Model studies of diffusion in glassy and polymer ion conductors

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ABSTRACT

Ion–conducting glasses and polymer systems show several characteristic peculiarities in their composition–dependent diffusion properties and in their dynamic response. First we give a brief review of the current understanding of the ion dynamics in network glasses in terms of stochastic theories. Secondly, a model for PEO(polyethylene-oxide)–based polymer electrolytes is described. The equation of state is calculated from the quasichemical approximation. Using this information together with Monte Carlo simulations of diffusion at constant volume, we obtain constant–pressure results for polymer chain and ion diffusion as a function of ion concentration. This theory allows us to make comparison with experiments which are carried out at constant pressure.

1. INTRODUCTION

Ion conducting glassy[1–3] and polymeric[4,5] materials show a large variability in their chemical composition, local structure, ion diffusion properties and in many other physical properties.[6] Investigation of these amorphous systems and of the relevant ion transport mechanisms thus constitutes a wide and active area of research.

Generally, ion migration in these materials is connected with slow relaxation processes on time–scales much larger than microscopic times. A well-known example occurs in glasses, whose low–frequency dynamic response appears to slow down continuously as temperature is lowered.[7,8] A quite different situation is known for polymer electrolytes, where ions are strongly coupled to the polymer network. Therefore, ion diffusion slows down and gets almost suppressed when approaching the glass transition temperature.[9,10] Theories, which aim at a description of ionic motions on such extended time–scales, will have to eliminate all fast (e.g. vibrational) degrees of freedom from the outset. One then arrives at coarse–grained models based on stochastic ionic moves in an environment that reflects the characteristic local structure of the system.

Adopting this point of view, we shall first focus on several transport anomalies in glasses and discuss the respective state of stochastic modelling (section 2). In section 3 we introduce a lattice model for polymer electrolytes which emphasises the mutual influence of ion and polymer chain dynamics.[11,12] Monte Carlo simulations of diffusion in an (NVT)–ensemble will be supplemented by calculations of the equation of state via the quasichemical approximation (QCA) in the version of Guggenheim[13] and Barker.[14] Combination of both methods will enable us to obtain transport properties in an (NpT)–ensemble. Consideration of a constant pressure p is important when comparing theory with experimental trends under varying composition, such as the increase in the glass transition temperature or the decrease in ionic mobilities upon adding salt.[10,15]

2. ION TRANSPORT ANOMALIES IN GLASSES

Alkali–doped network glasses (oxide- or sulphide–glasses, like the systems $M_2O - SiO_2$ or $M_2S - SiS_2$, where M represents the alkali ion) exhibit several peculiar features in their diffusion properties:

i) The activation energy $E(c)$ for dc–transport markedly decreases with increasing alkali concentration c for dilute systems (small c), while it saturates for strongly doped samples. This behaviour results in a very sensitive c–dependence of the ambient–temperature dc–conductivity.[2]

ii) The Haven–ratio $H(c)$ shows a steep decrease with c and also saturates for larger c.[16]

iii) Conductivity dispersion is an important effect where, apparently, different mechanisms are active. At lower frequencies, Jonschers' 'universal ac–response' applies (power–laws in frequency, with exponents $n_\sigma \simeq 0.6$ to 0.7[17,18]), while at high frequencies one observes a 'nearly constant–loss'–type response, characterized by an exponent $n_1 \simeq 1$.[8,19] When temperature gets lowered, the latter process dominates the conductivity spectra.

iv) Dynamical processes which govern the ac–conductivity spectra also manifest themselves in quasi–elastic neutron scattering, ultrasonic attenuation and nuclear–spin relaxation.[20]

v) Mixed–alkali systems, e.g. $(Na_2O)_x(K_2O)_{1-x}$–SiO_2, show a highly nonlinear dependence of Na– and K–diffusion constants and of other physical properties on the ratio of mixing x.[21]

Up to now, no theory exists that accounts for all of these features. Nevertheless, deeper insight into their microscopic origin has emerged from specific model studies. Here, we only briefly address some of the most recent approaches and refer the interested reader to the original literature.

