

Fast and Slow Dynamics in Metasilicate Glasses

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Molecular dynamics (MD) simulations of lithium metasilicate (Li_2SiO_3) glass has been performed. Dynamics of lithium ions in metasilicate glass were found to divide into fast and slow ones in the glassy state. We have divided the particles into type A (slow dynamics) and B (fast dynamics). We have examined the characteristics of the dynamics and structure with distinguishing between type A and B particles. Type A particles are located within neighboring sites during a 1 ns run. Such particles show only single jumps and tend to return to their previous sites due to low dimensional local paths. The particles with long waiting time of the jump motion is also included type A particles. On the other hand, type B particles show accelerated dynamics. Cooperative jumps (simultaneous jumps of neighboring ions or occurring within several ps before the relaxation of the jump sites) cause the acceleration. Power law distributions of the displacements reveal that the fast dynamics is characterized as Lévy flight. Short intervals of the jump events also take place in the fast dynamics at short time region. We have found the difference in the medium range structure concerning type A and B particles. The structure for type B particles seems to be favorable to cause the cooperative jumps.

§1. Introduction

Dynamics in lithium metasilicate (Li_2SiO_3) glass, which is made up of cations and a framework structure consisting of chains made of SiO_4 units, has been examined by MD simulations. Both slow (type A particles) and fast (type B particles) dynamics of Li ions have been observed in Li_2SiO_3 glass.^{1),2)} The slow dynamics is characterized by lithium ions showing single jumps, which localizes due to a locally low dimensional path^{1),3)} and long waiting times. Both spatial (geometrical) and temporal terms determines the character of the slow dynamics. On the other hand, type B particles show accelerated dynamics due to cooperative jumps.^{1),3)} Power law distributions of the displacements revealed that the fast dynamics can be characterized as Lévy flight.^{4),5)} The distribution are related to the geometry of the jump motions. In the present work, we have examined the characteristics of the dynamics and structures of type A and B particles.

§2. MD simulation

MD simulations were performed in the same way as in previous studies.^{1)-3),6)-10),12)} The numbers of the particles in the basic cube being 144 M (= Li), 72 Si and 216 O of M_2SiO_3 . The volume was fixed as that derived by NPT (con-

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stant pressure and temperature) ensemble simulation. Pair potential functions of Gilbert-Ida type¹¹⁾ and r^{-6} terms were used. The parameters of the potentials used were previously derived on the basis of *ab initio* molecular orbital calculations,¹⁰⁾ and their validity was checked in the liquid, glassy and crystal states under constant pressure conditions. The volume was fixed as that derived by the NPT (constant pressure and temperature) ensemble simulation. The glass transition temperature was approximately 830 K for the Li system. The run up to 1 ns (250,000 steps) for the Li_2SiO_3 at 700 K was analyzed.

§3. Results and discussion

3.1. Characteristics of fast and slow dynamics

In previous works on Li_2SiO_3 ,¹⁾⁻³⁾ the dynamics of the lithium ions were found to divide into two types in the glassy state. The plot of displacements of Li ions against jump angles between successive jumps (measured using a fixed scale during 1 ns at 700 K) showed clear two regions as shown in Fig. 1. The component around $\theta/2\pi = 0.2$ meant a larger forward correlation probability of jumps, while the component at around $\theta/2\pi = 0.5$ indicated a larger back correlation probability of jumps. Since the displacements and angles are measured using the fixed scale (the length is half of the first maximum of the $g(r)$ Li-Li), the separation of the dynamics is related by geometrical character of the jumps.

Since many particles keep their characteristics for a fairly long time in glassy state, we have divided the particles into type A (slow dynamics) and B (fast dynamics). Type A particles are located within neighboring sites during a 1 ns run, therefore, do not contribute to diffusion or DC but can contribute to AC. Such particles show only single jumps and tend to return to their previous sites due to low dimensional local paths. On the other hand, type B particles can go to second neighboring sites or to further sites by cooperative jump motions and thereby contribute to the long time diffusive dynamics by using three dimensional jump paths.¹⁾

The typical motions of type A and B particles in the r - θ phase were shown in Fig. 1(b). Type A particles tend to be trapped in the $\theta=0.5$ region, while the displacements of type B particles tend to change in low θ region, however, sometimes these were trapped in $\theta=0.5$ region. The motion of type B particles is not a Gaussian type. Since displacements of particles show a power law distribution in the longer r region, the accelerated dynamics caused by the cooperative jumps was characterized as Lévy flight.⁵⁾ Blumen⁴⁾ has treated the systems where both temporal and spatial factors play roles by the continuous time random walk (CTRW) extended on the fractal structures.^{4),5)} When the waiting time distribution is represented by $t^{-1-\gamma}$ form and the first moment of the waiting time distribution is infinite ($\gamma < 1$), the relation,

$$R^2 \sim t^{2/d_w \cdot \gamma} \quad (3.1)$$

is obtained where d_w are the fractal dimension of the random walk. We have separated these exponents²⁾ by plotting MSD against $N(t)$ (accumulated number of jumps until t) and by plotting the $N(t)$ against t in log-log scales. The equation is

found to be valid for the both slow and fast dynamics. The slopes were obtained for type A and B particles, in the region from 50 to 300 ps. The slope for the temporal term of type A ion was about 1 while that of spatial term was smaller than 1. Therefore, behavior of these type A ions in this time region is mainly characterized by a geometric factor (backward correlation of the jump motion).

