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MOLECULAR DYNAMICS STUDY OF DYNAMICAL HETEROGENEITY IN ION CONDUCTING GLASSES

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Abstract

Molecular dynamics (MD) simulations of lithium metasilicate (Li_2SiO_3) glass have been performed. Dynamic heterogeneity of lithium ions has been examined in detail over 4 ns at 700 K. Particles showing displacements less than the distance at the first minimum of $g(r)^{\text{Li–Li}}$ during a given time T(=920 ps) were defined as type A. Particles showing a displacement greater than the distance of the first minimum of $g(r)^{\text{Li–Li}}$ during T were defined as type B. The type A particles show slow dynamics in accordance with a long tail of waiting time distribution of jump motion and localized jumps within neighboring sites (fractons), while the type B particles show fast dynamics related to the co-operative jumps with strong forward correlation probability (Lévy flights). The mutual changes of two kinds of dynamics with a relatively long time scale have been observed.

The 'mixed alkali effect' in the $LiKSiO_3$ system can be explained by the mutual interception of jump paths. The paths of lithium and potassium are nearly independent in a relatively short time scale while the mixing of the jump paths occurs in a long time scale. The mixed alkali system also shows a kind of heterogeneity.

The heterogeneity can be realized only when the 'memory' of the characteristics of the dynamics is longer than the relaxation time for the mixing. Observation of the heterogeneity also depends on the time (or spatial) resolution.

Keywords: heterogeneity, ionics, mixed alkali effect, silicate glass

Introduction

Thermodynamic properties of glasses are closely related with the microscopic motion of atoms. Recently, Odagaki and Yoshimori [1] has proposed a general framework of calculating the specific heat of the system, where the dynamics of the representative point can be separated into fast motion in a basin of energy landscape and the slow stochastic jump motion among basins. A low energy excitation (boson peak) is also discussed in relation with the anomaly in the specific heat of the glass [2].

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The lithium ions in lithium metasilicate (Li_2SiO_3) glass exhibit the dynamical heterogeneity due to the coexistence of the fast and slow components.

In the present work, fluctuations between these components in a longer time region have been examined in detail by molecular dynamics simulations (MD). The existence of heterogeneity in the glassy state due to slow and fast dynamics was observed in many glass forming liquids [3–8] near the glass transition regime. The results in single alkali metasilicate glass (Li_2SiO_3) are compared with those in lithium potassium metasilicate glass ($LiKSiO_3$), which also shows a kind of heterogeneity due to nearly independent jump paths of Li^+ ions and K^+ ions. Cooperative jumps (simultaneous jumps of neighboring ions or those occurring within several pico-seconds before the relaxation of the jump sites [9, 10]) play important roles in the dynamics. Relationships between the heterogeneity and the functional forms of the decays will be discussed.

MD simulation

MD simulations in Li_2SiO_3 were performed in the same way as in previous studies [10–17]. The number of particles in the basic cube was 432 (144 for Li, 72 for Si and 216 for O). The volume was fixed as that derived by NPT (constant pressure and temperature) ensemble simulation. The glass transition temperature is approximately 830 K. Pair potential functions of Gilbert–Ida type [18] and an r^{-6} term were used. The parameters of the potentials used were previously derived on the basis of *ab initio* molecular orbital calculations [17], and their validity was checked in the liquid, glassy and crystal states under constant pressure conditions. A run, up to 4 ns (1 000 000 steps), was performed at 700 K. The number of jumps for each ion was counted in a similar manner that in the previous works [11–15, 19, 20]. Namely, the displacement greater than 1/2 of the distance of first maximum of the pair correlation function, $g(r)^{\mathrm{M-M_{max}}}$, was judged as the jump, where the positions of atoms were averaged for several pico-seconds to remove the effect of the small displacement due to the thermal vibration, the near constant loss and the low energy excitation.

Particles showing displacements less than the distance at the first minimum of $g(r)^{\mathrm{Li-Li}}$ during a given time (T) were defined as type A. That is, the ion is located within neighboring sites during T. Particles showing a displacement greater than the distance of the first minimum of $g(r)^{\mathrm{Li-Li}}$ during T were defined as type B. The definition of the types A and B depends on the T and time windows used [12, 14]. In the present work, T was set to be 920 ps and the time window was set to be 80 ps as the definition II in [14] in each 1 ns time region, unless otherwise stated.