Properties of dispersive transport and composition–dependent effects in single–alkali glasses can be understood with reasonable accuracy from stochastic lattice gas models based on structural disorder and Coulomb–interactions.[22-24] In particular, the 'counter–ion model' has proved successful in explaining the behaviour of weakly doped glasses.[25] It also proposes a mechanism for the 'nearly constant loss' response in terms of correlated, dipolar reorientation processes.[26] On the other hand, for explaining mixed–alkali–effects, a quite different approach in terms of the 'dynamic structure model' has been suggested, which involves the concept of lattice mismatch and a dynamical adjustment of the local structure to each ionic species.[27,28] The design of a unique model by a proper combination of these ideas remains a task of future research.

3. LATTICE MODEL OF POLYMER IONIC CONDUCTORS

As pointed out in the Introduction, ionic and network degrees of freedom in polymer ionic conductors are strongly coupled and influence each other in a fundamental way. For example, in PEO (polyethylene–oxide)–based electrolytes, binding of cations to the electro–negative oxygen atoms in the chain molecules can introduce crosslinks into the polymer network. Local fluctuations of chains, which are essential for providing open pathways for the ions, therefore get reduced and ionic mobilities decrease. At the same time the network viscosity rises. Clearly, with increasing ion concentration c these effects get enhanced, but they are expected to saturate when the number of cations approaches the number of binding sites. Some of these aspects have been studied recently with the aid of stochastic models consisting of an interacting system of lattice chains and two species of point particles, representing cations and anions, respectively. Details of this model and the simulation technique are described in Ref..[11] Our aim here is to investigate a somewhat simplified model which contains only one species of point–particles ("ions") which can bind to the chains. This simplification, of course, ignores all features connected with anion diffusion, yet it allows us to investigate the profound influence of ions on the polymer network rigidity. In addition, it greatly facilitates the problem to convert results for diffusion at constant volume to the corresponding results for constant pressure. This will enable us to describe experiments on polymer electrolytes under varying salt content, which normally are carried out under constant pressure.

The model we consider involves lattice polymer chains (on a simple cubic lattice of spacing a) which consist of two types of beads, C–beads which do not interact with the point–particles and X–beads which attract point–particles with strength ϵ. In analogy to PEO the sequence of beads is taken as $C(XCC)_n$, so that the length of chains is given by $r = 3n + 1$. Throughout this work we assume $r = 13$. All the beads repel each other with a common strength, which again is taken as ϵ. In our simulations, see section 5, the equilibration procedure and the rules for elementary chain and ion motions are taken as in Ref..[11]

4. EQUATION OF STATE

To extract the pressure from Monte Carlo runs for a lattice system normally is a difficult task, although several methods are known in principle.[29–31] One reason is the problem of thermalization following a stochastic volume change. Therefore, with respect to the equation of state of our model, we shall rely on the quasi–chemical approximation (QCA), which requires solving a set of nonlinear equations for the quantities N_{ij}, which denote the number of nearest neighbour pairs consisting of molecules of type i and j. The version by Barker,[14] which we adopt here, allows us to deal with heterogeneous chains as described in the foregoing section.[32]

Rather than going into details, we merely give the final result for the pressure p, obtained from

$$-\frac{pa^3}{k_B T} = \ln\left(\frac{N_0}{M}\right) + \frac{z}{2}\ln\left(\frac{2N_{00}M}{zN_0^2}\right) \qquad (1)$$

Here M, N_0 and N_{00} denote the numbers of lattice sites, vacant sites and vacancy pairs, respectively, to be calculated from the QCA–equations as a function of the numbers of molecules and temperature.

