diffusion-fundamentals

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

Anomalous Diffusion in Ionically Conducting Glasses

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1. Introduction

Molecular Dynamics Simulation has been done to clarify the complicated dynamics of ions in ionically conducting glasses. The system chosen was a lithium metasilicate which contains Li ions and networks composed of SiO_4 units.

2. Results and Discussions

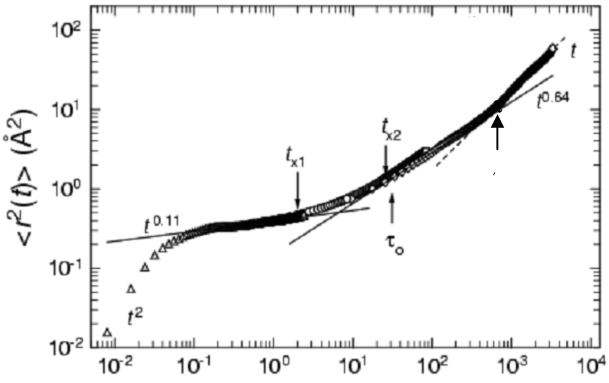

Fig. 1: Several time regions found in MSD of Li ions in Li_2SiO_3 glass at 700 K.

Several time regimes in mean square displacement (MSD) of Li ions, $<r^2>$, at 700 K are shown in Figure 1. At the very short times we see the ballistic motion that has $<r^2> \propto t^2$, followed by an apparent overshoot corresponding to the boson peak. At times 0.4 ps to 1.6 ps, there is an extended time regime that the MSD increases very slowly with time approximately as t^α with $\alpha \approx 0.11$, which is identified with the nearly constant loss (NCL). The properties of the NCL differ in many respects from the ion hopping transport contribution. Using the self-part of the van Hove function $G_s(r,t)$ of Li ions, we conclude that almost all ions are still within their cages in this region, although the contribution of jumps to MSD is non-negligible. The motions of the caged Li^+ ions are correlated with the matrix atoms, particularly the oxygen. In fact, the NCL and the accompanying Lévy distribution of length scales disappear if the oxygen atoms are frozen in a simulation. This suggests that the NCL originates from anharmonic interaction of the caged Li^+ ions with the surrounding matrix atoms executing correlated movements. The NCL as defined no longer holds after t_{x1}, as indicated in Fig.1 when the MSD deviates from the $t^{0.11}$-dependence. The process is followed ($t_{x1}<t<t_{x2}$) by some independent jumps of ions contributing a linear t term to the MSD. Then, cooperative ion jumps start with the MSD initially ($t_{x2}<t<\tau$) having the t^θ -dependence ($0<\theta<1$) and finally, when $t>\tau$, the steady state diffusion regime is reached and the MSD is proportional to time[1].

Figure 2 shows the self-part of the van Hove function of Li ion at 700 K. The function is compared with the Gaussian propagators having the same diffusion coefficient. Bifurcation of the dynamics into slow and fast ions is clearly observed in the function. Slow part consists of waiting time distribution with long tail and localized jumps within the neighbouring sites. Latter can be attributed to fracton of jump version. The fast ions show the longer scale motion with the successive jumps caused by the cooperative jumps of several ions characterized as Lévy flights. With elapse of time these motions are mixed and non-Gaussian parameters tend to decrease. Thus the dynamics has a hierarchy structure, which consists of diffusive motions and localized motions.

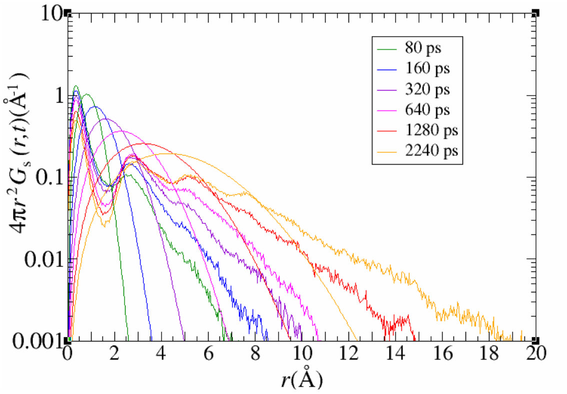

Fig. 2: Self-part of the van Hove function of Li ion in Li_2SiO_3 glass. Curves for the Gaussian type diffusive motions are also shown.

We have visualized the topological structure of the dynamics of single particle motion using the phase-space plots[2] using the principal components obtained by Singular Spectrum Analysis (SSA)[3]. The motion represented in this way is for one particle, but it reflects the cooperative dynamics in a correlated domain. A deterministic character of several motions is shown by these plots.

3. Conclusion

Several time regimes in mean square displacement (MSD) of Li ions are clarified and characterized in detail. The motion of the lithium ion in lithium metasilicate glass is found to be highly heterogeneous. Coexistence of slow and fast dynamics and exchanges between them are examined by several methods such as van-Hove functions, SSA (singular spectrum analysis). The ionic motions are highly cooperative with matrix atoms and have a deterministic character.

References

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