MD simulations in $LiKSiO_3$ were performed in the similar manner as the single alkali system. The number of particles in the basic cube was 432 (72 for Li, 72 for K, 72 for Si and 216 for O).

Results and discussion

In our previous works, coexistence of the slow and fast dynamics of Li^+ ions was found in the glassy lithium silicate [11–15]. The heterogeneity of the positions of types A and B particles during 1 ns run at 700 K has been observed clearly in space. Mixing of both types of trajectories was observed in a limited space region, which suggests the existence of fluctuations of the dynamics. Fluctuations between fast and slow dynamics in a longer time scale are examined in the present work.

Characteristics of the fast and slow dynamics so far studied were summarized as follows.

The slow dynamics are mainly caused by the single jumps, where the localized motions within neighboring sites and the waiting distribution having a long tail play important roles. On the other hand, the fast dynamics are mainly caused by the cooperative jumps of neighboring particles, which resulted in a large forward correlation probability of the successive jumps. The dynamics has been characterized as a kind of Lévy flight since the power law distribution of the displacements of the ions has been observed [13].

Since many particles keep own characteristic for a fairly long time in the glassy state, we have divided the particles into types A and B. Type A particles are located within neighboring sites during 920 ps, while type B particles visit second or further neighboring sites. Plots of the evolution of displacements of Li ions *vs*. jump angles between the successive jumps (measured using a fixed scale during 1 ns at 700 K) showed two regions [14]. Thus these two kinds of dynamics are distinguishable clearly, although the definition of type A and B depends on the choice of T and the time window used. The restricted jump angles observed are characteristics for the glass where the framework made by SiO_4 chains is fairly stable and therefore the structure of the jump paths has much a longer life time compared with the time scale of the jump motion of the lithium ion.

Fluctuations between fast and slow dynamics

Details of the fluctuations between fast and slow dynamics were examined as follows. A successive 4 ns simulation run at 700 K was divided into four regions. Particle types were distinguished by the squared displacement during 920 ps in each 1 ns region. Figure 1 shows a plot of the squared displacement of each lithium ion *vs.* the number of jumps in each time region. The mean squared displacement (MSD) of particles is a linear function of an accumulated jump number in a long time region, at least in macroscopic point of view. However, we can find wide distribution of points in Fig. 1 in a limited time scale. There are particles with long waiting time and those repeating jump motion within neighboring sites, which have been characterized as fractons [13]. Both kinds of localized particles contribute to the slow dynamics. On the other hand, particles with large displacements, which show medium jump frequencies were also observed. The large displacements are caused by the strong for-

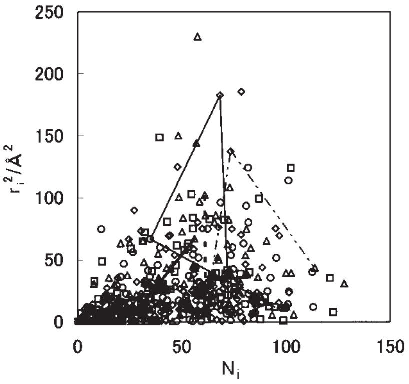

Fig. 1 Squared displacement of each lithium ion is plotted *vs.* the number of jumps in each (1 ns) time region. □ – 0–1 ns; o – 1–2 ns; ◇ – 2–3 ns and Δ – 3–4 ns regions. The data points during 4 ns are connected for the arbitrarily chosen six particles

ward correlation due to cooperative jumps and the dynamics have been characterized as Lévy flights [13].

A pattern of the distribution is kept unchanged through four regions. In the Fig. 1, points in the four time regions are connected for the six arbitrarily chosen Li ions. The changes among three kinds of dynamics are observed. The behavior with large N_i and small r^2 region is found to switch to that with medium N_i and large r^2 values of type B motion with accelerated dynamics. The changes between localized (back-correlated) motion and accelerated (forward-correlated) motions are related with the spatial (geometrical) character of the jump motion. Some slow particles tend to keep their characters over 4 ns, since they do not cause the change in their own environment. However, changes of the jump frequency were observed for some other particles. Large displacements of B type particles seem to cause large changes of their environment by themselves. Namely, the change of the type of the dynamics occurs during nano-seconds runs at 700 K.

