

Charge Transport in Polymer Ion Conductors: a Monte Carlo Study

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Abstract

Diffusion of ions through a fluctuating polymeric host is studied both by Monte Carlo simulation of the complete system dynamics and by dynamic bond percolation (DBP) theory. Comparison of both methods suggests a multiscale-like approach for calculating the diffusion coefficients of the ions.

1 Introduction

Chain polymers carrying electro-negative atoms (e.g. oxygen or nitrogen) in their repeat unit can act as solvents for certain salts. Well-known examples are Li-salts dissolved in polyethylene-oxide (PEO). At temperatures sufficiently above the glass-transition temperature these polymer-salt solutions show significant DC ionic (Li^+) conductivities. Such "polymer electrolytes" offer widespread applications in batteries, sensors and fuel cells. From the scientific point of view, an important goal is to improve our understanding of the electrical conduction mechanism in polymer electrolytes, and in particular to elucidate the interplay between ion diffusion and the polymer network dynamics.

Dynamic Monte Carlo (MC) simulation of the diffusion coefficient of few particles (ions) in a rearranging environment of polymer chains is hampered by the need to move every monomer (polymer bead or ion) with the same probability. Therefore most of the computational time is spent moving the polymeric host without affecting the ionic configurations. On the other hand, earlier studies indicate that important features of the ion diffusion within a dynamical matrix of chain molecules can be described by a more coarse-grained model[1]. The idea is to map the diffusion process onto DBP-theory [2, 3] and to determine the central quantity entering this theory, the renewal time distribution $\psi(t)$, from the time dependence of the local occupational correlation function due to the polymer chain dynamics. In this communication we perform tests of such a procedure for a hard-core lattice gas and for tracer diffusion in systems of athermal lattice polymers. It turns out that the DBP-concept compares favourably with simulations of the complete system dynamics and thereby saves about one order of magnitude in computer time.

2 Hard-core lattice gas

In order to explain our procedure we treat the simple case of a hard-core lattice gas, i.e. point particles moving on a lattice with no interaction besides hard core repulsion. The tracer

diffusion constant $D(c)$ as a function of concentration c is known to a high degree of accuracy via dynamic pair approximations [4–6] which yield a tracer correlation factor

$$f(c) := \frac{D(c)}{D_0(1-c)} = \frac{1 + \langle \cos \Theta \rangle}{1 - [(3-2c)/(2-c)]\langle \cos \Theta \rangle}, \quad (1)$$

with $\langle \cos \Theta \rangle \approx -0.209$ for a simple cubic lattice.

Now we consider a lattice with static disorder in which randomly chosen sites are blocked and thus not accessible for the tracer particle. For this standard percolation problem we denote the mean square displacement of the tracer by $\langle r^2(t) \rangle_0$. If on the other hand the blocked sites are globally and instantaneously rearranged according to an arbitrary waiting-time distribution $\psi(t)$, generalized DBP-theory yields the following diffusivity at zero frequency in $d = 3$ dimensions [3]

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

Our aim is to map the complete system of coupled ions and lattice chains onto this coarse-grained DBP-model. While $\langle r^2(t) \rangle_0$ can be obtained in a straightforward manner from simulations of ion diffusion in the frozen network, the determination of $\psi(t)$ requires more explanation. Within the spirit of previous work on the hard-core lattice gas we propose to determine $\psi(t)$ from the local occupational correlation function $\langle n_i(t)n_i(0) \rangle$ of a site i adjacent to a fixed tracer position. Let us introduce the probability $\Phi(t)$ that no renewal takes place within the time interval $[0, t]$ after a previous renewal at an arbitrary $t_0 < 0$. The joint probability $\langle n_i(t)n_i(0) \rangle$ that the lattice point i is occupied at $t = 0$ and at t (not necessarily by the same particle) consists of two distinct contributions. The first one is the probability that i is occupied at $t = 0$ and that no renewal occurs until t , which is given by $c \Phi(t)$. The second contribution describes the situation where one or more renewals have taken place until t . The corresponding probability is given by $c^2(1 - \Phi(t))$. Hence $\Phi(t)$ is related to $\langle n_i(t)n_i(0) \rangle$ via

$$\Phi(t) = \frac{\langle n_i(t)n_i(0) \rangle - c^2}{c(1-c)} \quad (3)$$

According to [3], $\psi(t) = \Phi''(t)\bar{\lambda}^{-1}$ where $\bar{\lambda} = \int_0^\infty t\psi(t)dt$ denotes the mean renewal time. Equation (2) thus can be rewritten as

