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Monte Carlo study of diffusion in polymer electrolytes

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Abstract

Polymer chain and ion dynamics properties are investigated in a lattice model of polymer electrolytes, which emphasizes the difference in cation–polymer and anion–polymer interactions. The assumption of specific binding sites for cations on the chain molecules leads to a reduction of chain mobilities, which in turn suppresses diffusion of ions. We find a correlation between cation and chain diffusion constants, both of which closely follow a Vogel–Tammann–Fulcher (VTF) law with a common VTF-temperature, which increases with ion concentration. These findings are discussed in connection with recent experiments revealing a salt-induced change of the glass transition temperature and a pronounced asymmetry in the cation and anion diffusion constants. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Chain polymers containing ether-groups in their repeat units, such as PEO or PPO, are known to dissolve some salts, as a consequence of a difference in cation–polymer and anion–polymer interactions. Above their glass transition temperatures such polymer–salt solutions can show significant ionic conductivities [1]. The investigation of ion transport mechanisms including the detailed interplay between ionic and polymeric degrees of freedom has remained an active area of research, which has important implications with respect to the design of polymer electrolyte materials suitable for application in electrochemical devices [2].

In this communication we investigate a lattice model of an ion–polymer mixture. Interactions among all molecular units in the model, namely polymer beads and ions, are taken into account. The essential ingredient, which introduces the

mentioned fundamental asymmetry in the behaviour of cations and anions, are specific beads on the polymer chains which attract cations. This feature of the model mimics the role of the effective negative charge on the oxygen atoms in PEO- or PPO-based electrolytes. Our model is an extension of previous work by Olender et al. [3,4] who considered a single solute particle embedded in a polymer host. Using Guggenheim's quasichemical approximation in connection with simulation methods these authors could explain certain unexpected experimental trends [5] with temperature in ion solvation and dissociation equilibria, as a result of a reduction of chain entropies due to cation–chain interactions.

Here we consider diffusion properties, assuming chain lengths substantially shorter than the entanglement length. The first question we address is chain diffusion, which is shown to follow the Vogel–Tammann–Fulcher (VTF) law. Upon addition of ions chain mobilities are found to be reduced. This effect manifests itself experimentally in an increase of the glass transition temperature, T_g .

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Clearly, this question is important in view of the fact that high ionic conductivities are expected only at temperatures sufficiently above T_g . Moreover, to get further insight into factors determining the ionic transport we study the detailed correlation between ionic and chain diffusion constants.

2. Model

The system we consider consists of N_p lattice chains of equal length r (self-avoiding walks with r steps) and N_I point particles, cations and anions of equal number, $N_+ = N_- = N_I/2$. Ions and the elementary beads of the chain molecules occupy sites of a simple cubic lattice with spacing a . In our simulations at constant volume the system is confined in a cube of size La , and periodic boundary conditions are employed. The total concentration of occupied lattice sites therefore is $c = c_p + c_I$, with $c_p = rN_p/L^3$ and $c_I = N_I/L^3$. All beads of the chains (irrespective of their nature, see below) repel each other with a common strength $\epsilon > 0$. Although this choice for bead–bead interactions seems somewhat artificial from a microscopic point of view, we use it here to model in a simple manner the possibility of a continuous freezing transition of the system of chains, when temperature is decreased, see Section 3. With respect to their interactions with ions we distinguish two kinds of beads, namely C-beads which do not interact with ions, apart from the site exclusion requirement, and X-beads, which attract cations with strength $-\epsilon_0 < 0$ and repel anions with strength ϵ_0 . All these interactions only act between nearest neighbours. In addition we include Coulomb forces between the ions carrying charges $\pm q$. To reduce the number of interaction parameters in our model, we assume here for simplicity that $q^2/a = \epsilon_0 = \epsilon$.

In analogy to PEO-based polymer electrolytes our chain molecules have the form $C(XCC)_n$ such that $r = 3n + 1$. Most of our calculations are done for short chains with $r = 13$. The dynamics of these chains is affected by kink-jump, end-jump and crankshaft moves, as described in Ref. [6], while ions perform nearest-neighbour hops. Terminal sites in all cases must be vacant. The probabilities for these elementary moves are chosen according

to the Metropolis algorithm. For generating thermalized initial configurations we use the configurational bias method [7,8].

