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Dynamics in pure and mixed-alkali glasses—spatial and temporal aspects

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Abstract. Long-time (~ 1 ns region) molecular dynamics (MD) simulations of lithium metasilicate (Li_2SiO_3) and a mixed-alkali silicate (LiKSiO_3) glass have been performed to confirm the mechanism of the ‘mixed-alkali effect’. The motion of lithium ions in lithium metasilicate (Li_2SiO_3) glass is divided into slow (A) and fast (B) categories in the glassy state. The waiting time distribution of the jump motion of each component shows a power-law behaviour with different exponents. The slow dynamics is caused by localized jump motions and by the long waiting time. On the other hand, the fast dynamics of the lithium ions in Li_2SiO_3 is characterized as Lévy flight caused by cooperative jumps. Short intervals between jump events also occur in fast dynamics, in the short-time region. The main diffusion and conduction processes of silicate glasses are not the single jumps but the cooperative jumps. A component with accelerated dynamics is almost absent in the mixed-alkali system. The contributions of the temporal and spatial aspects of the particle dynamics are separated. A large change in the spatial parameters has been observed on mixing, and interception of the jump path by other kinds of ion path suppresses the cooperative jump process. On the other hand, in longer-time regions, motion of the framework has been found to accompany the small number of events where alkali metal ions jump to unlike-ion sites. Thus both loosening of the glass structure and a reduction of ionic diffusion coefficients occur in the mixed-alkali system.

1. Introduction

Dynamical processes in disordered media differ from simple Brownian motion. Both slow (type-A particles) and fast (type-B particles) dynamics of Li ions have been observed in Li_2SiO_3 glass [1, 2], which is made up of cations and a framework structure consisting of chains made of SiO_4 units. Small γ' -values of the mean squared displacement (MSD) $\langle R^2(t) \rangle \sim t^{\gamma'}$ and small β -values (< 1) in the stretched-exponential ($\sim A \exp[-(t/\tau)^\beta]$) decay (α -relaxation regime) were observed for type-A particles. The slow dynamics is characterized by lithium ions with long waiting times and those showing localized single jumps due to a locally low-dimensional path [1, 3]. The γ' - and β -values depended on the geometrical correlation of successive jumps and the waiting time distribution of the jump motions. Thus both spatial (geometrical) and temporal terms determine the character of the slow dynamics. Blumen *et al* [4] have treated the systems where both temporal and spatial factors play roles by the continuous-time random-walk (CTRW) method extended to fractal structures [4, 5]. When the waiting time distribution is represented by a $t^{-1-\gamma}$ -form and the first moment of the waiting time distribution is infinite ($\gamma < 1$), the relation

$$R^2 \sim t^{(2/d_w)\gamma} \quad (1)$$

is obtained where d_w is the fractal dimension of the random walk. We have proposed a method for separating these exponents of the MSD by using the data obtained in MD simulation [2].

Such a treatment is also useful to characterize the fast dynamics of type-B particles [2]. Type-B particles show accelerated dynamics with $\gamma' > 1$, because cooperative jumps (simultaneous jumps of neighbouring ions or occurring within several ps, i.e. before the relaxation of the jump sites) cause acceleration, since the site needed for the backward jump of the first ion after a cooperative jump is already occupied by the second ion [1, 3]. Power-law distributions of the displacements and number of atoms participating in the cooperative jumps were observed [1, 3], so these fast dynamics have been characterized as Lévy flight [5]. The distributions are related to the geometry of the jump motions.

In many glasses, such as silicates, transport coefficients fall markedly when an alkali metal ion is mixed with other alkali metal ions; this phenomenon is known as the ‘mixed-alkali effect’ [7–11]. The effect is a key phenomenon in understanding the mechanism of ion conduction in glasses. The roles of the temporal and spatial terms in the glass transition problem and in the ‘mixed-alkali effect’ will be discussed here. Ingram [12] has reviewed recent developments related to the mixed-alkali effect. He has pointed out that the mixing of cations leads both to a loosening of the structure and, at the same time, to immobilization of the cations. In the present work, the results of MD simulation up to 1 ns have shown the relationships between the motion of alkali metal ions and the framework structure in the mixed-alkali glass.

