

Diffusion in polymer electrolytes and the dynamic percolation model[☆]

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Abstract

A semi-microscopic description of ionic transport in polyethylene oxide (PEO)-type electrolytes is presented, which is based on discrete stochastic moves of individual molecular units. Diffusion coefficients for ions and for the center of mass motion of chains are calculated by Monte Carlo simulation as a function of various model parameters, with emphasis on the incorporation of pressure effects. Within an even more coarse-grained description of diffusion in an athermal system of pointlike particles and chains we provide a quantitative verification of the concept of dynamic percolation (DP). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Within the ongoing search for polymer electrolytes with electrical and mechanical properties suitable for electrochemical devices, materials with increasing complexity in their chemical structure are being developed. Yet there is a need for improving our understanding of ionic transport mechanisms in simple model systems. Here we shall present two versions of a simplified, coarse-grained model that is based on discrete, stochastic motions of lattice chains (polymers) and pointlike particles representing the ions. The

first model involves microscopic interaction parameters, the main ingredient being an effective attraction between cations and polar groups in polyethylene oxide (PEO)-type systems. Using dynamic Monte Carlo simulations, it is shown that this model qualitatively reproduces several experimental trends in ionic and chain diffusion constants as a function of temperature, salt content and pressure.

In a second, even more coarse-grained description, we shall employ dynamic percolation (DP) theory. This concept has been proposed long ago in the context of polymer electrolytes [1], but to our knowledge it has not been tested with respect to its quantitative validity for ion diffusion through a fluctuating host of chain molecules. We propose a mapping of that problem onto DP-theory and show that the correlation factor for self-diffusion of pointlike particles can be reproduced quantitatively by this theory.

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2. Lattice model of a polymer electrolyte and equation of state

In our first model, chain molecules are represented by beads occupying a sequence of nearest-neighbour points on a simple cubic lattice of spacing a . To account for the chemical heterogeneity of PEO-like chains, we distinguish between C -beads and X -beads in sequences $C(XCC)_n$, where X corresponds to an oxygen atom. The total length of a chain is $r = 3n + 1$. In order to include the possibility of a transition from the fluid to a glassy state, we assume a common nearest-neighbour repulsion $\varepsilon > 0$ among all beads of the chain. Furthermore, since we are interested only in the cation motion and in effects due to their specific interactions with the chain, we take into account only one species of ions, which attract X -beads with strength $-\varepsilon_0 > 0$ [2]. In order to reduce the number of free parameters in our model, we simply assume that $\varepsilon_0 = \varepsilon$. Cations move via nearest neighbor-jumps while elementary moves of the chains follow the generalised Verdier–Stockmayer algorithm [3,4]. Transition probabilities in our dynamic Monte Carlo simulation are given by the Metropolis algorithm, and periodic boundary conditions are employed. Equili-

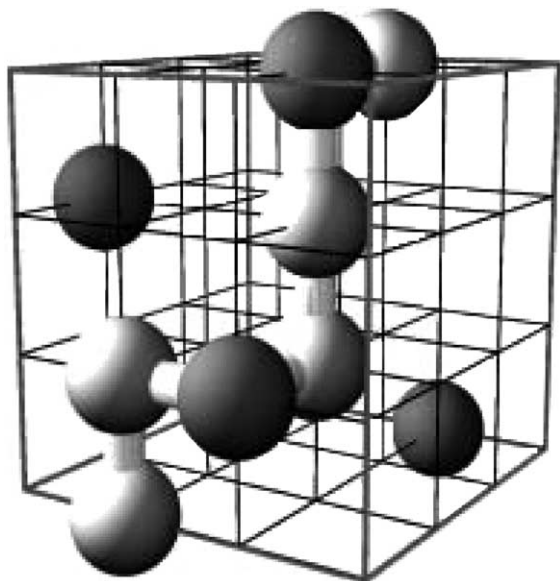


Fig. 1. Section of our lattice model, illustrating a lattice-chain of type $C(XCC)_n$, and pointlike particles.

bration steps are carried out independently with the help of the configurational bias method [5]. A section of this model is illustrated in Fig. 1. A similar model with mobile cations and anions has been studied previously with respect to ion solvation, dissociation and diffusion properties [6,7].