Isobars for different numbers of ions are shown in Fig. 1 at a fixed (reduced) pressure $pa^3/\epsilon = 0.35$. When we add ions at a high temperature, the system swells, but the amount of swelling is less than what one would expect for non–interacting point particles. This, clearly, is a consequence of the attractive ion–polymer interaction, which even leads to a reversed trend at low temperatures (see Fig. 1). Let us remark that inclusion of anions in an extended model would favour a volume increase.
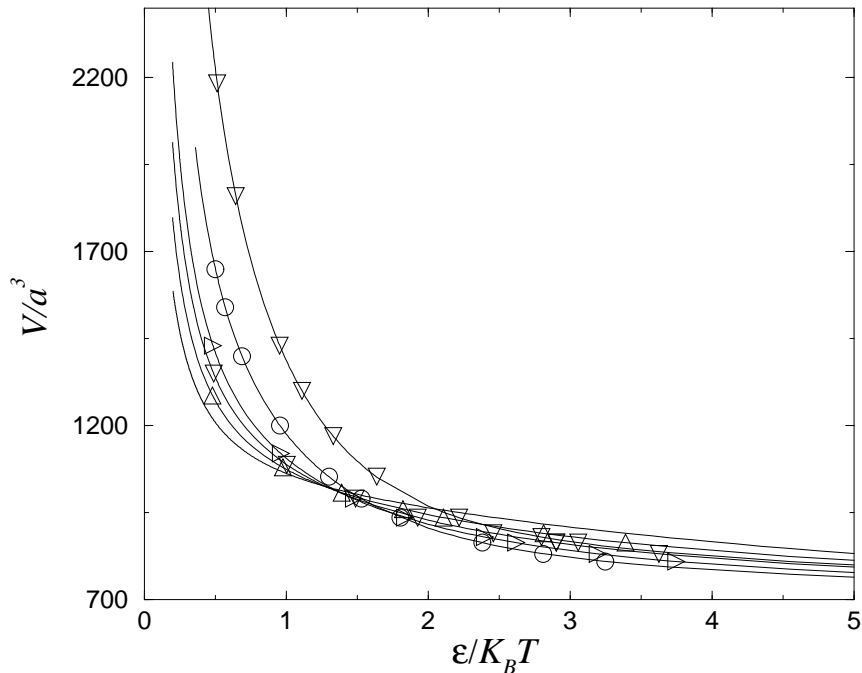

Figure 1: QCA–isobars ($pa^3/\epsilon = 0.35$) for different concentrations of point particles. Values for volume and temperature indicated by special points are used in the simulations for $D^{(P)}$ and $D^{(I)}$ shown in Fig. 2. At high temperatures ($\epsilon/k_B T \lesssim 1$) the different curves refer to (from below): $N_1 = 0, 20, 40, 60, 120, 240$.

5. DIFFUSION PROPERTIES UNDER CONSTANT PRESSURE

Next we turn to Monte Carlo simulations of the long–time diffusion constants $D^{(I)}$ and $D^{(P)}$ for ions and for the centres–of–mass of polymer chains, respectively. These quantities are deduced as usual from the corresponding time–dependent mean–square displacements.