Relationship between heterogeneity and functional forms of decays

Slow dynamics near the glass transition temperature for simple liquid are usually characterized by a stretched exponential form of the density-density correlation, $F(t)$ in α relaxation region.

$$F(t) \sim A\exp[-(t/\tau)^{\beta}] \tag{1}$$

with $\beta<1$. Such behavior is also observed for the lithium motion, although the contribution of fast component overlaps.

For the motion of Li ions in the present system, self-part of the wavenumber dependent density-density correlation function $F_s(k, t)$, can also be presented as a stretched exponential form in 20~300 ps region [11],

$$F_s(k, t) = A\exp[-C(t/\tau_k)^{\beta_k}] \quad (2)$$

where C is a constant and $\tau_k \sim k^{-n}$. The β value in the Eq. (1) corresponds to the averaged values of β_k.

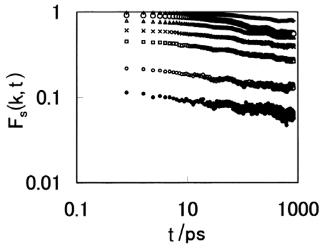

Fig. 2 Partial self-part of the density-density correlation functions, $F_s(k, t)$, at 700 K for Li ions of the type A. Decay for the type A is slower than the exponential type decay due to the back-correlated jump motion (fracton). The wavenumbers (k in Å^{-1}) are, 2π/10, 2π/5, 2π/3, 2π/2, 2π/1.5, 2π/1.0 and 2π/0.8, from the top to the bottom, respectively. A relatively small time window (80 ps) was used here to distinguish the types A and B clearly

Partial $F_s(k, t)$ functions for the types A and B of Li ions are shown in Figs 2 and 3, respectively. A relatively small time window (80 ps) was used to distinguish types A and B clearly. This causes the large fluctuations of the curves due to the time dependent phenomena in nano-seconds region.

The type A ions show slower decay than the exponential one, at any wavenumbers because of the correlation (backward jumps). The waiting time distribution with a long tail can also cause the deviation from the exponential decay in a long time region. Both temporal and spatial terms contribute to the slow dynamics. We have previously shown that a lithium ion moves with the center of the gravity of the coordination polyhedron made by the oxygen atoms. Each polyhedron shows stability, which depends on the geometrical degrees of freedom. The decay of each polyhedron was found to be exponential with a different rate, at least in the time region examined in [22]. This means that the stretched exponential decay due to the waiting time distribution can be decomposed into exponential ones, although the decay due to backward jumps is intrinsic non-exponential.

Table 1 Heterogeneity in single and mixed alkali silicate glasses

Time region	Li_2SiO_3	$LiKSiO_3$
In a shorter time scale	Coexistence of fast and slow dynamics	Independent path of Li and K ions ‘Mixed alkali effect in the ion transport’
In a longer time scale	Fluctuation between fast and slow dynamics	Mixing of jump path of Li and K ions ‘Mixed alkali effect in the viscosity’

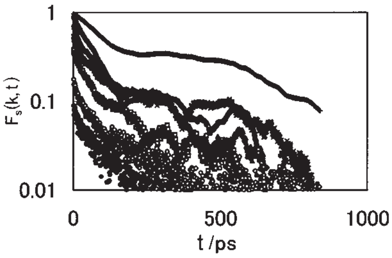

Fig. 3 Partial self-part of the density-density correlation function, $F_s(k, t)$, at 700 K for Li ions of type B. The recovery of the decay curves is caused by the mixing of the slow dynamics. The wavenumbers (k in Å^{-1}) are, 2π/10, 2π/5, 2π/3, 2π/2, 2π/1.5, 2π/1.0 and 2π/0.8. (The order of k at the initial part of the decay is the same as in Fig. 2)

As shown in Fig. 3, type B ions show faster decays than the type A ions and show recoveries of the curves due to mixing of the localized motion. The fluctuations due to the mixing are remarkable when the k values are between 2π/2 and 2π/5 (Å^{-1}) The k value 2π/3 corresponds to the typical jump distance (~2.77 Å). The contribution of the n<2 component found in the $F_s(k, t)$ in the lithium motion (which was obtained for all Li ions) [11] is attributed to the fast decay. Namely, the dynamics are the non-Debye types. Intervals of the jumps tend to be shortened by the cooperative jumps [12] and hence the dynamics are non-exponential types. The fast dynamics are related with the acceleration in both the temporal and spatial terms.