2. MD simulation

MD simulations were performed in the same way as in previous studies [1–3, 6, 10, 11, 13, 14]. The number of particles in the basic cube was 144 M (144 for Li in the pure lithium system; 72 for Li, 72 for K in the mixed-alkali system), 72 Si and 216 O for M_2SiO_3 . The volume was fixed as that derived by *NPT*-ensemble (constant-pressure and constant-temperature) simulation. Pair potential functions of Gilbert–Ida type [15] and r^{-6} -terms were used. The parameters of the potentials used were previously derived on the basis of *ab initio* molecular orbital calculations [14], and their validity was checked for the liquid, glassy and crystal states under constant-pressure conditions (ensemble simulation). The glass transition temperatures were approximately 830 and 850 K for the Li and the mixed systems, respectively. Runs up to 1 ns (250 000 steps) for the Li_2SiO_3 and for the mixed-alkali system both at 700 K were analysed.

2.1. Analysis of the jump motion

The number of jumps for each ion was counted. A displacement greater than 1/2 of the distance of the first maximum of the pair correlation function, $g(r)_{Li-Li}$, was taken as a jump, with the atom coordinates averaged over several ps to remove the effect of small displacements [6]. The particles showing a squared displacement less than the squared distance at the first minimum of $g(r)_{Li-Li}$ are defined as type A. That is, the ion is located within neighbouring sites during a given time, T . Particles showing a squared displacement greater than the squared distance at the first minimum of $g(r)_{Li-Li}$ are defined as type B and contribute to the long-time dynamics. Two kinds of definition of type A and B have been used in this work depending on the T and time windows used. In definition I, a time window was not used and $T = 1$ ns. (This definition is the same as that used in our previous work [1].) The numbers of particles of types A and B were 76 and 68, respectively. In definition II, a time window of 80 ps (100 points for initial t) was used and types A and B were distinguished by values of the averaged squared displacement over 920 ps. With this definition, the numbers of particles of A and B types were 85 and 59, respectively. The differences caused by these definitions have been discussed in the

previous paper [2]. Since no significantly different conclusions arise from these definitions, the results from both will be used in following sections case by case.

3. Results and discussion

3.1. Separation of time and space aspects

In previous works on lithium metasilicate (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 lithium ions against jump angles between successive jumps (measured using a fixed scale for 1 ns at 700 K) showed two clear regions (cf. figure 6 in [1]). The component around $\theta/2\pi = 0.2$ meant a larger forward-correlation probability of jumps, while the component near $\theta/2\pi = 0.5$ indicated a larger back-correlation jump probability. Since many particles keep their characteristics for a fairly long time in the glassy state, we have divided the particles into type A (slow dynamics) and B (fast dynamics). Type-A particles are located within neighbouring sites during a 1 ns run and, therefore, do not contribute to diffusion or a DC (direct current) but can contribute to an AC (alternating current). Such particles show only single jumps and tend to return to their previous sites due to the low-dimensional local paths. On the other hand, type-B particles can go to second-neighbouring sites or to further sites by cooperative jump motions and thereby contribute to the long-time diffusional dynamics by three-dimensional global jump paths [1]. This situation differs from that in the liquid state where no particle can be localized for a long period. Type-B dynamics also differs from that in the liquid state, where the motion of particles can usually be described by Gaussian dynamics. 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]. The non-Gaussian character of such motion will be discussed in a separate paper. The large forward-correlation probability (restricted angles of jump motion) and the power-law distribution of the characteristic jump lengths for the jump motions are criteria for Lévy flight dynamics.

Mean squared displacements (MSD), $R^2(t)$, of types A and B are shown in figure 1. Here the values are averaged using a time window of 80 ps for smoothing (definition II).

A plot of squared displacement against number of jumps for alkali metal ions during a 1 ns run at 700 K for Li ions of type A and type B in Li_2SiO_3 is shown in figure 2.

