

Dynamic percolation theory for particle diffusion in a polymer network

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Tracer-diffusion of small molecules through dense systems of chain polymers is studied within an athermal lattice model, where hard-core interactions are taken into account by means of the site exclusion principle. An approximate mapping of this problem onto dynamic percolation theory is proposed. This method is shown to yield quantitative results for the tracer correlation factor of the molecules as a function of density and chain length provided the non-Poisson character of temporal renewals in the disorder configurations is properly taken into account. © 2002 American Institute of Physics. [DOI: 10.1063/1.1481763]

I. INTRODUCTION

Atomic charge or mass transport processes in condensed systems often take place in a dynamically disordered host medium, whose microscopic structure fluctuates on a time scale of the order of the atomic hopping time. An example of current interest in materials science are polymer ion conductors.¹ These are solutions of ionic salts in a polar polymer that can possess significant ionic conductivities. It is well known that ionic motions in these materials are strongly coupled to motions of polymer chain segments, a situation which may be viewed as implying a continuing rearrangement of preferred ionic diffusion pathways through the host medium. At the glass transition temperature T_g , large scale segmental motions get frozen, suppressing long-range ionic diffusion. Other systems where atoms diffuse in a reorganizing host medium include permeation of small molecules through polymer films^{2,3} or ionic motions through protein channels passing biological cell membranes.⁴

Important progress in calculating the diffusion coefficient of a random walker in a dynamically changing environment emerged from dynamic percolation theory (DPT) and its generalizations. In its original form due to Druger *et al.*^{5,6} one considers the random walk in a bond percolation model, where configurations of open and blocked bonds are randomly renewed at a given rate λ . An important outcome of this model is the fact that the frequency-dependent diffusivity $D(-i\omega, \lambda)$ can be obtained by analytic continuation of the diffusivity $D_0(-i\omega) = D(-i\omega, 0)$ in the absence of renewals

$$D(-i\omega, \lambda) = D_0(-i\omega + \lambda), \quad (1)$$

irrespective of the precise form of the function $D_0(s)$ to be derived from a system with only static disorder.⁶ The same result (1) was independently obtained by Harrison and Zwanzig within effective medium theory⁷ assuming independent random renewals of individual bonds rather than global renewals as in Ref. 6, and also by Hilfer and Orbach.⁸ Sub-

sequent work on polymer ion conductors was focused on an identification of the central parameter of this theory, the renewal rate λ , from experimentally observed polymer viscosities⁹ and more recently from dielectric relaxation spectroscopy.¹⁰ In parallel, the theory was generalized considerably to off-lattice hopping,¹¹ spatially correlated renewals,¹² cases with distinct kinds of migration steps¹³ and, in particular, to non-Poisson renewal processes characterized by some waiting-time distribution $\psi(t)$.¹¹ In that case the zero-frequency diffusivity in $d=3$ dimensions is given by

$$D = \frac{1}{6} \frac{\int_0^\infty dt \psi(t) \langle r^2(t) \rangle_0}{\int_0^\infty dt t \psi(t)}, \quad (2)$$

where $\langle r^2(t) \rangle_0$ is the mean-square displacement of the random walker in a frozen environment.¹⁴ Note that in the case $\psi(t) = \lambda \exp(-\lambda t)$ Eq. (2) reduces to the zero-frequency limit of (1).

While DPT or, generally, dynamic disorder hopping theory¹¹ was developed as a framework for diffusion of small guest molecules in a fluctuating disordered host environment, it was also recognized that the basic idea underlying these dynamically disordered hopping models can provide an approximation to many-particle effects in transport processes in interacting lattice gases.¹⁵ A (pointlike) tracer particle in an interacting lattice gas can hop to a neighboring site provided the other particles have arranged such that this attempted site is vacant and that energetic conditions for the hop are fulfilled. The fact that the time scales for the changing environment and the tracer motion are interconnected offers a way to establish an effective dynamic bond percolation model for the tracer, involving a time constant λ . λ can be determined either self-consistently or by an ansatz based on the lattice coordination number. A many-particle effective medium theory for diffusion in interacting lattice gases emerges in this way.¹⁵

Besides these investigations for a lattice gas of point particles it seems that DP theories, although motivated by processes in polymer electrolytes, have never been tested

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quantitatively in the context of statistical polymer models. While the renewal processes associated with a system of point particles are sufficiently characterized by a single rate constant λ entering Eq. (1),¹⁵ we expect this equation to fail for the problem of diffusion through a polymer network because of the inherent distribution of relaxation times characterizing the chain motion. This should result at least in a more complicated form of the waiting-time distribution $\psi(t)$. The question now is how far Eq. (2) can describe the diffusion coefficient, when $\psi(t)$ is defined in a suitable way in terms of the actual dynamics of the polymer network.