$$D = \frac{1}{6} \frac{\int_0^\infty dt \Phi''(t) \langle r^2(t) \rangle_0}{\int_0^\infty dt t \Phi''(t)} \quad (4)$$

where we obtain $\Phi(t)$ from (3) by means of MC simulations for $\langle n_i(t)n_i(0) \rangle$. The resulting $\Phi(t)$ can be fitted with sufficient accuracy by a combination of P exponential functions,

$$\Phi(t) = \sum_{i=1}^P a_i \exp(-\lambda_i t) \quad (5)$$

On the other hand, $\langle r^2(t) \rangle_0$ can be expressed in terms of the simulated mean square displacement $\langle r_n^2 \rangle_0$ of a tracer particle making n steps in a frozen network via

$$\langle r^2(t) \rangle_0 = \lim_{N \rightarrow \infty} \sum_{n=0}^N \frac{(\omega_0 t)^n}{n!} \exp(-\omega_0 t) \langle r_n^2 \rangle_0 \quad (6)$$

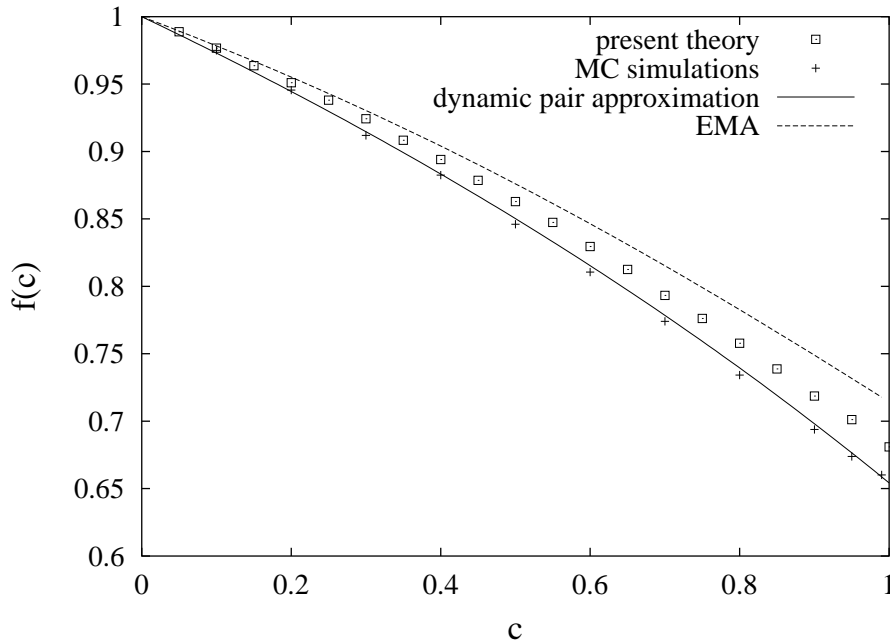


Figure 1: Test of DBP-theory against simulations of the complete system and the dynamic pair approximation equation (1). The quantity shown is the tracer correlation function $f(c)$ as a function of concentration. Also plotted are results obtained recently from a many-particle effective medium approximation[8].

where ω_0 is the attempt frequency of the tracer. Inserting (5) and (6) into (4) and carrying out the integration one gets

$$\frac{D}{\omega_0} = \frac{1}{6} \lim_{N \rightarrow \infty} \sum_{i=1}^P \left(\frac{\lambda_i}{\omega_0}\right)^2 a_i \sum_{n=0}^N \frac{\langle r_n^2 \rangle_0}{(\lambda_i/\omega_0 + 1)^{n+1}} \quad (7)$$

Independent calculations for $c \rightarrow 1$ showed that in order to keep the error caused by the finiteness of N and p below the statistical error, values of $P = 3$ and $N = 40$ were sufficient. Note that the main decay of $\Phi(t)$ is roughly represented by a single exponential with decay rate $\lambda_0 = -(d\Phi/dt)_{t=0} = (5/6)\omega_0$.