On the other hand, type B ions showed accelerated dynamics with $2/d_w \cdot \gamma > 1$, where the large slopes (> 1) for both terms contributed to the acceleration. The large slope in the spatial term is explained by the forward correlated motion of successive jumps. The motion is caused by cooperative jumps, since the site required for the backward jump of the first ion after a cooperative jump has been already occupied by the second ion. The large slope of the time dependent term means that the jump interval of the successive jumps tends to be shortened than the previous jump interval. The motion is also explained by the cooperative jumps, since the second (or higher order) particle activated for the cooperative jumps can easily continue the jump without large activation energy using the site previously occupied by the leading particles.⁸⁾ Such tendency was also confirmed by the following analysis of the waiting time distribution of the jump motions.¹²⁾ The mean waiting time of the jump motion $\langle t \rangle$ is usually defined by $\langle t \rangle = \int_0^\infty t' \phi(t') dt'$ and $N(T)$ is obtained from

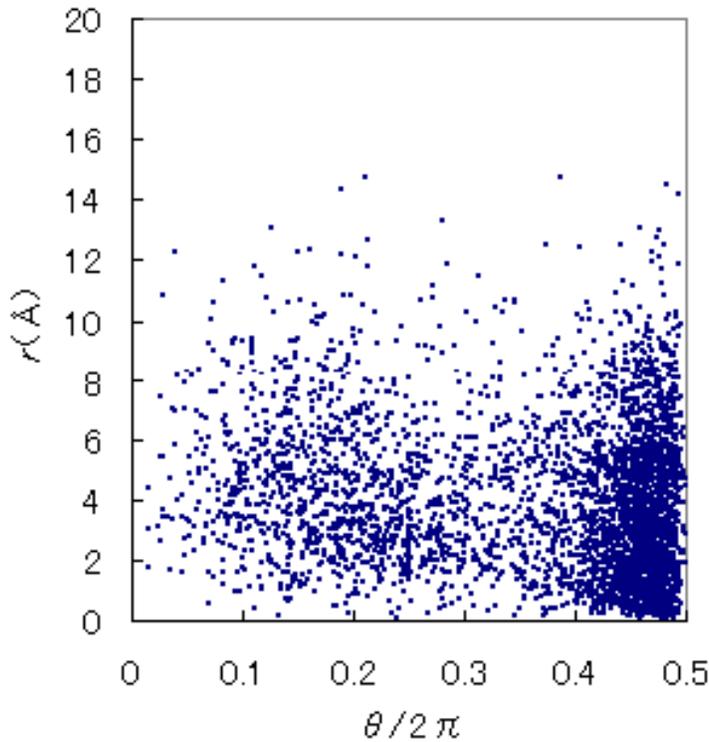


Fig. 1. Displacements against angles between successive jumps for Li^+ ions.

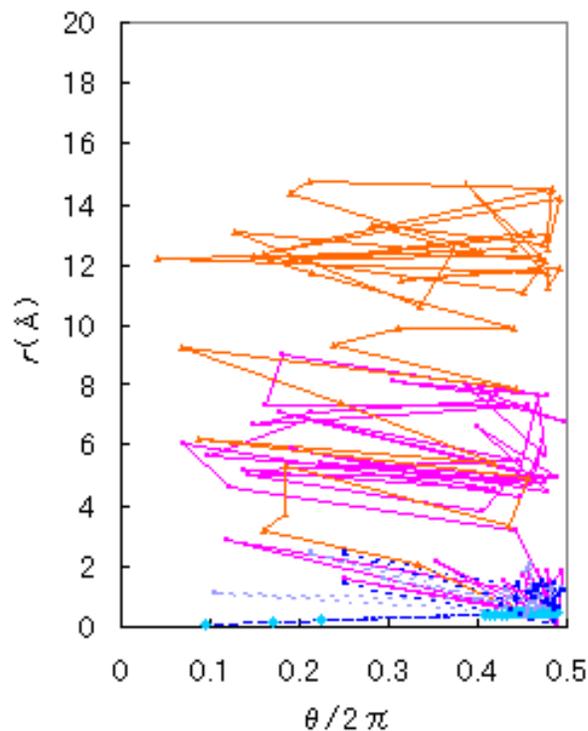


Fig. 2. Typical motions of Li^+ ions of type A and B in r - θ phase. — (pink and orange) for type B and \cdots (violet), --- (blue) and $- \cdot - \cdot -$ (pale blue) for type A.