To elucidate this question, we investigate in this article an athermal lattice model, defined in Sec. II, which consists of lattice chains with varying density and chain length and a sufficiently dilute system of point particles. Both chains and point particles undergo diffusion via elementary stochastic moves. This model is a special case of a more general lattice model of chains and point particles with specific interactions, used previously to describe the influence of temperature, pressure and salt content on diffusion and network relaxation properties of polymer electrolytes.^{16,17}

In the present work, we first obtain diffusion coefficients from dynamic Monte Carlo simulation of our model. These results serve as a reference with respect to the subsequent approximation method based on dynamic percolation theory. To implement this theory, we determine by simulation (i) the waiting-time distribution $\psi(t)$, which we define in terms of the occupational correlation function of a site next to a fixed point particle and (ii) the mean-square displacement $\langle r^2(t) \rangle_0$ of point particles for static disorder (frozen chains). These steps are computationally much less demanding than the full simulation. Comparison of both methods via Eq. (2) provides a sensitive test for the applicability of DP theories to diffusion in a fluctuating polymer host. We find excellent agreement between the tracer correlation factors as a function of density and chain length, as obtained from those two methods. Temporal correlations, reflected in the nonexponential character of $\psi(t)$, are found to be crucial in this analysis.¹⁸

In Sec. III we specialize to a chain length $r=1$ which corresponds to a system of point-particles only, before we present in Sec. IV our full analysis for chains up to a length $r=20$. Some further conclusions are drawn in Sec. V.

II. SIMULATION METHOD AND IMPLEMENTATION OF THE DYNAMIC PERCOLATION CONCEPT

Consider a system of lattice chains on a three-dimensional simple cubic lattice of spacing a . The chains are made of beads, assigned to lattice sites, and linearly connected via nearest-neighbor bonds. Apart from site exclusion, which mimics a hard-core repulsion, no explicit interactions between beads are assumed. For M chains each with r beads in a box of linear size La , the concentration of occupied lattice sites is simply given by $c = Mr/L^3$. In addition, our system contains pointlike tracer particles, again subjected to site exclusion, with a concentration $c_t \ll 1$ sufficiently small so that correlations among them are negligible. Most of our simulations were carried out with $L=10$, $r=1$ to 20, $c_t = 10^{-2}$, and periodic boundary conditions are employed. After preparation of the system with the desired number of

chains, equilibration and the subsequent dynamics at equilibrium are based on the generalized Verdier–Stockmayer algorithm, which employs end-bond motions, kink-jumps and crankshaft rotations.^{19–21} Point-particles individually perform nearest-neighbor hops. In the special case $r=2$ (moving dimers) only the end-bond motion is active, which then is a 90 degree rotation of the dimer about one of its end-points. As usual, introducing

$$D(s) = \frac{s^2}{6} \int_0^\infty dt e^{-st} \langle r^2(t) \rangle, \quad (3)$$

we can obtain the diffusion coefficient of point-particles, $D = \lim_{s \rightarrow 0^+} D(s)$, from their simulated mean-square displacement $\langle r^2(t) \rangle$. To separate the average effect of blocking, contained in a factor $1-c$, one introduces the tracer correlation factor $f(c) \leq 1$ according to

$$D = D^{(0)}(1-c)f(c), \quad (4)$$

where $D^{(0)} = \Gamma a^2$ denotes the diffusion coefficient for infinite dilution ($c \rightarrow 0$), with Γ the bare hopping rate.

Our aim is now to map the complete system dynamics onto a disordered single-particle model, where disorder configurations are globally renewed according to some appropriate waiting-time distribution $\psi(t)$. In order to test the validity of this idea against full simulations, we have to extract the input quantities to Eq. (2), $\langle r^2(t) \rangle_0$ and $\psi(t)$, from our polymer model. While $\langle r^2(t) \rangle_0$ can be obtained in a straightforward manner from separate simulations with frozen chains, there is no unique (rigorous) route to determine $\psi(t)$ so that we have to employ some physical arguments. As indicated already in the Introduction, we propose to determine $\psi(t)$ from the local occupational correlation function $\langle n_i(t)n_i(0) \rangle$, where $n_i(t)$ is the occupation by chain beads of a site i adjacent to a fixed tracer position. To simulate $\langle n_i(t)n_i(0) \rangle$ chains were first equilibrated while keeping the tracer fixed. Such a procedure is perfectly in the spirit of dynamic percolation theory based on renewals as “seen” by the tracer in its immediate neighborhood.

At this point let us recall some relationships from renewal theory. Let $\phi(t)$ with $t > 0$ be the probability density for the first renewal event, when the foregoing renewal took place at an arbitrary time $t_0 < 0$. Then

$$\Phi(t) = 1 - \int_0^t dt' \phi(t') \quad (5)$$

is the resulting probability that there is no renewal within the interval $[0, t]$. Following Refs. 11 and 22,

$$-\frac{d\Phi}{dt} = \bar{\lambda}\psi(t), \quad (6)$$

where $\bar{\lambda}^{-1} = (\phi(0))^{-1} = \int_0^\infty dt \psi(t)$ denotes the mean renewal time.