Both long-life (low-frequency and small-displacement) and localized (high-frequency and small-displacement (due to fractons [1])) components are observed for the Li ions in Li_2SiO_3 . Thus both temporal and geometrical randomness contributes to the dynamic behaviour of this system. In the medium- N region, component B had large displacements—larger than the squared distance at $g_{\text{Li-Li}}(r)_{\text{min}}$. Separation of the time and spatial exponents in MSD was achieved by plotting the accumulated number of jumps against time and plotting the MSD against the accumulated number of jumps using log–log scales. The slopes thus obtained for type-A and type-B particles, in the region from 50 to 300 ps, are given in table 1 for definition

Table 1. Contributions of temporal and spatial parts to the MSD in Li_2SiO_3 in the region 50–300 ps in definition II.

Component	Slope		
	$\log N/\log(t/\text{ps})$	$\log(R^2/\text{Å}^2)/\log N$	$\log(R^2/\text{Å}^2)/\log(t/\text{ps})$
A	1.03	0.66	0.68
B	1.30	1.19	1.55

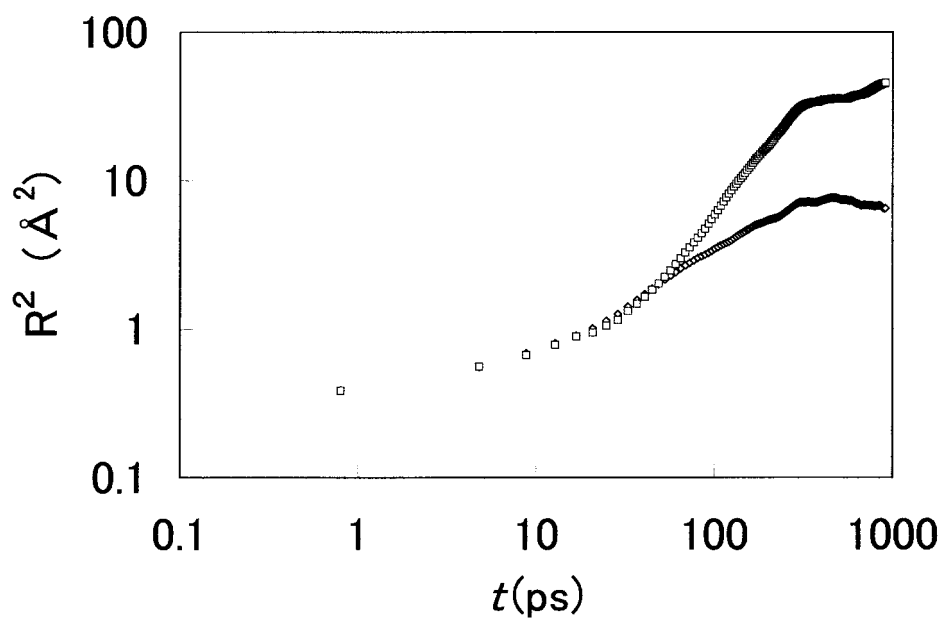


Figure 1. Mean squared displacements of Li ions in Li_2SiO_3 for types A and B at 700 K. A: lower curve; B: upper curve.