Of primary interest in this work are diffusion properties of ions and chains under varying temperature, salt content and pressure. Dynamic simulations, however, are normally carried out for a fixed volume of the system, while in experiment, the pressure p is kept constant. Because of the lack of efficient algorithms for dynamical properties in a lattice system under constant pressure [8], we perform constant volume simulations but choose the volume V for given T and p from the equation of state (EOS). The EOS on the other hand, can be obtained with reasonable accuracy from the quasi-chemical (QCA) approximation in the version by Barker [9] for systems involving heterogeneous chains. Details are deferred to a forthcoming publication so that we proceed directly to our results.

3. Results for chain and ion diffusion

Diffusion coefficients for chains and ions are deduced from their mean-square displacements in the long-time limit. Calculations are carried out for a system with $N_p = 31$ chains of length $r = 13$ and with varying concentration x of ions. Here x is defined as the ratio between the number of ions and the number of X -beads in the system. For a given pressure p and temperature T we first calculate the volume $V(p, T)$ from the QCA approximation. A nearly cubic simulation box is then chosen, with size $a^3(L_1 \times L_2 \times L_3) = V(p, T)$, and periodic boundary conditions are employed in all three directions. For example, if $p = 0.35\varepsilon/a^3$, $x = 0.16$ and $k_B T/\varepsilon \approx 0.915$ we find $V = 1100a^3$ so that we can choose $L_1 = 10$, $L_2 = 10$, $L_3 = 11$.¹

Fig. 2 shows the T -dependence of the diffusion coefficients for chains and ions at a given pressure $p = 0.35 \varepsilon/a^3$ for various ionic concentrations [2]. In

¹ In fact, values for p are taken such that this procedure yields integers L_1 , L_2 and L_3 which are close to each other.

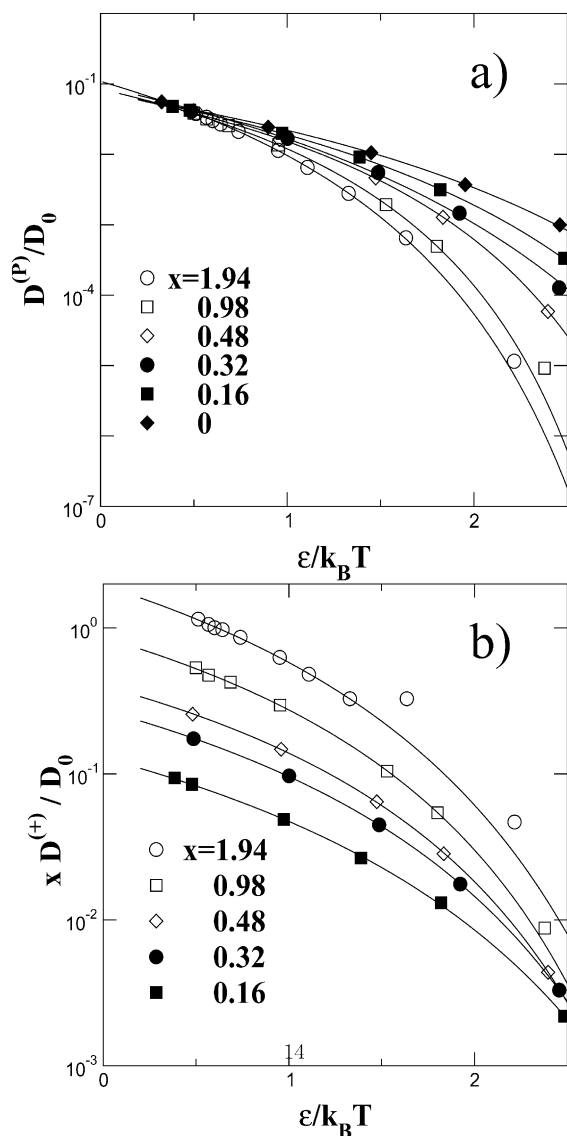


Fig. 2. Arrhenius representation of normalised diffusion coefficients at fixed pressure $p=0.35\epsilon/a^3$ of (a) the center of mass motion of chains and (b) of ions for different ion concentrations x . Data in (b) have been multiplied by x and thus reflect the conductivity. Continuous lines are fits to the VTF-Eq. (1).