Thus ion dynamics in the present system in both fast and slow components obey the non-exponential decays and are explained by a combination of special and temporal characters.

Blumen *et al.* have extended the continuous time random walk (CTRW) to the dynamics on fractal structures [23], where the contribution of spatial (α) and temporal (γ) parameters are taken into account.

That is,$<r_i^2(t)>\sim t^{\alpha\gamma}$, in a certain time regime, where the α corresponds to $2/d_w$ (d_w is a fractal dimension of the random walk), while γ is the exponent related with the waiting time distribution of the jump motions. Quite similar discussions hold for the decay curves. Each parameter in MSD was separately evaluated using the results of MD simulations [12–15]. The fast decay observed in Fig. 4 corresponds the dynamics with α>1 and γ>1 accelerated by the cooperative jumps.

Richert [24] used the terms heterogeneous scenario and homogeneous scenario to classify the type of non-exponential relaxation near the glass transition region, in which ‘heterogeneous’ was used for the superposition of exponential relaxation processes with different rates, while ‘homogeneous’ was used for the identical intrinsically non-exponential relaxation processes. However, our concept of heterogeneity does not directly involve the origin of a stretched exponential form, because the heterogeneity in the present system is a superposition of non-exponential decays.

The heterogeneity comes simply from the existence of the distinguishable types of dynamics in the glassy state.

The heterogeneity in the mixed alkali system

Mixed alkali effect (MAE) is a key phenomenon to understand the ionics in the glass where transport coefficient reduces in non-linear way by mixing of more than two kinds of alkali metal ions [25]. The mechanism of the MAE so far studied is summarized as follows.

The jump paths of lithium and potassium ions in the $LiKSiO_3$ system are nearly independent in a relatively short time scale [16]. Balasubramanian and Rao [26] have also shown similar results for the related compounds. Park and Cormack [27] have shown that the environments of the different alkali types differ from each other. Greaves [28] has also shown that the existence of local structure of each alkali metal environment and selectivity in hopping of alkali metal ions. The mixed alkali systems exhibit the heterogeneity in a wide sense.

The interception of the mutual jump paths causes the suppression of the cooperative jumps, and therefore the motion of Li becomes more localized by the mixing [14, 15]. The maximum of the Haven ratio experimentally observed [29] in the mixed alkali system can be explained by the suppression of the fast dynamics. Both the Kohlrausch exponent β and Haven ratio are considered to reflect the degree or coupling between the mobile ions in the glass [30].

Ingram [31] has pointed out that the mixed alkali system showed the reduction of the ion dynamics and the loosening of the framework (reduction in viscosity) at the same time. We have explained this by the mixing of the jump paths occurring in a long time scale, which accompanied with the jumps between unlike ion sites [32]. The heterogeneity in the mixed alkali system will be lost, if the dynamics are averaged for a longer time.

Comparison of the heterogeneity in single and mixed alkali systems is given in Table 1. The heterogeneity can be realized only when the 'memory' of the characteristics of the dynamics is significantly longer than the relaxation time for the mixing. Observation of the heterogeneity also depends on the time (or spatial) resolution.

Conclusions

The dynamics of lithium ions in a metasilicate glass have been examined at 700 K by MD simulations. The heterogeneity due to coexistence of fast and slow dynamics and the fluctuations between them in nano-seconds region have been observed. Both spatial and temporal terms determine the characteristics of each dynamics.

The stretched exponential form of the decay is caused by the superposition of non-exponential decays of both dynamics. The fast dynamics may be represented by a superposition of exponential decays with different effective jump distances and/or different waiting times. On the other hand, slow dynamics contains both localized motion and a long waiting time component. Decay curves for the former is intrinsic non-exponential functions due to contribution of backward jumps, while the latter can be decomposed into exponential contributions with different life times. Therefore, the coexistence of the fast and slow dynamics and the origin of a stretched exponential form should be treated separately, although the stretched exponential type decay tends to be discussed in relation to the heterogeneity of the dynamics due to two exponential decays.

The mixed alkali effect is caused by the mutual interception of the jump paths, which is nearly independent in a shorter time scale. Therefore, the system shows a kind of heterogeneity. A mixing of such paths occurs at a longer time scale. The heterogeneity is related with the 'memory' of characteristics of the dynamics and also depends on the time (or spatial) resolution.

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