Our basic idea is now to identify renewal events with occupational changes at site i next to a fixed tracer. We argue that with probability $\Phi(t)$ the occupation at site i does not change within $[0, t]$ so that the stochastic variable $n_i(t)$ (with possible values 0 or 1) preserves its initial value, $n_i(t) = n_i(0)$ and $n_i(t)n_i(0) = (n_i(0))^2 = n_i(0)$. Conversely, with

probability $1 - \Phi(t)$, one or more renewals occur within $[0, t]$. Then, since configurations are randomly reassigned, $n_i(t)$ can be replaced by its average, c . Hence, in this case, $n_i(t)n_i(0) = cn_i(0)$. Averaging in addition over the initial occupation $n_i(0)$, we obtain for the correlation function

$$\langle n_i(t)n_i(0) \rangle = c[\Phi(t) + c(1 - \Phi(t))]. \quad (7)$$

This can be rewritten as

$$\Phi(t) = \frac{\langle n_i(t)n_i(0) \rangle - c^2}{c(1 - c)}, \quad (8)$$

consistent with the requirements $\Phi(0) = 1$ and $\Phi(t) \rightarrow 0$ as $t \rightarrow \infty$. Combination of (5), (6), and (8) yields

$$\psi(t) = \bar{\lambda}^{-1} \Phi''(t) = [\bar{\lambda}c(1 - c)]^{-1} \frac{d^2}{dt^2} \langle n_i(t)n_i(0) \rangle. \quad (9)$$

After insertion into (2) the prefactors drop out. Equation (9) completes the implementation of DP theory to our many-particle model. In the next sections we test the performance of this approximation scheme to a simple hard-core lattice gas and to a polymeric system.

III. HARD-CORE LATTICE GAS

As a first application let us briefly examine the special case of nonconnected beads, $r = 1$, which is identical to the conventional hard-core lattice gas of point-particles. The tracer correlation factor $f(c)$ in that case is known to a high degree of accuracy via dynamic pair approximations,^{23–25} giving

$$f(c) = \frac{1 + \langle \cos \Theta \rangle}{1 - [(3c - 2)/(2 - c)] \langle \cos \Theta \rangle}, \quad (10)$$

and through simulations.²⁶ In Eq. (10), which becomes exact as $c \rightarrow 1$, the quantity $\langle \cos \Theta \rangle$ characterizes the average directional change in two consecutive steps of the tracer due to the presence of one vacancy. For a simple cubic lattice, $\langle \cos \Theta \rangle \approx -0.209$. An effective-medium approximation to $f(c)$ was obtained recently¹⁵ from dynamic percolation theory using the Harrison Zwanzig approach.⁷

In what follows we apply the approach outlined in Sec. II to the same problem. $\langle r^2(t) \rangle_0$ is obtained from simulating a single mobile particle in the frozen configuration of the background particles. $\Phi(t)$ is deduced from Eq. (8) where $\langle n_i(t)n_i(0) \rangle$ is obtained from a short time simulation of a lattice gas with one fixed tracer particle, as described above. These simulations were carried out within a cubic box of length $L = 10$ and periodic boundary conditions. Note that collective properties of a hard-core lattice gas with symmetric transition rates show a relaxational behavior independent of concentration.^{27,28} The function $\Phi(t)$ as determined from (8) is therefore c -independent and thus can be determined from single particle random walk theory. Within that framework $\Phi(t)$ can be interpreted as time-dependent probability of return of a single random walker to site i , taking into account that one site adjacent to i is blocked by a fixed tracer. In Appendix A we briefly indicate how $\Phi(t)$ can be calculated exactly or how one can generate efficient analytic approximations.

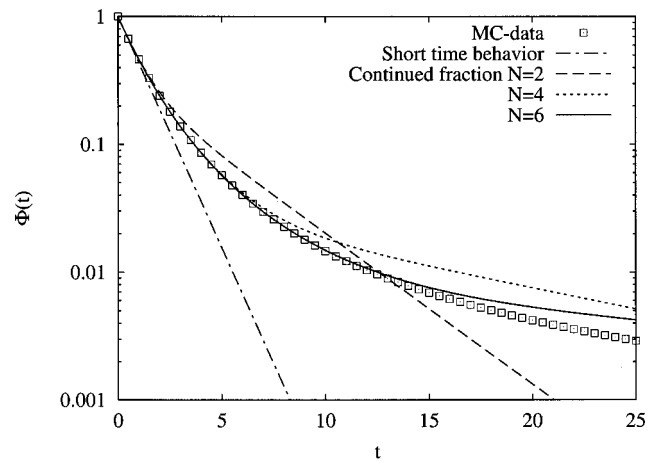


FIG. 1. Semilogarithmic plot of the function $\Phi(t)$ [see Eq. (8)] for the hard-core lattice gas. Monte Carlo data are obtained by simulating the probability of return of a single random walker starting next to a blocked site. Dashed–dotted line: single exponential approximation as determined by the initial slope [see Eq. (11)]. The other lines represent continued fraction approximants up to order $N = 6$ (see Appendix A). Here and in subsequent plots we take $\Gamma = 1$ for the bare hopping rate.