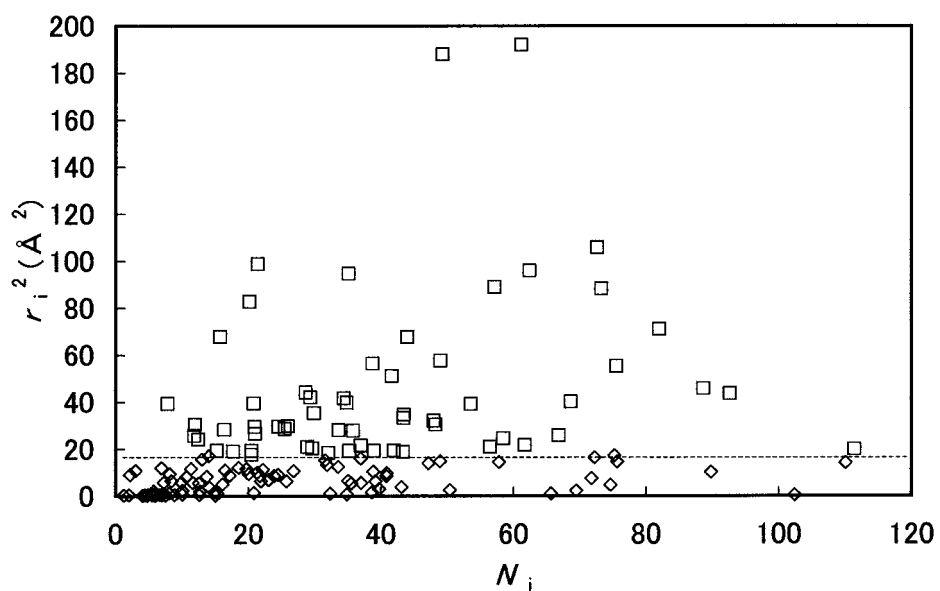


Figure 2. Squared displacement against number of jumps for alkali metal ions during a 1 ns run at 700 K for Li ions of type A (\diamond) and B (\square) in Li_2SiO_3 .

II. The slope for the temporal term of type-A ions was about 1 while that of the spatial term was smaller than 1. Therefore, the behaviour of these type-A ions in this time region is mainly characterized by a geometric factor (backward correlation of the jump motion). The

large slopes for the space terms, shown in table 1, for type-B ions can be explained by the forward-correlated motion of successive jumps caused by cooperative jumps. The bigger slope (larger than 1) of the time-dependent term of type-B ions means that the jump interval between successive jumps tends to be shorter than the previous jump interval in a certain time region. Details of such acceleration in temporal terms have been discussed in [16]. The slopes of these plots for lithium and mixed compounds are given in table 2.

Table 2. Contributions of temporal and spatial parts to the MSD.

System	Region	Slope			
		$\log N/\log(t/\text{ps})$		$\log(R^2/\text{\AA}^2)/\log N$	
		Li	K	Li	K
Li_2SiO_3 (700 K)	~ 300 ps	1.10	—	0.99	—
Li_2SiO_3 (700 K)	~ 300 ps	0.72	—	0.31	—
LiKSiO_3 (700 K)	~ 300 ps	0.95	0.90	~ 0.50	~ 0.46
LiKSiO_3 (800 K)	~ 300 ps	0.94	0.87	0.79	0.70

4. Slowing down of the dynamics and loosening of the structure in the mixed-alkali glass

The slowing down of the dynamics near the glass transition temperature has been explained by the trapping diffusion model (TDM) [17], where the waiting time distribution of the jump motions (temporal term) plays a dominant role. The ‘mixed-alkali effect’ (a large decrease in ion dynamics in the mixed-alkali glasses) [7–9] is another example of slow dynamics in a glass. The slowing down of the diffusion of alkali metal ions in LiKSiO_3 has been explained by the blockage of cooperative jumps by interception of the jump paths of different kinds of alkali ion [2, 3, 10, 11, 13]. Preferred diffusion paths for each type of ion have been discussed by several authors [18, 19, 22, 23]. In contrast with the case for the glass transition described by the TDM, change in the geometrical term plays an important role in the ‘mixed-alkali effect’.

In our previous work [3, 10, 11], a mechanism of the mixed-alkali effect has been explained as follows. In LiKSiO_3 glass, each cation has an individual jump path. These paths are intercepted by each other. The interceptions of such paths result in a decreased number of cooperative jumps, which was found to be a main mechanism of ion conduction in the pure systems [1]. Single jumps do not constitute a main mechanism since they have a large back-correlation probability.

Plotting squared displacements against jump frequency number for the mixed-alkali system for 1 ns showed that the jump frequency of a lithium ion is about half of that for pure silicate, which corresponds to the fact that there are about half as many possible jump sites as compared with the pure Li_2SiO_3 system, since other sites are for K^+ ions. An even more pronounced feature is that the component with large displacements (corresponding to type-B particles) is not found in this case [2]. Only localized particles with power-law distribution of the jump frequency were observed. That is, accelerated dynamics due to cooperative motion is suppressed in the mixture.

