



Evidence of active regions for ion transport in lithium silicate glasses using the isoconfigurational ensemble. Part II



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ABSTRACT

In the context of the ionic transport in glasses, the concept of conduction channels (or pathways) has proved to be useful to rationalize both experimental and computational results. While the concept of a transport “channel” is well defined for crystalline solid conductors, for the case of glasses this concept mainly refers to a finite region of the sample (at least in the diffusive time scale) in which mobile ions have a convenient environment to perform the electrical transport.

In the previous work, we present an alternative way to put into evidence the existence of such regions in the diffusion time scale during a molecular dynamics experiment. In fact in that work [1] we use the so-called isoconfigurational ensemble method (ICEM) and the associated concept of particle propensity, both recently introduced by Harrowell and co-workers [2]. Then the notion of particle propensity to movement—immerse in the ICEM—was employed to find the existence of regions which are dynamically more active for the moving particles: the conduction channels.

In the present paper we provide more computational evidence to support our alternative way to make evident the existence of channels that we presented in [1]; we show in this paper that our procedure is exactly equivalent to the approach previously adopted by other authors in the literature. This coincidence between the two searching strategies allow us to add more information about the nature of the channels. In fact, we can state now for the first time that the existence of the channels is defined at the very beginning of the dynamics and they remain almost unchanged even in the diffusive (nanosecond) scale. Besides, it was shown that a channel is a region of a sample which is also highly correlated dynamically during the trajectory of the moving ions.

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1. Introduction

Lithium metasilicate glass proves to be a paradigmatic system for the study of charge transport in ionic conducting inorganic glasses. Several authors have shown in this system the existence—in the diffusional time scale—of preferred transport pathways for moving lithium ions which are responsible for charge transport. Well in contrast with crystalline solid electrolytes, pathways in glasses can be characterized in a statistical way due to the inherent complexity of these systems and the channel topology [3]. In our previous work we used the molecular dynamics (MD) formalism and the isoconfigurational ensemble method (ICEM) introduced by Harrowell and co-workers [2] as an alternative way to demonstrate the existence of these channels. The ICEM formalism is directly bounded to the notion of propensity to movement of the particles. Consequently, in our previous work we introduced the high propensity cluster (HPC) concept, which defines a topological region of the glassy matrix characterized by its high ability to promote the faster motion of lithium ions or channels for ionic transport.

The ICEM allowed us to put into evidence the existence of these pathways at the very beginning of the dynamical evolution of the system. Or—in other words—the exploration of the dynamics in the picosecond time window (40 ps) allowed us to predicate about the dynamics in the diffusional scale (here, the value of 40 ps corresponds to the time when the non-Gaussian parameter—which characterizes the deviation of the dynamics from the Gaussian behavior—reaches its maximum value t^* and defines a time interval in which the behavior of the system is dynamically heterogeneous [1,4,5]). Moreover, the analysis of the propensities at *different time intervals* supports the idea that for the present system the long time dynamics (diffusive) of the entire network is implicit in the short time scale [1].

Up to the present, channels were put into evidence in a direct manner. Jund et al. [6] and Heuer et al. [7] have respectively concluded about the existence of channels for ionic conduction in alkali silicates using MD simulations by analyzing a complete trajectory in the nanosecond scale (the diffusive behavior). Rao et al. [8] applying the bond valence formalism showed another alternative way of identifying ionic conduction channels. More recently it was shown that the complex multiparticle dynamics could be equivalently described as a single particle “vacancy” dynamics in a disordered energy landscape including all the information about Coulomb interaction [9].

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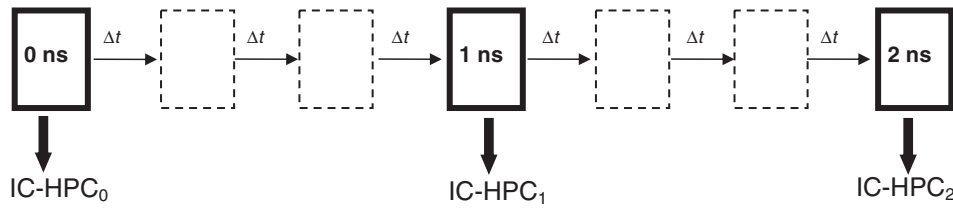


Fig. 1. Schematic representation of our procedure.

Then, this paper should be considered as a continuation of our first one [1]. In fact, the aim of the present work is to provide the necessary additional computational evidence to support that our alternative description of a channel using the IC is adequate. To accomplish this task we consider it necessary to address two remaining questions:

- I) Is the exploration of a narrow time window (picosecond) enough to define a HPC (channel) that is supposed to prevail in the diffusive (nanosecond) scale?
- II) Are these topological regions, involved in the dynamics of the diffusive scale (nanosecond), the channels for ionic transport as defined by other authors [7]?