Results for $\Phi(t)$ obtained both from Monte Carlo simulation and from these approximations are plotted in Fig. 1. As seen from the figure, the main decay of $\Phi(t)$ at short times is fairly well represented by an exponential with decay rate

$$\lambda_0 = -(d\Phi/dt)_{t=0} = (\frac{5}{6})\Gamma. \quad (11)$$

The factor $\frac{5}{6}$ simply arises from the fact that one of the six bonds in the simple cubic lattice connected to site i is blocked by the tracer. The actual decay of $\Phi(t)$ is approached gradually by continued fraction approximants of increasing order N , which were derived according to Appendix A. The asymptotic decay of $\Phi(t)$ at long times is governed by diffusion, giving $\Phi(t) \propto (\Gamma t)^{-3/2}$, which, however, cannot be accounted for by a finite continued fraction. Nevertheless, for the purpose of practically evaluating (2) we find that it is sufficient to approximate $\Phi(t)$ in terms of a superposition of three exponentials.

Figure 2 shows the c -dependent tracer correlation factor obtained in this way. The agreement of data points from our DPT with the full curve representing the dynamic pair approximation Eq. (10) is quite satisfactory. For completeness we also included Monte Carlo data for the full hard core lattice gas. The DPT result for $c = 1$ with value $f \approx 0.6802$ was obtained analytically, see Appendix A, whereas the exact value is $f(1) = (1 + \langle \cos \Theta \rangle)/(1 - \langle \cos \Theta \rangle) \approx 0.654$. Also shown are diffusion constants calculated from the effective medium approximation as described in Ref. 15, which is based on only one time constant for renewal events. With $\lambda = \lambda_0$ as given by (11) this theory yields the dashed curve whose deviations from Eq. (10) in the high-concentration regime are larger than the deviations of our DP theory. [On the other hand, merely fitting λ to the exact value of $f(1)$, giving $\lambda \approx 0.62\Gamma$, turns out to give very good agreement with Eq. (10) in the whole concentration range.]

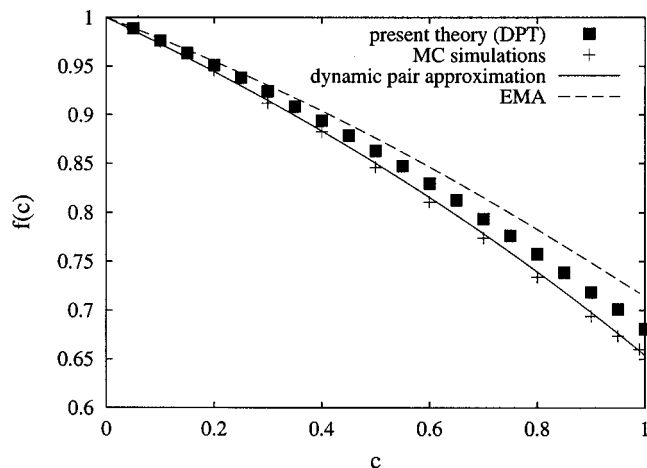


FIG. 2. Tracer correlation factor $f(c)$ of the hard core lattice gas against concentration, obtained by different methods (see text). Full curve [Eq. (10)] and MC simulation data serve as reference for the performance of the present DP theory and the EMA as described in Ref. 15.

These results confirm the conclusion in Ref. 15 that dynamic percolation theory can reasonably describe diffusion in many-particle systems. At the same time our results indicate that the theory significantly improves when the non-Poisson character of renewal processes is taken into account. For the problems in the next section this last aspect will become much more important.

IV. LATTICE POLYMERS

For the hard-core lattice gas ($r=1$) the procedure described obviously bears no computational advantage over existing methods. The situation changes, however, when we go over to $r>1$. The correlation factor $f(c)$ now depends on r and no analytic approximation equivalent to Eq. (10) is available for this case. At the same time full simulations of the diffusional dynamics become more demanding because of the internal degrees of freedom of the host molecules and the larger statistical errors connected with the small concentration of tracer particles. Here our approximate DPT-based computational scheme is potentially useful. In this section we examine the performance of this scheme.

Figure 3 summarizes our MC simulation results, again represented in terms of the correlation factor $f(c)$, Eq. (4), for different chain lengths r up to $r=20$. The full lines are fits to the simple functional form $f(c)=(1-\alpha(r)c)/(1-\beta(r)c)$ with fit parameter α , β that depend on the chain lengths r . These results will be used as a basis for assessing the performance of the approximate DP-based approach. As discussed above, this approach is based on evaluating the waiting time distribution $\psi(t)$ according to Eq. (9) and the mean-square displacement $\langle r^2(t) \rangle_0$ of a tracer in the presence of a frozen solvent. Figure 4 shows typical results for the function $\Phi(t)$, see Eq. (8), obtained for chains with length $r=10$ for several concentrations, while our simulation results for $\langle r^2(t) \rangle_0$ are shown in Fig. 5 for the same r -values as in Fig. 4. Substitution of these results into Eqs. (2) and (4) yields our DP-approximation for the correlation factor $f(c)$, which is shown in Fig. 6 together with the “exact” MC