In Figure (1) we compare the results of this theory with MC simulations (see also [7]) and the dynamic pair approximation equation (1) and also with an existing effective medium approximation (EMA) for a percolating lattice renewing itself with only one rate constant $\lambda = 5/6\omega_0$ [8]. As one can see, using more than one rate constant in the representation of $\Phi(t)$ according to (5) improves the results significantly. This observation suggests to apply the generalized DBP-theory to the situation described in the next section where the non-exponential character of the renewal process is even more pronounced.

3 Results for athermal chains and conclusion

In the case of a hard-core lattice gas the procedure described bears no computational advantage over existing methods but was merely considered as a test case. The situation changes, however, when we apply our approach to ion diffusion in a polymer network. No analytic approximations for $D(c)$ of a quality similar to (1) are available then, and full sim-

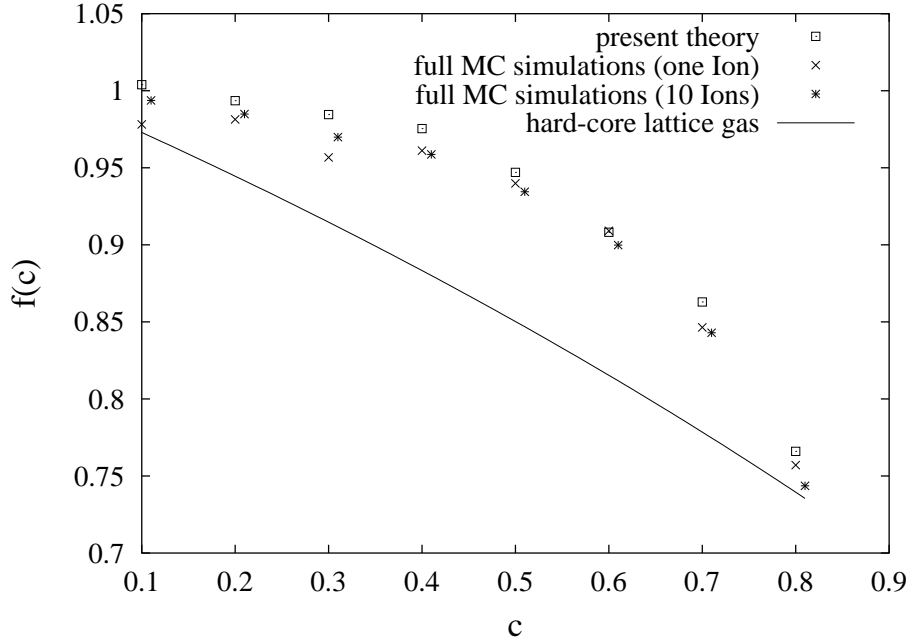


Figure 2: Comparison of the present theory with full MC simulation using ion concentrations $c_{\text{ion}} = 10^{-3}$ (one ion) and $c_{\text{ion}} = 10^{-2}$ (10 ions). For comparison the result of equation (1) for a hard-core lattice gas is also included.

ulations of D become much 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.

Let us consider, for example, a system where the chains are made of ten beads, assigned to lattice sites, and linearly connected via nearest-neighbour bonds. Apart from site exclusion, which mimics a hard-core repulsion, no explicit interactions between beads are assumed. The size of the simulation box is $L = 10$ and periodic boundary conditions in all directions are employed. For the chain dynamics we use the standard algorithm as described in Ref. [9–11], while point-particles individually perform nearest-neighbour hops.

To apply our theory we again determine $\Phi(t)$ in analogy to the hard-core lattice gas, see (5), which is now highly non-exponential, indicating the importance of temporal correlations in the associated renewal processes. A superposition of three exponential functions in (5), however, still gives a good description of $\Phi(t)$. Mean-square displacements $\langle r_n^2 \rangle_0$ of ions within a frozen network of chains are determined using $N = 200$ steps, and the diffusion constant is calculated as before via equation (7). In Fig.(2) we compare our results for the tracer correlation factor as a function of the total concentration of occupied sites, c , with full MC simulations. Due to the connectivity of chains blocking effects at a given c on average are reduced and the correlation factor $f(c)$ is larger than in the case of point particles, at least as long as $c \lesssim 0.8$. More important from the computational point of view is the fact that DBP-theory very well agrees with the full simulations, but saves about one order of magnitude in computer time. Mapping that problem onto a coarse-grained DBP-model thus appears to constitute an accurate and efficient method for investigating diffusion through a dynamic host of chain molecules. To support this conclusion further work is being carried out, in particular under varying chain lengths.

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