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# On the nature of the heterogeneous dynamics of ions in ionic conducting glasses ☆

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**Abstract**

Molecular dynamics simulations were performed to study the complex and heterogeneous dynamics of ions in ionically conducting glasses. The dynamics of Li ions in lithium silicate glasses have been characterized by van-Hove functions, fractal dimension of random walks, multifractal analysis of density profile, and principal component analyses of time series. Hierarchy dynamics with local and successive jumps, which are followed by cooperative jumps involving more ions, are observed in the self-part of the van-Hove functions and in trajectories where they form a multifractal density profile. Fractal dimensions of the random walks can be used to characterize the motions of ions in both the short and long length-scale regions. Difference between them becomes clearer in the glassy state, and the corresponding power law dependences of the mean squared displacements can be well explained by these exponents. Phase-space plot using the de-noised data obtained by principal component analysis reveals that the trajectory extending from the short time to the long time dynamics in the plot is continuous and has long term memory. The motion examined by the principal component analysis of the time series shows the deterministic character of the single particle ion dynamics. Each ion moves among domains of collective motion. Recurrence plot and mutual information function shows long correlation of the dynamics. Therefore, the cause of the dynamic heterogeneity is rather deterministic in nature.


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## 1. Introduction

Dynamics of ions in ion conducting materials show complex but universal properties, which are similar to many other systems such as glass-forming substances, colloidal glasses, turbulent flows, etc. This similarity suggests the existence of the common underlining dynamics [1]. One such similar property is the non-exponential and heterogeneous nature of the dynamics. Our goal is to characterize and understand the non-exponential and heterogeneous ion dynamics in an archetypal glassy ionic conductor, namely the lithium metasilicate system, which shows large fluctuation of the dynamics both in time and space. Molecular dynamics (MD) simulation is a useful technique that yields information on the dynamics of ions not accessible by experiments or theoretical models. We have carried out reliable MD simulations with the parameters derived from the *ab initio* molecular orbital calculation [2] and validity of the parameters was checked in a crystal structure under constant pressure conditions. If the quality of the parameters were not good enough, the structure would not be stable under such conditions. Thus the system is not only a realistic glass to recapture the commonly observed behaviors in experiments, but is also a model glass to explore other properties inaccessible by other means.

☆ I have a long and continuing collaboration with Kia Ngai in the study of the dynamics of ions in ionically conducting materials. It is a pleasure for me to contribute to the Festschrift honoring him an article to present extensions of the works that we have collaborated and published together in the past recent years.

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Dynamical heterogeneity [3,4] seems to be one of the common properties of relaxation and diffusion in many-body interacting systems including disordered ionic conducting materials. However, up till now, the definition of dynamic heterogeneity can differ widely from one researcher to another. In the present work, we focus our attention to the heterogeneous dynamics of diffusing ions in glassy Li metasilicates, $Li_2SiO_3$. Several methods are applied to characterize the heterogeneity of dynamics and, consequently the nature of the heterogeneity is made more precise. Fast and slow ions related to both temporal and spatial factors are coexistent in the ion conducting glasses. These basic features of heterogeneous dynamics are supplemented by new data which enable us to compare the power law exponents of mean squared displacement and the fractal dimension of random walks, to perform time series analysis of cooperative jumps of two ions, and to construct recurrence plots and averaged mutual information function. The MD simulation data obtained in previous works are also reexamined in conjunction with some additional data at longer time scales for the present purposes. The paper is organized as follows. In Section 2, the aforementioned methods used to analyze MD data are explained. The results are described in Section 3.

In Section 3.1, typical behavior of ions in the glassy state found in the mean squared displacement, the van-Hove self-correlation function, $G_s(r,t)$, and the non-Gaussian parameter are summarized for the $Li_2SiO_3$ system at several temperatures to show the macroscopic distribution of the heterogeneous dynamics.