Thereby we choose a system with $N_P = 31$ chains of length $r = 13$ and with a varying number N_1 of ions. Given a fixed pressure p and temperature T, we carry out these simulations by choosing a nearly cubic simulation box of size $L_1 \times L_2 \times L_3 = V(p, T)/a^3$ (with periodic boundary conditions) such that the volume $V(p, T)$ corresponds to that obtained from the QCA (see Fig. 1). Fig. 2 shows the T–dependence of both $D^{(I)}$ and $D^{(P)}$ at a pressure given by $pa^3/\epsilon = 0.35$ for various amounts of ions. As T goes to infinity, we approach the dilute limit ($V \to \infty$), and chain diffusion constants for different N_1 assume a common value (that corresponds to the athermal limit). As temperature is lowered, the different curves in Fig. 2 show a downward curvature of a form which is well represented by the Vogel–Tammann–Fulcher (VTF) law,
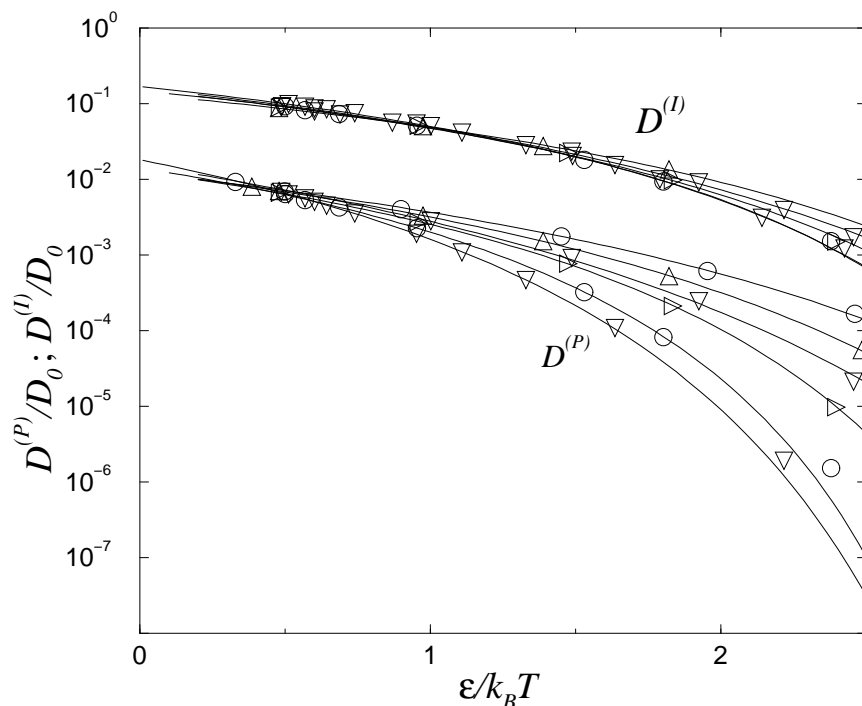

Figure 2: Simulated polymer chain and ion diffusion constants, $D^{(P)}$ and $D^{(I)}$, versus inverse temperature at a constant pressure, $pa^3/\epsilon = 0.35$. The different sets of data and (fitted) curves refer to different numbers of ions (from above): $(N_1 = 0(\bigcirc), 20(\triangle), 40(\triangledown), 60(\triangleright), 120(\bigcirc), 240(\triangledown)$. At a given temperature, the sizes of simulation cells were chosen according to the volumes deduced from the QCA, see the special points and corresponding symbols in Fig. 1. Continuous lines represent fits in terms of the VTF–law.

$$D^{(\alpha)}(T, N_1) = D_\infty^{(\alpha)} \exp\left(-\frac{E^\alpha(N_1)}{T - T^{(\alpha)}(N_1)}\right) \qquad (2)$$

Here α stands for I and P. The quantities $D_\infty^{(\alpha)}$ denote the diffusion constants at infinite temperature, $D_\infty^{(I)} = D_0$ being the diffusion constant of a free particle, and $D_\infty^{(P)}/D_0 \simeq 10^{-2}$. $E^\alpha(N_1)$ is an energetic parameter and $T^{(\alpha)}(N_1)$ the VTF–temperature.