3. Simulation results

Our first objective is the long-time diffusion constant of the chain molecules, to be obtained from the time-dependent mean-square displacement of their center-of-mass, $\mathbf{R}_i(t)$; $i = 1, \dots, N_p$,

$$D^{(p)} = \lim_{t \rightarrow \infty} \frac{1}{6tN_p} \sum_i \langle (\mathbf{R}_i(t) - \mathbf{R}_i(0))^2 \rangle. \quad (1)$$

Because of the repulsive bead–bead interactions in our lattice system, a pronounced short-range order in the pure polymer solvent ($N_I = 0$) develops at concentrations close to $c_p = 0.5$, which suppresses diffusion. Since we want to simulate an amorphous system without ordering effects we choose a somewhat smaller concentration $c_p = 0.403$ ($N_p = 31$). Fig. 1 shows the diffusion constant, $D^{(p)}$, on a logarithmic scale normalized with respect to the diffusion constant, D_0 , of non-interacting point particles, as a function of the inverse temperature. In the temperature range considered

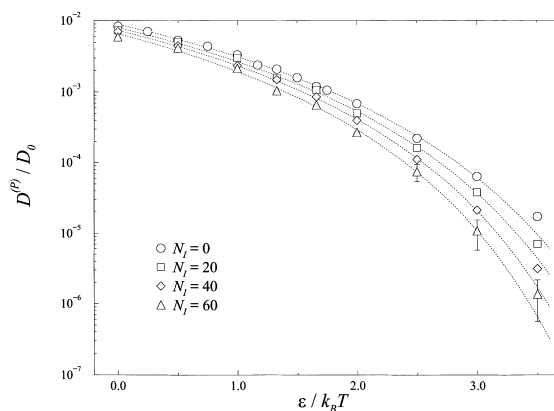


Fig. 1. Temperature dependence of the center-of-mass diffusion constant $D^{(p)}$ (Eq. (1)) of chains ($N_p = 31$, $r = 13$) at constant volume ($L = 10$) for various salt concentrations $c_I = 0, 0.02, 0.06$ (corresponding to $N_I = 0, 20, 60$). D_0 denotes the diffusion constant of a single free particle on the lattice and the dotted lines represent VTF fits according to Eq. (2) (For parameters see Table 1). The typical size of error bars indicated for $N_I = 60$ applies to all data sets.

$D^{(P)}$ varies over about three orders of magnitude in a manner which is well described by the VTF law of the general form

$$D(T) = D_{\infty} \exp \left[-\frac{B}{k_B(T - T_0)} \right]. \quad (2)$$

Here D_{∞} represents the diffusion constant for $T \rightarrow \infty$, and B is an energetic parameter that in comparison with $k_B T_0$ determines the fragility of the system. T_0 denotes the Vogel–Fulcher temperature, for which we find in the case of polymer chain diffusion $k_B T_0^{(P)} \simeq 0.157\epsilon$. This kind of temperature dependence in our model of chains corresponds to the well-known experimental behaviour of fragile glass-forming systems. Upon adding ions ($N_I \neq 0$) the diffusion constant of chains decreases, as seen from the additional data in Fig. 1 for three different ionic concentrations in the range $0.02 \leq c_1 \leq 0.06$.

Concerning the behaviour of $D_{\infty}^{(P)}$, this decrease is merely a consequence of having additional blocked sites. Generally, however, $D^{(P)}$ depends on c_1 more strongly than one would expect merely from site blocking. It turns out that the decrease of $D^{(P)}$ with temperature in that range of c_1 s can again be represented by the VTF-law. Evidently, the VTF-temperatures, $T_0^{(P)}(c_1)$, increase with the ion concentration, c_1 , see the parameters in Eq. (2) as a function of c_1 as listed in Table 1. These findings clearly indicate an increased rigidity of the polymer network under addition of ions, an effect which is consistent with the idea that cations provide crosslinks between chains due to bond formation with X-beads. In an earlier study of a simplified model, which involved only one species of point particles, we have shown that for even larger ion-polymer interactions ($\epsilon_0 > \epsilon$) the T -de-

pendence of $D^{(P)}$ becomes more like an Arrhenius function [9].

