

Heterogeneity, Multifractality and Cooperativity in Ionically Conducting Glasses

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Heterogeneity, multifractality and cooperativity, which come from the complicated motions and landscape of the disordered materials, are key features to understand dynamics of the ions in the ion conducting glasses. We have examined the landscape structure of the lithium metasilicate (Li_2SiO_3) glass by molecular dynamics simulations. The dynamics has similarities to that found in super-cooled liquid near the glass transition [1] of simple glass forming liquid, although the size of the cooperatively rearranging region is relatively small [2]. Complicate dynamical potential surface, which is obtained as the accumulated positions of Li ions during an MD run, has been characterized [3] by multi-fractal analysis using singularity ($f(\alpha)$) spectra [4]. Then single and collective motions of Li ions on the surface have been examined by the singular spectral analysis (SSA) and multi-channel singular analysis (M-SSA) [5]. The former is a principal component analysis for the time series and the latter is its extension to the temporal-spatial data.

Mean squared displacements (MSD), van-Hove functions and non-Gaussian parameters of the Li ions show complex behaviour due to coexistence of the fast and slow ions in temporal and spatial terms.

Fig. 1 shows the time dependence of the singularity spectra at 700 K. $f(\alpha)$ corresponds to the fractal dimension of the set of small cells with a singularity strength α , and they are obtained as the function of the moment q . When the system is mono fractal, the spectrum converges to a point. Therefore, the convex curves mean the multi-fractality, that is, the mixing of the more than two fractals with the different exponent. The left part of the spectrum is concerning with the localized motion while the right part is concerning with the diffusive motion. The left end of the singularity spectrum corresponds to the most dense part, while the right end of the value corresponds to the most rarefied part, which means the long length scale of the motion. With elapse of time, the spectrum develops towards the right direction and this clearly means the importance of the motion with longer length scale in the longer time scale region. Thus the multi-fractality is a description of the fractal dimension of pattern made by dynamical heterogeneity.

The ($f(\alpha)$) value at $q=0$ (at maximum) corresponds to the capacity dimension, representing the fractal dimension of the jump path connecting sites, which is related to the percolation of the path. Actually, at about 500 ps (where linear time dependence in long time region begins in MSD), the $f(\alpha)$ value becomes 2.5, which coincident with the percolation threshold of three

dimension. In other words, when the jump path dynamically percolates, diffusive regime is attained. The $f(\alpha)$ values in larger α region are smaller than the value at $q=0$ but is still non-negligible. Concerning this region, the motion should be treated with proper weight because of longer length scale of the motion and diffusivity is related to the square of the length.

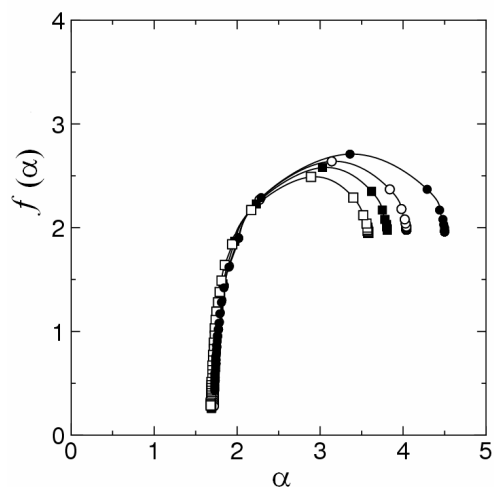


Fig. 1 Time dependence of the singularity spectra of the Li ions at 700 K. Squares: 250 ps, filled squares: 500 ps, circles: 1 ns, and filled circles: 4 ns.

Single particle motion of ions on such surface has been examined [6] by the phase-space plot using the de-noised data obtained by SSA. The plots have clear structures of long jumps, localized jumps and localized motions within sites. This means a deterministic nature of the motion. The motion represented in this way is for one particle, but it reflects the cooperative dynamics in a correlated domain. M-SSA is found to be useful to characterize the collective motion of ions.

References

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