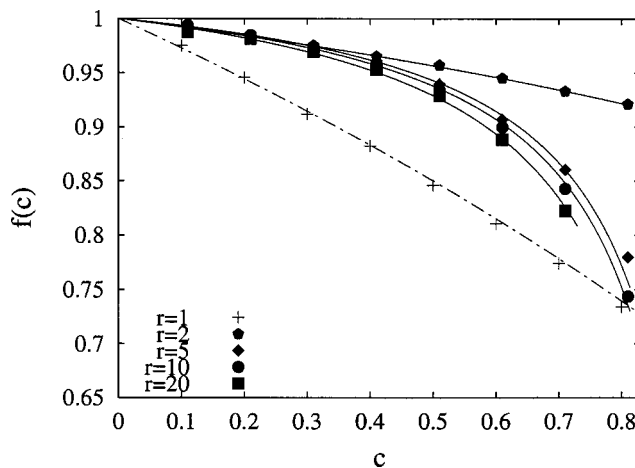


FIG. 3. Simulated tracer correlation factor $f(c)$ for different chain lengths $r=2, 5, 10$, and 20 . Full lines refer to the fit function $f \approx (1 - \alpha c)/(1 - \beta c)$, where for $r=5, 10$, and 20 the fit parameters are $\beta=1$ and $\alpha=1.057, 1.062$, and 1.071 , respectively. This implies that the diffusion constant (4) is approximately linear in c , $D(c) \approx D_0(1 - \alpha c)$. On the other hand, for $r=2$ we find $\alpha=0.391$ and $\beta=0.318$. For comparison we also show simulation data for $r=1$ (hard core lattice gas) together with Eq. (10) (dashed-dotted line).

results of Fig. 3. (For clarity, only the full lines from Fig. 3, representing the fitted data as discussed above, appear in Fig. 6.) Evidently, the DP approximation agrees very well with the full simulation for all r . Some further observations are noteworthy:

- (a) From the MC simulation results for $f(c)$ (Fig. 3) an interesting picture emerges concerning the effect of host connectivity on the tracer diffusion. Focusing first on chains with $r \geq 5$ we see that for $c \leq 0.8$, $f(c)$ and hence the diffusion constant are larger than in the hard-core lattice gas (Sec. III).²⁹ Thus, in this density range chain connectivity facilitates diffusion of tracer particles relative to the hard core lattice gas ($r=1$) with the same average site occupation c . For larger site oc-

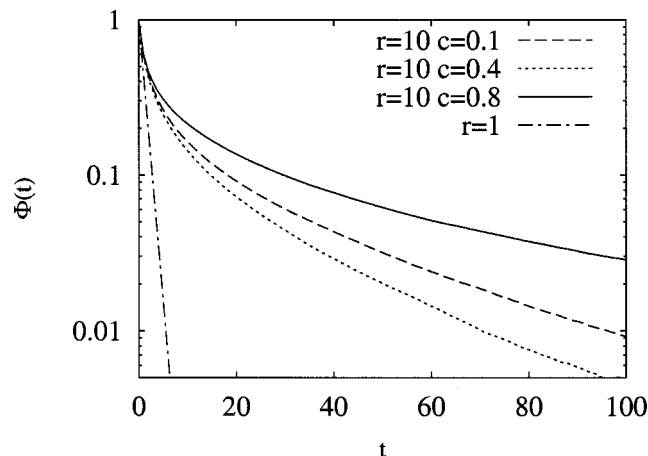


FIG. 4. $\Phi(t)$ for chains of length $r=10$ for three different concentrations $c=0.8, 0.1$, and 0.4 (from above). Also shown is the short time behavior of the c -independent function $\Phi(t)$ for $r=1$ (dashed-dotted line), reproduced from Fig. 1.

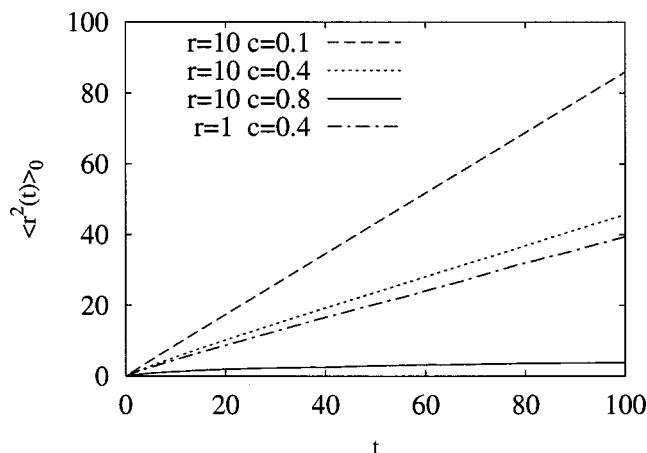


FIG. 5. Mean-square displacement $\langle r^2(t) \rangle_0$ of walkers in a frozen chain network. Network parameters are as in Fig. 4. For $c=0.4$ a comparison is made with the case $r=1$.

cupations, however, correlation factors $f(c)$ for lattice polymers seem to drop below those of the hard core lattice gas ($r=1$).