the Arrhenius plots of Fig. 2, the data points show a downward curvature and can well be represented by the Vogel–Tammann–Fulcher law,

$$D^{(\alpha)}(T, x) = D_{\infty}^{(\alpha)} \exp\left(-\frac{E^{(\alpha)}(x)}{T - T^{(\alpha)}(x)}\right) \quad (1)$$

where α distinguishes polymer chains ($\alpha=P$) and ions ($\alpha=+$). The quantities $D_{\infty}^{(\alpha)}$ denote the diffusion coefficients at infinite temperature, $D_{\infty}^{(+)}=D_0$ being the diffusion coefficient of free monomer particles and $D_{\infty}^{(P)}/D_0 \approx 10^{-2}$. $E^z(x)$ is an energetic parameter and $T^{(\alpha)}(x)$ the VTF-temperature. One important observation is that both $D^{(+)}$ and $D^{(P)}$ are reduced when we increase the amount of ions. This is to be expected from the assumptions of our model, since an ion which binds to an X -bead of the chains will reduce the chain mobility. As a consequence, we observe that VTF-temperatures $T^{(\alpha)}(x)$ increase with x , as displayed in Fig. 3. Generally, the VTF-temperature represents a lower bound to the glass transition temperature T_g . Our simulations with respect to the diffusion of chains are therefore consistent with the experimentally observed increase in T_g with the ion content [10,11]. Yet one has to be aware of the fact that experimentally the difference between both temperatures, $T_g - T^{(\alpha)}$, may not remain constant during the variation of system parameters [12]. Interestingly, for weakly doped polymers with $x \ll 1$ the VTF-temperatures $T^{(P)}$ and $T^{(+)}$ roughly coincide, indicating a strong coupling between ions and chains. However, as the number of ions becomes comparable to or larger than the number of X -beads ($x \geq 1$), ion and

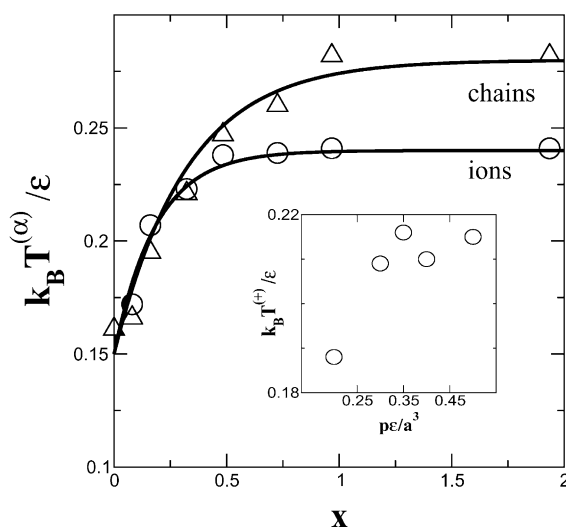


Fig. 3. VTF-temperatures for chains and ions versus ion concentration x at fixed pressure $p=0.35\epsilon/a^3$. The inset shows the variation of $T_0^{(+)}$ with pressure at $x=0.16$.

chain motions get decoupled (for a review see Ref. [13]), as seen from Fig. 3. The corresponding VTF-temperatures saturate for large x , with $T^{(+)} < T^{(P)}$, which means that for temperatures $T \sim T^{(P)}$ the ions maintain a certain mobility while the system of chains gets frozen. These results correctly describe experimental trends in the glass transition temperature of PEO-based electrolytes.

Fig. 4 displays the pressure-dependence of ionic diffusion constants for various temperatures in a semilogarithmic representation. Over the major part of the pressure range considered, we find an exponential decrease of $D^{(+)}$ with growing p ,

$$D \propto e^{-p/p_0(T)} \quad (2)$$

again in qualitative agreement with several experimental observations [14,15]. Note that the pressure ε/a^3 corresponds to a physical pressure roughly of the order of 1 kbar. This estimate is obtained by noting that $k_B T_g \sim k_B T^{(P)} \sim 0.2\varepsilon$, see Fig. 3, and by using experimental values $T_g \approx 200$ K for short chains and a bond length $a \approx 2$ Å. On the other hand, the steep rise of D with decreasing pressure for small p ($p \lesssim 0.1\varepsilon/a^3$) seen in Fig. 4 seems to be an artefact of our model, which contains only repulsive interactions among the chains. This causes an unrealistic volume expansion for small p so that the density falls below reasonable melt densities.