A first important observation is that both $D^{(I)}$ and $D^{(P)}$ are reduced when we increase N_1, as a result of an increased number of cations which bind to the chains (X–beads) and possibly form crosslinks. As a consequence, we observe rising VTF–temperatures $T^{(\alpha)}(N_1)$, 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 therefore are consistent with the experimentally observed increase in T_g with the ion content. Interestingly, for weakly doped polymers ($N_1 \lesssim 60$), $T^{(I)}(N_1)$ and $T^{(P)}(N_1)$ roughly coincide, which is indicative of a strong coupling between ions and chains. However, as N_1 becomes comparable with the number of X–beads, which in the present case is $4N_P = 124$, the influence of N_1 on the ion and chain mobilities diminishes, as seen by comparing the data for $N_1 = 120$ and $N_1 = 240$ in Fig. 2. Simultaneously, the VTF–temperatures saturate, as shown in Fig. 3. At saturation, $T^{(I)} < T^{(P)}$, which means that for $T \simeq T^{(P)}$ the ions maintain a certain mobility while the system of chains freezes. The reason is that in the strongly doped regime only part of the ions will bind to the X–beads. These results correctly describe the experimental trend in the glass transition temperature of PEO–based electrolytes as a function of ion content in an appropriate regime of doping.[10,15] At even larger ion concentrations, however, the experimental T_g drops after passing a maximum. This is possibly due to ion clustering effects, not taken into account in the present model.
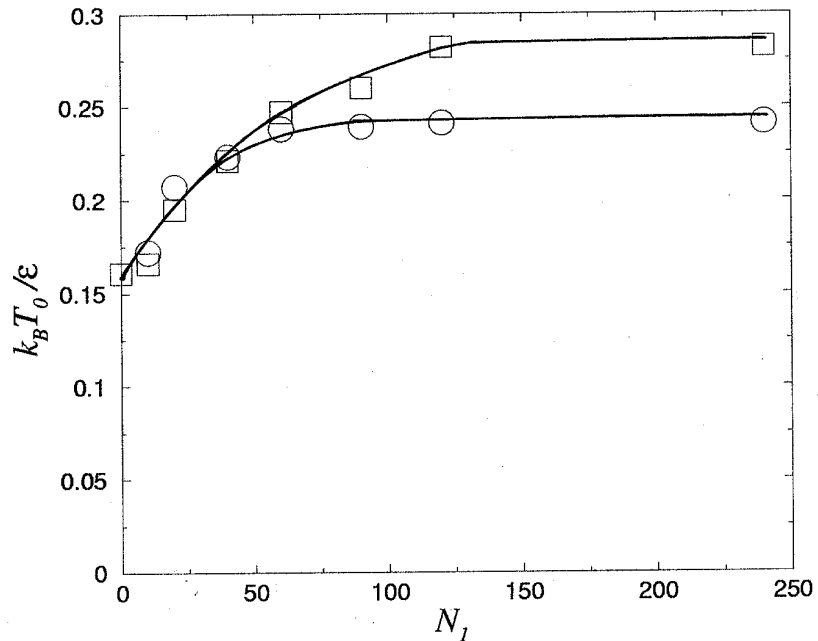

Figure 3: VTF–temperatures for ions ($T^{(I)}$) and polymer chains ($T^{(P)}$) versus the number of ions, as deduced from the data in Fig. 2. (Continuous lines are guides to the eye.)

6. SUMMARY AND OUTLOOK

Diffusion properties of amorphous solid electrolytes were discussed, emphasizing the actual capabilities of semi–microscopic (stochastic) models and Monte Carlo simulation to account for the experiments. Naturally, in this context we were interested only in experimental key features, which are common to many different materials.

After pointing out several characteristic ion transport properties of glasses together with successes and persisting problems in their theoretical understanding, we turned to a specific model for PEO–based polymer electrolytes. Composition–dependent diffusion properties and the tendency to undergo a glass–transition were studied under constant pressure. This was achieved by combining constant–volume simulations with the equation of state derived from the QCA.

The model we studied contains only one species of particles (cations) besides the polymer chains and hence does not allow us to investigate simultaneously the diffusion of anions. A simplified treatment of anion diffusion in an otherwise realistic model of a polymer electrolyte might be developed with the help of the concept of dynamic bond percolation.[33–35]

Acknowledgements

References

[1] C. A. Angell, Chem. Rev. **90**, 523 (1990)

[2] M. D. Ingram, Phys. Chem. Glasses **28**, 215 (1987)

[3] K. M. Shaju, S. Chandra, Solid State Ionics **86-88**, 453 (1996)

[4] F. M. Gray, "Solid Polymer Electrolytes" (VCH Publishers, New York, 1991)

[5] M. A. Ratner, D. F. Shriver, Chem. Rev. **88**, 109 (1988)

[6] Recent reviews are contained in:
"Superionic Solids and Solid Electrolytes", edited by A. L. Laskar and S. Chandra (Academic Press, 1989);
"High Conductivity Solid Ionic Conductors - Recent trends and applications", edited by T. Takahashi (World Scientific, Singapore, 1989)