- (b) These findings for $r \geq 5$ are in contrast to the behavior found for $r=2$, which is a special case concerning the allowed elementary moves (see Sec. II). For all concentrations c considered, $f(c)$ now remains larger than 0.9; see Fig. 3. Dimers therefore induce only minor backward correlations in the tracer motion. Intuitively, from the point of view of the tracer, only one monomer of the dimer molecule effectively suppresses tracer forward motion by a nearest-neighbor hop, while its second monomer is shielded.
- (c) The main feature seen in Fig. 4 is the highly nonexponential decay of the function $\Phi(t)$ for the chain systems, indicating the importance of temporal correlations in the associated renewal processes. Furthermore, in contrast to the case $r=1$ with c -independent $\Phi(t)$, we observe for $r=10$ a decay of $\Phi(t)$ that depends on

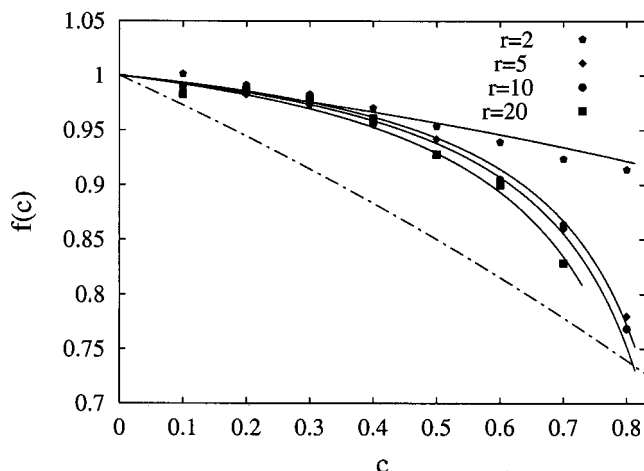


FIG. 6. Comparison of tracer correlation factors from DP theory for chains of different lengths (data points) with results from full simulations. Full lines represent fit functions for the simulation data, reproduced from Fig. 3. Again, the dashed-dotted lines represents Eq. (10).

c . Two opposing trends seem to be the reason for a nonmonotonous c -dependence. First, we argue that at an intermediate concentration $c=0.4$ the relaxation is faster than for $c=0.1$ because of the more homogeneous distribution of monomers in the surroundings of the tracer, allowing enhanced occupational fluctuations. Second, going to higher concentrations, all polymer modes slow down and thereby diminish the decay of $\Phi(t)$ (see the case $c=0.8$ in Fig. 4). The final result for $f(c)$, however, remains monotonous in c because of the stronger c -dependence of $\langle r^2(t) \rangle_0$ (see below). For dimers ($r=2$) we have found that $\Phi(t)$ decays even somewhat faster than in the case $r=1$ and is only weakly c -dependent. To elucidate in this context the role of the fixed tracer, we have performed additional simulations for the correlation function $\langle n_i(t)n_i(0) \rangle^{(0)}$ in the absence of the tracer, which follows from the unperturbed polymer dynamics. The corresponding functions $\Phi^{(0)}(t)$, see Eq. (8), generally show a similar but somewhat faster decay than $\Phi(t)$. We have found that using $\Phi^{(0)}(t)$ instead of $\Phi(t)$ in calculating $f(c)$ causes deterioration of the good quantitative accuracy of the DPT scheme.

- (d) The mean square tracer displacement $\langle r^2(t) \rangle_0$ in a frozen host, plotted in Fig. 5, shows with increasing c a crossover from diffusive behavior, $\langle r^2(t) \rangle_0 \sim t$, to a localized random walk $\langle r^2(t) \rangle_0 \rightarrow \text{const}$ as $t \rightarrow \infty$, as expected for a percolative network. It is expected that this crossover takes place at some critical concentration c_{crit} . A precise determination of the percolation threshold $c_{\text{crit}}(r)$ for walks through a frozen network of chains of length r is beyond the scope of this article, yet rough estimates are presented in Appendix B for two- and three-dimensional systems. In $d=3$ dimensions, c_{crit} appears to increase with r , indicating again that for given c the frozen chains are less prohibitive to tracer diffusion than a frozen background of independent monomers. For example, for $r=10$, the concentration $c=0.8$ clearly exceeds $c_{\text{crit}}(r=10)$; see Fig. 5 and the estimates in Appendix B.
- (e) As already noted, the DP approximation agrees very well with the full simulation for all r (see Fig. 6). This remains true even in the special case of lattice dimers ($r=2$). In particular, following the analysis contained in Figs. 4 and 5, it is easy to understand the marked drop in $f(c)$ for large c , i.e., near and above the percolation threshold, shown by the data for $r \geq 5$. Because of the absence of diffusion in the frozen lattice with $c > c_{\text{crit}}$ (see Fig. 5), long-range tracer motion solely relies on network fluctuations which, however, become slow in that regime (see Fig. 4). The r -dependence ($r \geq 5$) of our results in Fig. 6 follows from the fact that the dynamics in high-density lattice polymer systems slow down further as r increases at constant density c .³⁰