It is generally observed that polymer rigidity increases with salt content [2,10]. McLin et al. [11] have reported that the glass-transition temperature, T_g , of solutions of LiClO₄ in PPO increases with salt content for molar fractions of salt less than about 0.3. The trend which we find for $T_0^{(P)}(c_1)$ in our model appears to be consistent with these experiments.

We next turn to ion diffusion and its dependence on temperature and ion concentration. Results are shown in Fig. 2. Again we observe a VTF dependence. Cation and anion diffusion differ, thus indicating two distinct transport mechanisms for each ion type. First of all, at low temperatures anion diffusion is much faster than cation diffusion, in agreement with recent diffusion

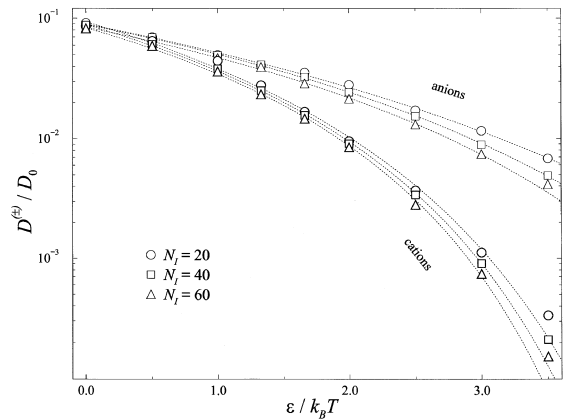


Fig. 2. Selfdiffusion constants D_{\pm} of ions as a function of inverse temperature for the same systems as in Fig. 1. Thin and thick symbols refer to anions and cations, respectively. Statistical errors are of the order of the symbol size.

Table 1

Parameters of the VTF – fits according to Eq. (2) for the diffusion of chains (Fig. 1) and ions (Fig. 2). In these fits data points for $\epsilon/k_B T = 3.5$ were omitted. Errors in VTF parameters are estimated to be about 5%

N_I	$D_{\infty}^{(P)}$	$B^{(P)}/\epsilon$	$k_B T_0^{(P)}/\epsilon$	$D_{\infty}^{(-)}$	$B^{(-)}/\epsilon$	$k_B T_0^{(-)}/\epsilon$
0	8.89×10^{-3}	0.879	0.157	–	–	–
20	8.10×10^{-3}	0.922	0.163	8.97×10^{-2}	0.493	0.094
40	7.40×10^{-3}	0.944	0.175	8.86×10^{-2}	0.497	0.115
60	6.80×10^{-3}	0.975	0.184	8.43×10^{-2}	0.503	0.127

studies by Vincent [12] on PEO-based electrolytes with low salt concentration, using the pulsed-field gradient nuclear magnetic resonance technique. These experiments also revealed the trend, that diffusivity of either ionic species decreases if the salt concentration is increased, which agrees with our data in Fig. 2. Closer analysis of this data yields a VTF temperature, $T_0^{(+)}(c_1)$, for the cations nearly identical with $T_0^{(P)}(c_1)$ for the three concentrations c_1 , whereas the corresponding quantities, $T_0^{(-)}(c_1)$, for anions are much less, see Table 1. These effects allow us to conclude that cation motions and chain motions are correlated, whereas anions are less strongly coupled to the chains, a fact, which is intuitively clear from the opposite signs of cation- and anion-polymer interactions in our model. Nevertheless, we do observe a dependence of $T_0^{(-)}$ on c_1 . Since the overall ion concentration in our model is always small direct interaction effects among ions remain negligible, so that the observed c_1 -dependence of $T_0^{(-)}$ again is due to the stiffening of the polymer network under the addition of ions.