The slope of the MSD of lithium ions in the pure lithium-containing glass (figure 1) changed at about 300 ps in the present case. The inflection is caused by overlap of the localized motion and the diffusive motion due to cooperative jumps [1]. The motion of silicons and oxygens changes at about 100–200 ps. The slopes in longer-time regions were negligibly small, as expected for the glassy state. The larger slopes for silicons and oxygens at short times

are due to localized motion of the chains. The changes of the slopes for silicons and oxygens were not smooth, due to restricted spring motion arising from the chain structure.

On the other hand, the motion of alkali metal ions in the mixed-alkali system was one order of magnitude less than in the pure systems. Simultaneous (or nearly simultaneous) changes of slopes of all species were found at about 600 ps even after an averaging procedure using a time window of 80 ps. This indicates the existence of cooperative motion of all species, although the number of events is small. The cooperative motion of the cations and chain structure is one of the characteristics of loosening of the framework structure.

We have examined the changes in the framework structure made up of SiO_4 units for Li_2SiO_3 and LiKSiO_3 , both at 700 K [20]. In spite of the large movement of oxygen atoms, the positions of the silicons were almost fixed for the Li_2SiO_3 . On the other hand, motions of both oxygen and silicon were small and the chain structure seems to move collectively in LiKSiO_3 . To learn the details of these motions, Van Hove functions have been examined. The distinct part of the Van Hove function is defined by

$$G_d^{\alpha'\beta'}(r, t) = (1/N_{\alpha'}) \sum_{i=1}^{N_{\alpha'}} \sum_{j=1}^{N_{\beta'}} \langle \delta(r - r_i^{\alpha'}(0) + r_j^{\beta'}(t)) \rangle. \quad (2)$$

In the Van Hove function of the Li–Li and K–K pairs for the LiKSiO_3 , peaks at $r = 0$ appear, which indicate that ions move into sites previously occupied by the same kinds of ion. We observed broadening of the first peak of the Van Hove function at 3.6 Å for Li–Li pairs, and new shoulders appeared at 1.5 Å with a lapse of time. New shoulders were also observed for the K–K pair. These results mean that the paths of both cations change gradually during 1 ns. In the functions for the Li–K and K–Li pairs, we have observed new peaks due to the $\text{Li}/\bar{\text{K}}$ jumps and $\text{K}/\bar{\text{Li}}$ jumps during a 800 ps run, where $\bar{\text{A}}$ means the site previously occupied by A, although we did not observe such events over 192 ps in the previous work [10]. Such jumps have also been observed at higher temperature (at 800 K) [3, 11]. Since no shoulders in the functions for Li–Li and K–K pairs were observed for a 1 ns run with pure salts at 700 K, the change must be related to the jump events among unlike-ion sites. In the Van Hove functions (distinct part) of the Si–Si pair in Li_2SiO_3 , the height of the first peak was nearly constant from 200 to 800 ps. This means that the structural relaxation of the chain is nearly frozen. On the other hand, in the Van Hove functions (distinct part) of the Si–Si pair in the LiKSiO_3 system, the first peak became lower and broader with a lapse of time. A similar tendency was observed for the Li–O, O–O and Li–Si pairs. These results mean that the structural relaxation of the chains still occurs, though at longer times in the mixed-alkali system, i.e., a loosening of the framework structure is taking place. Direct calculations of the viscosity of the moving structures have not been carried out yet since these require much longer simulations. Here the structural changes in the chain are accompanied by the jumps among unlike-ion sites, which because of the large size difference of lithium and potassium causes strain, as has been discussed by LaCourse [21]. He assumed the formation of ‘mixed-alkali defects’ in mixed-alkali glass, which decreased the viscosity. The magnitude of the effect will depend on the electrical and mechanical strain caused by defect formation, and the rate of stress relaxation in the neighbourhood of the defects.