V. SUMMARY AND OUTLOOK

A method has been proposed how to map particle diffusion through a fluctuating network of polymer chains onto

dynamic percolation theory (DPT). As input quantities this theory requires the particles' mean-square displacement $\langle r^2(t) \rangle_0$ in the frozen network and the waiting time distribution $\psi(t)$ for network renewals. We proposed to relate $\psi(t)$ to the occupational correlation function of a site next to the tracer particle so that it reflects the temporal distribution of pathway openings seen by the fixed tracer. In contrast to the standard hard core lattice gas, $\psi(t)$ decays in a highly non-exponential fashion when longer chains are considered. This feature of the fluctuating network appears to be crucial in implementing dynamic percolation theory to chain systems. When properly taken into account, the DP model gives quite accurate results for the tracer correlation factor in its variation with concentration c and chain length r . We have verified this by comparing the results of DPT with Monte Carlo simulations of the complete system dynamics. Thereby it turns out that the DPT scheme saves about one order of magnitude in computing time relative to full simulations.

Our studies so far are limited to an athermal system and therefore are not yet in the position to make a direct comparison with experiments or molecular dynamics (MD) studies of diffusion through real polymer systems. Under this aspect it would be very interesting to extend our studies by applying DP theory with non-Poisson renewals to interacting systems as a first step in approaching real materials. The method in principle can also be applied to questions of dispersive transport.

Information on the mean-square displacement of guest molecules in a frozen polymer matrix with Lennard-Jones interactions has recently been obtained from MD simulations, and has been utilized in building a model to interpret experimental diffusion data for noble gases in polymers.³¹ Tentatively, from the point of view of the present theory, we can regard $\langle r^2(t) \rangle_0$ to be known for that system, while information on $\Phi(t)$ is lacking. For purely qualitative purposes we may assume a single renewal rate λ and employ Eq. (1) ($\omega=0$). Comparison with the measured diffusion constant yields a renewal time λ^{-1} , which turns out to be of the order of magnitude of the crossover time, beyond which the mean-square displacement in the model of Ref. 32 reflects long-time diffusion.³³ This apparent consistency with Refs. 31 and 32 supports our conclusion that the DP concept could become a promising tool in studies of diffusion through real polymeric systems.

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APPENDIX A: HARD-CORE LATTICE GAS-SUPPLEMENTARY RESULTS

Regarding the hard-core lattice gas, the quantity $\Phi(t)$ given by (8) is equal to the probability of return to site i after time t in the case of a single random walker. Here site i is next to a site blocked by a fixed tracer. In calculating $\Phi(t)$,

the effect of the blocked site can be taken into account by standard defect matrix theory.³⁴ This yields an expression for $\Phi(t)$ in terms of the solution of a 3×3 matrix equation, whose coefficients are determined by unperturbed lattice Green functions up to third-neighbor distances. The calculation is straightforward and will not be reproduced here.

In the present context it is sufficient to obtain an accurate approximation for $\Phi(t)$ only until it decays to about 10^{-2} . Computationally it is then advantageous to represent its Laplace transform $\hat{\Phi}(s)$ as a continued fraction of the type $\hat{\Phi}(s) = a_0(s + b_1 - a_1(s + \dots)^{-1})^{-1}$, generated by a short time expansion of $\Phi(t)$.³⁵ Time derivatives $\Phi^{(n)}(t=0)$ with $0 \leq n \leq 2N-1$ are easily obtained by enumerating closed paths of the walker which avoid the blocked site. Specifically, we use

$$\Phi(t) = \sum_{n=0}^{\infty} \Phi_n \frac{(\Gamma t)^n}{n!} e^{-\Gamma t}, \quad (\text{A1})$$

where Φ_n is the probability of return to the origin after n steps.

At stage N the continued fraction is terminated such that $\hat{\Phi}(0)$ agrees with the exact result from defect matrix theory (see above) which, at $s=0$, is determined in terms of Watson-type integrals. Figure 1 contains a plot of the N th-order approximants for $\Phi(t)$ up to $N=6$. For $N=6$ the simulations are accurately represented up to $\Gamma t \approx 15$.

Finally we comment on the limit $c \rightarrow 1$, where the correlation factor from DPT can be evaluated analytically. Obviously, the mean-square displacement $\langle r^2(t) \rangle_0$ of a tracer in a frozen lattice is determined in that limit by successive exchanges with one neighboring vacancy. This gives $\langle r^2(t) \rangle_0 = ba^2(1-c)(1 - \exp(-2\Gamma t))/2$, where Γ is the jump frequency. From (8) together with the above-mentioned results for $\Phi(t)$ we obtain $f(1) = 0.6802$ as given in Sec. III.