Comparing in Fig. 4 different isotherms for the diffusion coefficient, we observe that the character-

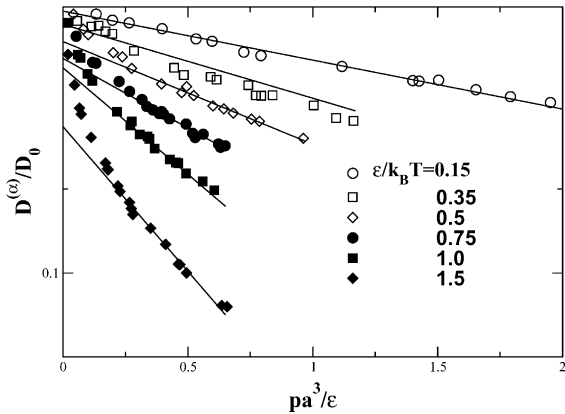


Fig. 4. Ionic diffusion coefficient $D^{(+)}$ on a logarithmic scale versus pressure for different temperatures.

istic pressure $p_0(T)$ significantly increases as temperature is lowered. This is to be expected from the T -dependence contained in the VTF-law (1). For a further analysis of Eq. (1) in combination with Eq. (2), we first note that in our model $T^{+}(p)$ is a weak function of pressure, see the inset of Fig. 3. Assuming $T^{+}(p)$ independent of p [14,15], compatibility of both Eqs. (1) and (2) requires that

$$E^{(+)} = E_0 + Ap; \quad (p_0(T))^{-1} = \frac{A}{T - T_0} + B \quad (3)$$

where E_0 , A and B are constants.² Our calculations for D as a function of p are, however, limited to $T \geq T^{(+)}$ so that Eq. (3) cannot be verified explicitly from the present data for $p_0(T)$.

4. Mapping of ion diffusion onto dynamic percolation theory

In a polymer electrolyte, the ions undergo hindered diffusion in a dynamically disordered environment where pathways continually rearrange due to the segmental motion of polymer chains. To account for this general aspect, several authors [1,16–18] have developed a dynamic percolation (DP) model. In contrast to the familiar problem of a random walk on a lattice in the presence of static percolative disorder [19], DP-theory is based on temporal renewals of disorder configurations. This means that the property of lattice bonds either to be open (allowing a step of the walker) or to be blocked will be reassigned in time according to stochastic rules. The most common assumption are global, instantaneous renewals characterized by some waiting time distribution $\psi(t)$ [16]. One central result of this theory is the following expression for the long-time diffusion coefficient of the walker in a 3-dimensional lattice

$$D = \frac{1}{6} \frac{\int_0^{\infty} dt \psi(t) \langle r^2(t) \rangle_0}{\int_0^{\infty} dt t \psi(t)} \quad (4)$$

where $\langle r^2(t) \rangle_0$ denotes the mean-square displacement for frozen disorder. In the special case of Poisson

² The analysis of Ref. [15] amounts to $B=0$.

renewal processes, we have $\psi(t) = \lambda e^{-\lambda t}$, and Eq. (4) reduces to the zero-frequency limit of the analytic continuation rule discussed in Ref. [1].

In this section, we perform a test of DP-theory in the case of an athermal model for diffusion of point-like particles and lattice chains, where only hard-core (excluded volume) interactions are taken into account. Clearly the quantity $\langle r^2(t) \rangle_0$ can be obtained in a straightforward manner from simulations of particle diffusion in the frozen network. To determine $\psi(t)$, we propose to consider a site i adjacent to some fixed position of the walker and to analyse the occupational fluctuations $\langle n_i(t)n_i(0) \rangle$ due to the motion of chain segments. These fluctuations reflect the opening and closing statistics of the bond connecting the walker with site i . Let us introduce, for $t \geq 0$, the probability $\Phi(t)$ that no renewal takes place within the time interval $[0, t]$ after a previous renewal at an arbitrary time $t_0 < 0$. The joint probability $\langle n_i(t)n_i(0) \rangle$ that the lattice point i is occupied both at $t=0$ and at some $t > 0$ (not necessarily by the same particle) consists of two distinct contributions. The first one is the probability that site i is occupied at $t=0$ and that no renewal occurs until time t , which is given by $c\Phi(t)$, where c is the mean occupation of a site. The second contribution describes the situation where one or more renewals have taken place until time t . The corresponding probability is given by $c^2(1 - \Phi(t))$. Hence,