[7] B. Roling, H. Happe, K. Funke, M. D. Ingram, Phys. Rev. Letters **78**, 2160 (1997)

[8] A. S. Nowick, A. V. Vaysleyb, Wu Liu, Solid State Ionics **105**, 121 (1998)

[9] P. G. Bruce, C. A. Vincent, J. Chem. Soc. Faraday Trans. **89**, 3187 (1993)

[10] J. Fan, R. F. Marzke, E. Sanchez, C. A. Angell, J. Non–Cryst. Solids **172-174**, 1178 (1994)

[11] P. Pendzig, W. Dieterich, A. Nitzan, J. Non–Cryst. Solids (1998), in press.

[12] R. Olender, A. Nitzan, J. Chem. Phys. **100**, 705; **101**, 2338 (1994)

[13] E. A. Guggenheim, "Mixtures" (Oxford, 1952)

[14] J. A. Barker, J. Chem. Phys. **20**, 1526 (1952)

[15] M. G. McLin, C. A. Angell, Solid State Ionics **53-56**, 1027 (1992)

[16] J. E. Kelly III, J. F. Cordaro, M. Tomozawa, J. Non–Cryst. Solids **41**, 47 (1980)

[17] A. K. Jonscher, "Dielectric Relaxation in Solids", (Chelsea Dielectrics Press, London 1983)

[18] K. Ngai, J. Non–Cryst. Solids **203**, 232 (1996)

[19] C. H. Hsieh, H. Jain, J. Non–Cryst. Solids **203**, 293 (1996)

[20] For a review, see K. Funke, Progr. Solid State Chem. **22**, 111 (1993)

[21] D. E. Day, J. Non–Cryst. Solids **21**, 343 (1976)

[22] P. Maass, J. Petersen, A. Bunde, W. Dieterich, H. E. Roman, Phys. Rev. Letters **66**, 52 (1991)

[23] J. Petersen, W. Dieterich, Phil. Mag. **65**, 23 (1992)

[24] P. Maass, M. Meyer, A. Bunde, Phys. Rev. B **51**, 8164 (1995)

[25] D. Knödler, P. Pendzig, W. Dieterich, Solid State Ionics **86-88**, 29 (1996)

[26] P. Pendzig, W. Dieterich, Solid State Ionics **105**, 209 (1998)

[27] P. Maass, A. Bunde, M. D. Ingram, Phys. Rev. Letters **68**, 3064 (1992)

[28] A. Bunde, M. D. Ingram, P. Maass, J. Non–Cryst. Solids **172**, 1222 (1994)

[29] R. Dickmann, J. Chem. Phys. **87**, 2246 (1987)

[30] A. D. Mackie, A. Z. Panagiotopoulos, S. K. Kumar, J. Chem. Phys. **102**, 1014 (1995)

[31] P. Pendzig, W. Dieterich, A. Nitzan, J. Chem. Phys. **106**, 3703 (1997)

[32] We have tested the QCA for a polymer electrolyte model with coordination number $z = 26$ against numerical simulations, which were based on the configurational bias method, as described by Siepmann et al..[36] It turned out that due to the neglect of three–particle and higher–order correlations in the QCA the volume is slightly overestimated, see W. Dieterich, O. Dürr, P. Pendzig, A. Nitzan, Proc. of the XI-th Max Born Symposium, "Anomalous Diffusion: from Basis to Applications", Ladek Zdroj, Poland (May 1998); Lecture Notes on Physics (Springer-Verlag), in press

[33] S. D. Druger, M. A. Ratner, A. Nitzan, Phys. Rev. B **31**, 3939 (1985)

[34] A. Nitzan, R. Granek, M. Ratner, J. Non–Cryst. Solids **131-133**, 1018 (1991)

[35] W. Dieterich, O. Dürr, P. Pendzig, A. Bunde, A. Nitzan, Physica A, in press

[36] J. I. Siepmann, D. Frenkel, Mol. Phys. **75**, 59 (1992)