APPENDIX B: PERCOLATION IN A FROZEN NETWORK

Calculation of the diffusion constant D from (2) requires knowledge of the mean square displacement $\langle r^2(t) \rangle_0$ of a tracer particle in a frozen network on time scales of the order of the decay time of $\psi(t)$. In this Appendix we estimate the critical concentration $c_{\text{crit}}(r)$ for percolation of a monomer particle through a frozen network of chains, which distinguishes diffusive from localized behavior of $\langle r^2(t) \rangle_0$ at long times. To our knowledge, this problem of correlated percolation has not been investigated before for general chainlength r . We do not, however, attempt any precise determination of $c_{\text{crit}}(r)$; rather we would like to point out some major qualitative trends in $c_{\text{crit}}(r)$ as a function of r in $d=3$ and $d=2$ dimensions.

In $d=3$, equilibrated chain configurations were prepared by the same algorithm as described in Sec. II, while in $d=2$ we used the algorithm by Siepmann *et al.*³⁶ For systems of varying size L , increased in steps ΔL , we determined the probabilities $P(r, c, L)$ of occurrence of a spanning cluster of vacant nearest-neighbor sites. For fixed r , we obtained points of intersection of successive curves $P(r, c, L)$ and $P(r, c, L - \Delta L)$ versus c , which give successive approximations for $c_{\text{crit}}(r)$.³⁷ Estimates for $c_{\text{crit}}(r)$ were deduced from calcula-

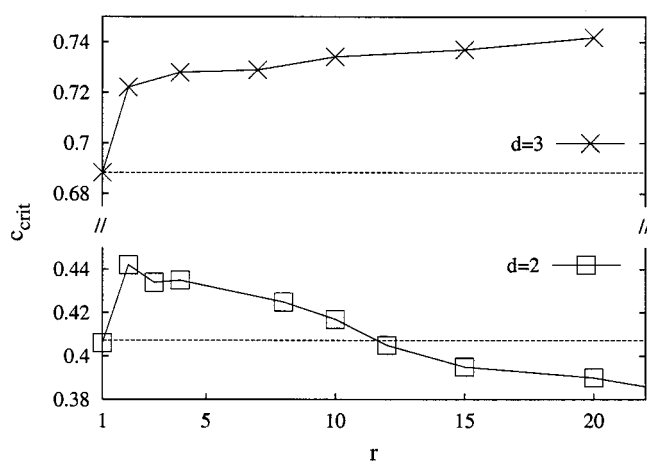


FIG. 7. Estimates for the critical concentration $c_{\text{crit}}(r)$ vs r for percolation of a monomer particle through a frozen network of chains of length r on a simple cubic ($d=3$) and a square ($d=2$) lattice.

tions with L -values up to a maximum L_{max} , to be adapted to r . For example, in $d=2$ we went up to $L_{\text{max}}=200$ for $r=20$, whereas $L_{\text{max}}=80$ for frozen dimers $r=2$. These values appeared sufficient to achieve reasonable convergence. In the limit $r=1$ we find $c_{\text{crit}} \approx 0.41$ for $d=2$ and $c_{\text{crit}} = 0.69$ for $d=3$, which reasonably agree with values $1-p_c$ given by the well-known thresholds p_c for site percolation on square and simple cubic lattices, respectively. The qualitative r -dependence of $c_{\text{crit}}(r)$ is shown in Fig. 7. In $d=3$, $c_{\text{crit}}(r)$ monotonously increases with r , which we interpret as a reduction of blocking of open pathways through the connectivity of chains. The most pronounced increase occurs already when going from monomers to $r=2$. In $d=2$ this argument again applies to the step from $r=1$ to $r=2$, but blocking becomes more effective for longer chains so that $c_{\text{crit}}(r)$ decreases, with $c_{\text{crit}}(r) < c_{\text{crit}}(1)$ for $r \geq 12$. For long chains, especially in $d=2$, it might be interesting to study $\langle r^2(t) \rangle_0$ near criticality on different length scales above and below the radius of gyration of chains, but this goes beyond the scope of this work.

Generally, for sufficiently long times and small $|c - c_{\text{crit}}|$ such that the correlation length becomes larger than the size of chains, one expects $\langle r^2(t) \rangle_0$ to follow the standard scaling forms for noncorrelated percolation, which imply associated scaling forms for the frequency-dependent diffusivity $D_0(-i\omega)$ as $\omega \rightarrow 0$. In applications of DP theory where the analytic continuation rule (1) holds at least for small λ , one can immediately predict the asymptotic forms of the long-time diffusion constant $D = D_0(\lambda)$ of a walker in the presence of slow ($\lambda \rightarrow 0$), Poisson-type network renewals.³⁸ The resulting scaling expressions for D are straightforward to write down from the corresponding expressions for $D_0(-i\omega)$ given in Ref. 39. Notable special cases depending on different limits in the scaling variable $z = (c - c_{\text{crit}})\lambda^{-k/(2\nu - \beta)}$ are

$$D \sim \begin{cases} \lambda^{1-k}, & z \ll 1, \\ \lambda(c - c_{\text{crit}})^{2\nu - \beta}, & c > c_{\text{crit}}; \quad z \gg 1, \end{cases} \quad (\text{B1})$$

where ν and β are the conventional static percolation expo-

nents for the correlation length and the order parameter, respectively, and k is the dynamic critical exponent for anomalous diffusion in a percolation system at criticality.³⁷

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