In Section 3.2.1, temperature dependence of the power law exponents and its relation with the fractal dimension of the random walks are shown. Spatial character of the motion observed in the trajectories is characterized by the fractal dimension, which is a good measure of the complexity of the motion and is directly related to the power law behavior in the mean squared displacement.

In Section 3.2.2, the multifractal [5,6] nature of the dynamical potential surface, which is obtained from the accumulated positions of Li ions, is shown. Structures of jump path and ion sites are characterized by the singularity spectra $f(\alpha)$ [6], which are useful to characterize the spatial heterogeneity of the density profile. Localization of the particles depends on both the complexity of the trajectories and the jump paths.

In Section 3.3, deterministic character of ionic motion and correlated motions of two ions in the glassy state will be shown by the phase-space plots using the de-noised data by singular spectrum analysis (SSA) [7].

In Section 3.4, long time correlation of the dynamics has been shown by recurrence plots [8] and by averaged mutual information (AMI) [9], which is a generalized correlation function. Temporal heterogeneity of the dynamics is characterized by the recurrence plot.

In Section 3.5, collective motion on the landscape was examined by a multi-channel singular spectrum analysis (M-SSA) [7]. Each ionic motion can be reconstructed by the small number of principal components of collective motions.

The results obtained are collectively discussed in Section 4 and the conclusion is given in Section 5.

## 2. Molecular dynamics simulations of $Li_2SiO_3$

New molecular dynamics (MD) simulations were performed in the same way as in previous studies [2,10–15]. Contained in the unit cell are 144 Li, 72 Si and 216 O for $Li_2SiO_3$. The system with larger unit cell (3456 particles total) is also examined. The volume was fixed as that derived by NPT (constant pressure and temperature) ensemble simulation. Pair potential functions of Gilbert–Ida type [16] and $r^{-6}$ terms were used. The parameters of the potentials used were previously derived on the basis of *ab initio* molecular orbital calculations [2] and the validity of the parameters was checked in molten, glassy, and crystalline states. The glass transition temperatures obtained by $T$–$V$ relation was approximately 830 K.

### 2.1. Data analysis

Fractal dimension of the random walks ($d_w$) has been determined by the divider methods [17] in similar manner as previous work [15]. Total (or mean) counts $N$ to cover the trajectories of ions are plotted against the length of a ruler $L$ in double logarithmic scales. The relation $N = aL^{-d_w}$ holds well (where $a$ is a constant) in both regions of short (<3 Å) and long (>3–10 Å) length scales, and the values of $d_{w1}$ and $d_{w2}$ were obtained for short and long length scales, respectively.

Spatial heterogeneity of the density profile was characterized by a multifractal analysis using the singularity spectrum, $f(\alpha)$. A direct method of determining $f(\alpha)$ by Chhabra and Jensen [5] was applied to the pattern made by the ions during the MD runs [18]. Using an MD basic box divided into cells with size $\delta$, the probability $p_i = (n_i/N)$ of the cell is measured, where $n_i$ is the number of times Li ions visit the $i$th cell during the run and $N$ is the total number of $n$. The number $n_i$ is also used to visualize the structures.

When the measure $p_i$ can be represented like $p_i = \delta^{\alpha}$, Hausdorff dimension of $\alpha$ is $f(\alpha)$. If we count the $N'(\alpha)$, where the probability $p_i$ has singularity strength between $\alpha$ and $\alpha + d\alpha$, $f(\alpha)$ is the fractal dimension of the subsystem with the singularity strength $\alpha$, by

$$N'(\alpha) \sim \boldsymbol{\delta}^{-f(\alpha)}. \tag{1}$$

Spatial heterogeneity is presented by the $f(\alpha)$ spectra, while tempo-spatial heterogeneity can be characterized by the recurrence plots (RP) [8], in which we can observe the correlation in the dynamics in a colored pattern. RP is a technique for the qualitative assessment of time series described by Eckmann et al. [8]. One-dimensional time series (which are obtained by MD in a three-dimensional real space) from a data file is expanded into a higher-dimen-