These aspects of ion-chain correlations become even more transparent, when we eliminate temperature and instead regard $D^{(\pm)}$ as functions of the chain diffusion constant, $D^{(P)}$. For cations the double-logarithmic plot in Fig. 3 infers a relationship of the form

$$\frac{D^{(+)}(T)}{D_0} = \alpha_+ \left[\frac{D^{(P)}(T)}{D_0} \right]^{n_+}, \quad (3)$$

which holds over at least three decades in $D^{(P)}$. Eq. (3) implies that $T_0^{(+)} = T_0^{(P)}$. The exponent, n_+ , is near unity for the dilute system with $c_1 = 0.02$, and becomes smaller as c_1 increases. Combination of Eq. (3) with the VTF representation for $D^{(P)}(T)$, see Eq. (2), and an analogous expression for $D^{(+)}(T)$ yields the relation $B^{(+)} = n_+ B^{(P)}$. These findings confirm that the behaviour of the diffusion constant, $D^{(+)}$, follows the slowing down in the polymer network dynamics as one decreases temperature and approaches T_g .

A different behaviour is observed for anion diffusion. Actually the plot in Fig. 3 shows that anion diffusion constants tend to fall on a common curve and hence depend both on temperature and ion concentration through $D^{(P)}$. In other words it appears that only one parameter is needed to describe the influence of the polymer network dynamics on the anion diffusion constants. This situation is reminiscent of the dynamic bond percolation (DBP)-model proposed long ago in connection with ionic transport in polymer electrolytes [13]. This model is based on diffusion of a single particle on a lattice containing a fraction, p , of randomly blocked bonds, but bond configurations are renewed in successive, independent steps at a rate determined by a certain renewal time, τ_R . Note that in attempting to establish a closer connection between anion diffusion in the present model and the DBP-model, involving the assumption $\tau_R^{-1} \propto D^{(P)}$, we would have to choose p larger than the threshold concentration p_c since $D^{(-)}$ seems to remain finite as $T \rightarrow T_0^{(P)} (\tau_R \rightarrow \infty)$.

4. Summary

A lattice model for polymer electrolytes has been studied where chain molecules consist of two types of beads, called ‘‘C’’ and ‘‘X’’. ‘‘X’’-beads are assumed to attract cations and thus mimic the role of the electronegative oxygen atoms in PEO-based complexes.

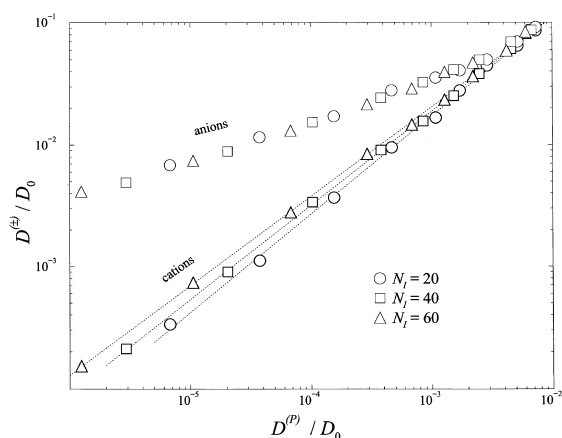


Fig. 3. Selfdiffusion constants D_{\pm} of ions plotted against chain diffusion constants D_P . For cations one observes a power-law relationship, see Eq. (3) as represented by the dashed curves.

Diffusion constants for the center-of-mass motion of polymer chains and for both species of ions are found to be consistent with the VTF-law. VTF temperatures, $T_0^{(P)}(c_1)$, for the chains increase with the amount of ions, which agrees with the experimental trend in the glass-transition temperature as a function of ion concentration.

While the VTF-temperatures for cation diffusion satisfy $T_0^{(+)}(c_1) \simeq T_0^{(P)}(c_1)$, which reflects strong coupling between cation motions and the center-of-mass motion of chains, the VTF temperatures for anion diffusion are substantially lower, $T_0^{(-)}(c_1) < T_0^{(P)}(c_1)$. Moreover, anion diffusion constants $D^{(-)}$ can be represented as a unique function of $D^{(P)}$ for all temperatures and ion concentrations studied. We conclude that $D^{(-)}$ is determined by just one parameter characterizing the network dynamics, in agreement with dynamic bond percolation ideas.

The above analysis is restricted to relatively short chains, much shorter than the entanglement length. In the opposite case of long chains we expect the ion diffusion to be decoupled from the (nearly) frozen center-of-mass motion of chains, but mediated by the local motion of polymer segments [12,14]. This situation, however, is outside the scope of our present investigation.

Acknowledgements

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