$T/\langle t \rangle$. Thus, $N(t)$ is related to $\phi(t)$. The log-log plots of jump intervals for the types A and B particles during 1 ns were linear. That is, $\phi(t)$, the probability of interjump intervals, had the form of $\phi(t) \sim t^{-(\gamma+1)}$, with the slopes for types A and B being -1.87 ($\gamma = 0.87$) and -2.13 ($\gamma = 1.13$), respectively. These results mean that long time intervals are frequently observed for the localized component, whereas short time intervals are frequently observed for the diffusive component. The $N(t)$ ($t \rightarrow \infty$) for different values of γ is known to be^{13),14)}

$$\langle N(t) \rangle \sim \begin{cases} (\sin \gamma \pi / A \gamma \pi) t^\gamma, & \gamma < 1 \\ \frac{t}{A \ln(t/A)}, & \gamma = 1 \\ t/(1 + \tau_1), & \gamma > 1. \end{cases} \quad (3.2)$$

The fractal time ($\gamma < 1$) is as usually observed in the slow dynamics in glasses. In the case, regenerative events occur on a random subset in time. This overcomes the divergence of the dynamics and time dependent character will be observed (probability of jump motion decreases and vanishes in the longer t limit). On the other hand, the mean waiting time in the case of $\gamma > 1$ (it may be described also as fractal time in a broad sense) is finite. In such a case, the long time behavior of the dynamics is

expected to become independent of time and to be a Debye type.^{5), 13), 14)} The large slope in log-log plot of N against t (>1) means that the waiting time of the jump is not a constant but a function of time in the observed short time region. In the present system, the next jump motion seems to take place more quickly as a result of the previous jump (due to cooperative jumps) and the waiting time distribution with $\gamma > 1$ consists of time dependent subsets. When the mean waiting time behaves as $\sim A + t^{\beta'}$ in a limited time region (where A is a constant), $N(t)$ becomes $\sim t^{1+\beta'}$. Thus the acceleration of the dynamics is caused not only by the forward correlated jumps but also by the change in frequency of jump events in a short time region.

3.2. Characteristics of the structures for fast and slow dynamics

We have examined pair correlation functions $g(r)$ with distinguishing between type A and type B particles. The function for A-O is practically identical with that of B-O.

There is no remarkable difference in the peak intensity of the first peak for A-A and B-B. On the other hand, the second peak for A-A is higher than that for B-B. Namely, each type A and B shows characteristic feature in medium range structure. This can be understood by the geometrical conditions where the cooperative motion is possible. The cooperative motion requires the packed structure for the neighbors and also requires the unoccupied site for the second neighbors. Therefore the obtained structure for type B seems to be suitable to cause the cooperative motion of two (or three) particles. On the other hand, the packed structure in the medium range seems to prevent the forward correlated motion for the type A particles.

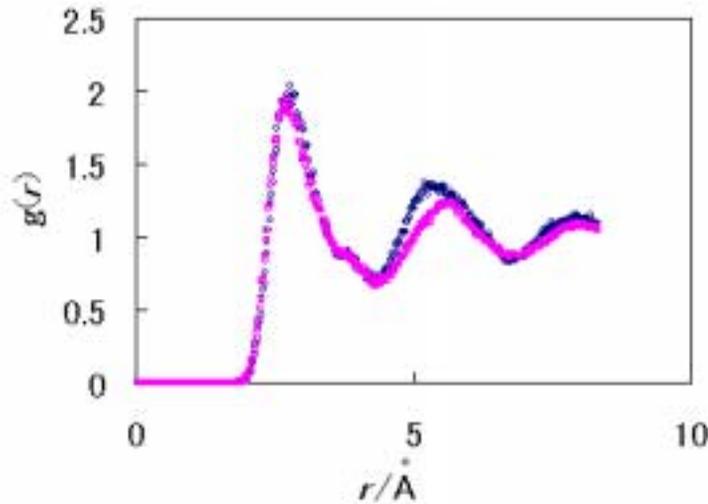


Fig. 3. Pair correlation functions $g(r)$ with distinguishing between type A and B particles; \circ (blue) for A-A and \square (pink) for B-B.

§4. Conclusion

Some characteristics of ion dynamics in a metasilicate glass have been examined. A large backward correlation probability and long intervals of the jumps contribute the slowing down of the dynamics the lithium ions. On the other hand, a large forward correlation probability and shorter time intervals of the jumps play roles in acceleration of the dynamics. The cooperative motion of like ions can accelerate the dynamics by both the factors. Therefore, both spatial and temporal factors are related to the fast and slow dynamics. The characteristics of the medium range structure concerning the type B particles seem to be suitable to cause the cooperative jump motions.

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