The verified coincidence between the two searching strategies, derived from an affirmative answer to the two previous questions, validates our approach and consequently allows us to add more relevant information about the nature of the channels. In fact, we can now state for the first time that the existence of the channels is defined at the very beginning of the dynamics and they remain almost unchanged even well into the diffusive (ns) scale. Or, in other words, our findings

put into evidence the role of the early local structure conditioning the long time dynamics.

2. Methods and computational details

Molecular dynamics calculations were performed on a system of 3456 particles (1152 Li, 570 Si and 1728 O) in the same way as in our previous work [1]. Briefly, the containing box ensures that the density corresponds to the experimental density of the glass [10]. The system $\text{Li}_2\text{O-SiO}_2$ we employed consists of a three-dimensional ensemble of particles interacting by the pair potential of Gilbert-Ida type [11] including the r^{-6} term:

$$U_{ij}(r) = \frac{q_i q_j e^2}{4\pi\epsilon_0 r} - \frac{c_i c_j}{r^6} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right). \quad (1)$$

The parameters of the potentials used were derived on the basis of ab-initio molecular orbital calculations by Habasaki [10]. The system was prepared by putting the atoms on a cubic box and assigning to each atom velocities drawn from a Maxwell-Boltzmann distribution corresponding to a temperature of 3000 K. The Verlet algorithm with a time step of 1 fs was used to integrate the equations of motion. Simulations were performed at 700 K, on a cubic box with periodic boundary conditions using the LAMMPS package [12].

The system was then firstly equilibrated at 3000 K in a 2 ns run using the NVE ensemble. Then, to reach the working temperature, it was cooled down from 3000 K to its final temperature 700 K in 2 successive cooling steps. Each cooling step (from 3000 K to 2000 K, and from 2000 K to 700 K respectively) consists of a 2 ns run using a thermostat to decrease the temperature linearly in the NPT ensemble. Two intermediate periods of equilibration consisting of a 2 ns run in the NPT ensemble were included at 2000 K and at 700 K to verify no pressure and temperature drifts. After cooling the system, alternate runs of 100 ps each in the NVE and NVT ensemble were successively repeated to complete 2 ns. After that, the system was equilibrated in a 2 ns run using the NVE ensemble. Finally, after this careful equilibration procedure, trajectories of 2 ns length were generated in the NVE ensemble for analysis [1].

The ICEM developed by Harrowell and co-workers [2] was used in the present work. Briefly, one performs a series of equal length MD runs from the same initial configuration; that is, always the same structure but each one with different initial particle momenta chosen at random from the Maxwell-Boltzmann distribution at the chosen temperature. Accordingly, the propensity of a particle for motion in the initial configuration for a fixed time interval of length t , has been defined as [2]:

$$\langle \Delta r_i^2 \rangle_{\text{IC}} = \langle |\bar{r}_i(t) - \bar{r}_i(0)|^2 \rangle \quad (2)$$

where $|\bar{r}_i(t) - \bar{r}_i(0)|^2$ is the squared displacement of particle i in such time interval) and $\langle \rangle_{\text{IC}}$ indicates the average over the ensemble.

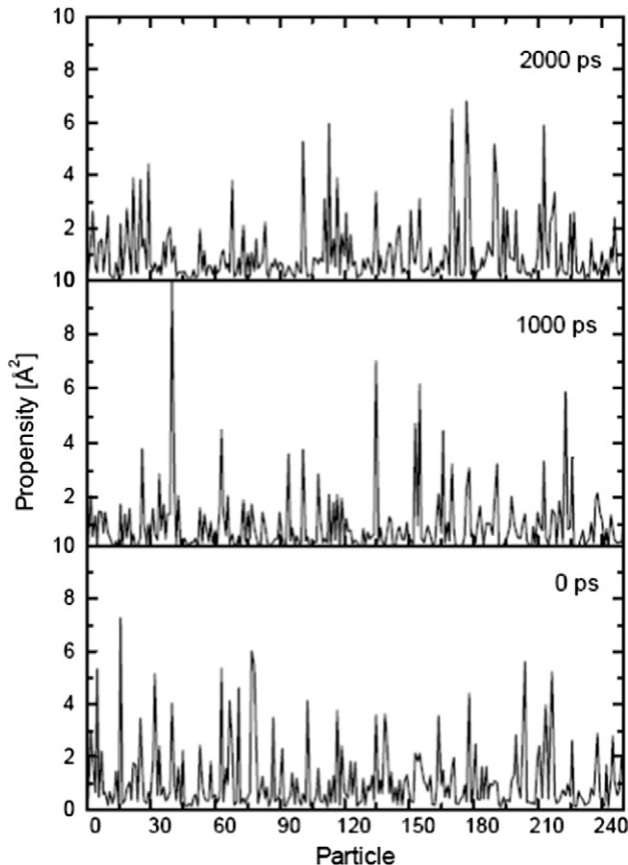


Fig. 2. Lithium ion propensity for 250 lithium ions selected at random at the experiments at 0, 1 and 2 ns respectively.

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