diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

A Microscopic Flow Model Based on Brownian Dynamics for Simulating Ionic Diffusion in Glasses

G. Darricarrere, J. Dutour[1] and F. Henn

Laboratoire LPMC, UMR CNRS 5617, Université Montpellier II, Pl. E. Bataillon, 34095 Montpellier cedex 05, France.

1.Introduction

The model, based on Brownian dynamics, is a first attempt [1] to simulate long-range ion transport in a 2D-channel geometry in which the ion velocity and displacement are determined by simple rules and random fluctuations which account for the ion-ion repulsion and the thermal bath, respectively. The simulation reports the influences of the ion density, of the amplitude of the stochastic force and of the geometry of the 2D-channel on the diffusion regime. A system constituted of two different types of ions is also investigated and the effect of the ion mixture is clearly outlined. In spite of its simplicity, the model yields interesting results which can be qualitatively compared to some experimental behaviors often observed in ionic glasses or melts such as conductive channels, mixed alkali effects, phase separation, or more commonly diffusion processes related to complex relaxation mechanisms.

2. Results and discussion

Two significantly different time scales can be distinguished in the problem of ionic diffusion, i.e. the waiting time in a given potential well and the transition time to a neighbouring position. Commonly, the waiting times are much longer than the transition times. We propose a model which avoids this difficulty in the diffusion problem. The main idea is to remove completely the waiting times from the problem and to take into account only the transition times. Therefore, the whole interval of waiting time collapses to zero and only the escape from one position to another is modeled. This approach is as considering the attraction force exerted by the opposite charges of the rigid framework to be averaged out all over the surface of the 2D-channel during the simulation time scale. Thus, there is no potential minimum due to the framework. This simple "toy" model is constructed to artificially magnify the role played only by the couplings between the moving ions and the confinement geometry considered here.

One of the first consequences of the model can be observed on the velocity distribution when comparing the data obtained with two mean values of $<\vec{F}_{stoc}(t)>$, the stochastic force. It can be seen that the width of the distribution of the velocity amplitude decreases when the density N increases for the smallest value of $<\vec{F}_{stoc}(t)>$. On the contrary, at larger values of $<\vec{F}_{stoc}(t)>$ there is no more broadening of the distribution of the velocity amplitude. For large values of $<\vec{F}_{stoc}(t)>$, heterogeneity in the mobile ions subnetwork will occur. This kind of heterogeneity is often observed with flow

---

[1] Present address: IREM, Bat. Lavoisier 45 Avenue des Etats Unis 78035 Versailles, France

models and is like a phase separation. In the case of amorphous ionic solids, i.e. glasses or polymers, where ions are highly mobile, this heterogeneity is comparable to the existence of ion-rich domains connected to each other or to the microsegregation of alkali cations, as reported in oxide glasses, which is known to play a key role on cooperative hopping mechanism.

Ions of different masses and radii are also investigated. The dynamics of each ion type is simply made different by varying the mean amplitude of the stochastic force. We simulate two systems containing 150 and 100 ions, respectively, and with the molar fraction of ion 2 varying from 0 to 1. The ions 1 and 2 mass ratio is chosen equal to 3.28 as it would be if ions 1 and 2 were Na^+ and Li^+ cations, respectively. The evolution of the global diffusion *D*, i.e. the mean square displacement as calculated for all the ions, indistinguishably goes through a minimum with the molar fraction. It is also emphasized that the exact behavior of *D* is dependent on the total number of ions. Likewise, further calculations show that the behaviour of *D* can be strongly influenced by the different simulation parameters, i.e. the amplitude of the stochastic white noise and the difference between the intrinsic velocities of ions 1 and 2. Our model clearly demonstrates that a non linear behaviour of the diffusion coefficient could arise from the dynamics of such mixed-ion systems and not from structural consideration only. This trend is comparable, for instance, to the well known mixed alkali effect observed in ionic glasses, ionic polymers or ionic melts where the mixture of two different mobile cations leads to a strong non-linear behaviour of the ionic conductivity as a function of the molar fraction (fig.1). These results emphasize the role of ion-ion coupling on the ion diffusion dynamics in glasses. Some similarities can also be found with the Monte-Carlo simulation carried out where it is pointed out that ion cooperative motions can be involved in the mixed alkali effect observed in glasses.

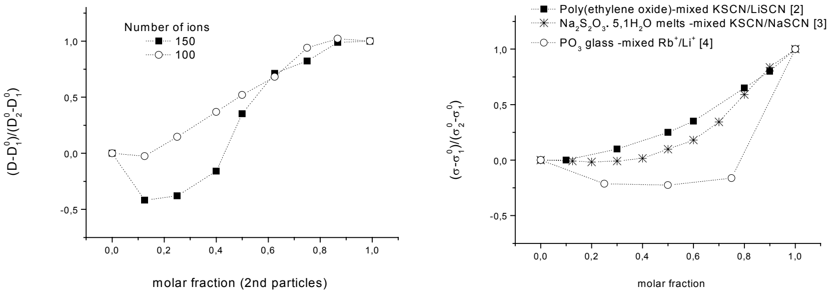

Fig.1: Qualitative comparison between simulated (a) and experimental (b) curves reporting the mixed cation effect.

References:

[1] F.Henn and j. Dutour, J. Non-Cryst. Solids, **351** (2005) in press

[2]S.S. Islam, K. Ismail, J. Chem. Eng. Data 35(1990)348

[3] M. Perrier, S. Besner, C. Paquette, A. Vallée, S. Lascaud, J. Prud'Homme, Electrochimica Acta 40(1995)2123

[4] C. Karlsson, A. Mandanici, A. Matic, J. Swenson, L.Börjesson, Phys. Rev.B 68(2003)064202