$$\langle n_i(t)n_i(0) \rangle = c\Phi(t) + c^2(1 - \Phi(t)) \quad (5)$$

According to Ref. [16],

$$\psi(t) = \frac{1}{\lambda} \Phi''(t) \quad (6)$$

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

Simulations for the local correlation function $\langle n_i(t)n_i(0) \rangle$ can be carried out quite efficiently. Using Eq. (5) we obtain $\Phi(t)$ whose decay is clearly non-exponential and slows down when chains get longer (see Fig. 5a). Eq. (6) then yields the waiting time distribution $\psi(t)$ which we insert into Eq. (4) to obtain the DP-approximation for D . To discuss its dependence on the concentration c , we introduce the correlation factor

$$f(c) = D(c)/(1 - c) \quad (7)$$

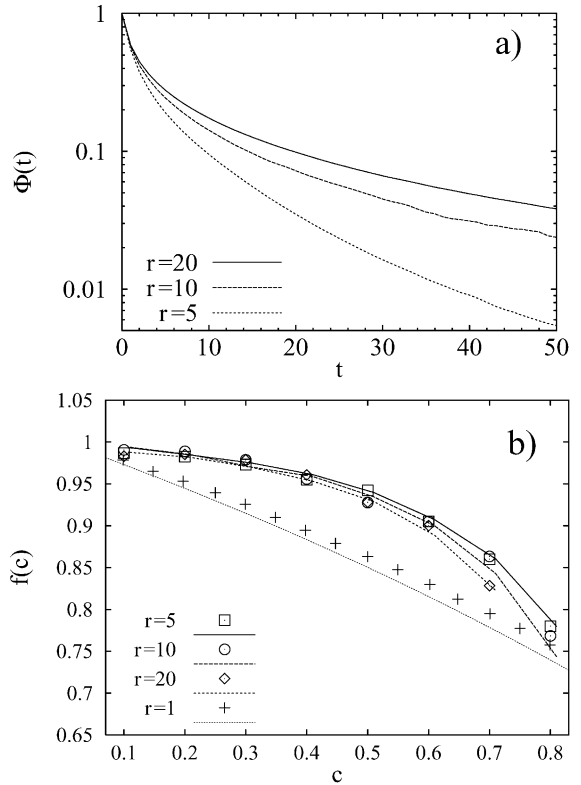


Fig. 5. (a) Probability $\Phi(t)$ (see text) versus time for varying chain lengths ($c=0.4$), illustrating the non-Poisson character of renewal events. (b) Comparison of concentration dependent correlation factors $f(c)$ for different chain lengths from DP-theory (data points) and from full simulations (lines). The case $r=1$ corresponds to tracer diffusion in the hard core lattice gas.

As seen from Fig. 5b, $f(c)$ as a function of c nicely agrees with simulation results for the complete system dynamics. It turns out that a single-exponential approximation for $\Phi(t)$, which would reflect Poisson-distributed renewals, is not sufficient to obtain accurate correlation factors. Indeed, setting $\Phi(t) = e^{-\lambda t}$ with λ determined either from the actual initial slope, $\lambda = \Phi'(0)$ or from the average relaxation time $\lambda^{-1} = \int_0^\infty \Phi(t)dt$, one would obtain correlation factors quite close to the hard-core lattice gas result ($r=1$), which is also shown in Fig. 5b for comparison. Temporal correlations in the renewal steps therefore have to be taken into account and their importance increases with growing chain length r .

5. Summary and conclusions

We have shown that a coarse-grained model of lattice-chains and pointlike particles based on simplified chemical interactions can account for several diffusion properties characteristic to PEO-type electrolytes. This includes VTF-behaviour of diffusion constants for chains and ions, an increase of VTF-temperatures with the ion content x and decoupling between ion and chain motions for large x . Thereby we focused on controlling the pressure p in our algorithm. By this we were able to deduce also an exponential decrease of ion diffusion constants with increasing p . On a qualitative level, these results compare favorably with several experiments.

Aiming at an even more coarse-grained description of ion transport in polymer electrolytes, we proposed a mapping of the coupled problem of ions and lattice chains onto DP-theory. Explicit calculations were carried out for an athermal system, suggesting that DP-theory yields a quantitative description of diffusion, provided the non-Poisson character of renewal events originating from the dynamics of chain molecules is properly taken into account.

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