Jumps among unlike-ion sites were also suggested in the dynamic structural model put forward by Maass *et al* [22, 23]. They assumed that ions A^+ and B^+ were able to move to each other’s sites and thus they actively interfere with each other’s conducting pathways. They also tried to explain the sharp decrease in the host-cation mobility in the dilute foreign alkali region by such motion. However, at least in a system containing both a network former and a modifier, the jumps among unlike-ion sites contribute to the loosening of the structure rather than decreasing the mobility. The situation is quite similar to that observed for the molten

state, where a fixed pathway was not observed [11]. Another possible explanation of the sharp decrease in the host-cation mobility is the fact that cooperative jumps are highly sensitive to blockage of the path. Evidence of this effect will be given in a later separate paper describing MC (Monte Carlo) simulations involving cooperative jumps. Cooperative jumps of one kind of cation have been confirmed to be the main mechanism of ionic diffusion in a pure system [1] and interception of the jump paths resulted in a decrease of the cooperative jump motion.

Thus it is evident that we must consider the role of cooperative jumps in the mixed-alkali effect. In the dynamic structure model, an A ion has a large probability of entering the site previously occupied by the same kind of ion. Such motion will be made more difficult by the existence of other ions. This is similar to some extent to (but not entirely the same as) the existence of the cooperative motion of ions in single-cation systems.

We can explain the difference between the dynamics for pure and mixed-alkali glasses as follows.

- (1) In a pure alkali metal glass, the conduction relaxation time ($\tau_c = \tau_{LiLi}$) is much shorter than that of the framework (τ_f). That is, $\tau_c \ll \tau_f$. The motions of alkali ions are accompanied by the motion of oxygen, but are not coupled with the motion of the whole chain structure as the positions of silicons are almost fixed.
- (2) In the mixed-alkali glass, the relaxation time due to jumps among unlike sites is of the same order as that in the chain structure, because these motions are cooperative, i.e., the size difference of unlike cations causes successive and/or simultaneous relaxation of chain structures. Even in the mixed-alkali system, the relaxation of Li/\bar{Li} and K/\bar{K} jumps can be faster than that of the framework, but the relaxation time of jumps among like-ion sites decreases considerably compared with that for the pure systems; that is, $\tau_c (= \tau_{LiLi}, \tau_{KK}) \leq \tau_{LiK} \sim \tau_{KLi} \sim \tau_f$ where τ_{LiK} and τ_{KLi} are the relaxation times of Li/\bar{K} and K/\bar{Li} jumps, respectively.

The de-coupling index $R = \log[\langle \tau_f \rangle / \langle \tau_c \rangle]$ is known to decrease in mixed-alkali systems considerably. The mechanism observed in the present work will probably be applicable to many pure and mixed-alkali glasses.

5. Conclusions

Some characteristics of the slow and fast dynamics in a metasilicate glass have been examined. Both the slowing down and the acceleration of the jump motion were related to both space and time terms. A large forward-correlation probability and shorter time intervals between the jumps due to cooperative jumps accelerate the dynamics of the lithium ions. By contrast, the large back-correlation probability and the long time intervals between individual jumps cause slowing down of the dynamics near the glass transition region. Thus there are two possible mechanisms for accelerating the jump diffusion process. One is the changing of the geometrical nature of the jump paths and motions. Another is the changing of the temporal character of the jump. The cooperative motion of like ions plays a role, accelerating both factors in the lithium metasilicate system.

In the simulation up to times of 1 ns, structural relaxation of the framework of the mixed-alkali glass is confirmed to occur. This relaxation can explain the loosening of the chain structure in the mixed-alkali system. Coexistence of the loosening of the structure and decreased mobility of cations in the mixed-alkali system can be explained as follows.

In a pure alkali system, the cooperative motion of the like ions causes accelerated dynamics and this motion is decoupled from the motion of the glass-forming structure. On the other hand, the jump paths of the two kinds of alkali ion are independent, at least on a shorter

timescale, and are intercepted by each other in the mixed-alkali system. This causes more localized motions of the alkali ions and decreases the transport coefficient. This effect is larger for the cooperative jump motion than for single-jump motion. At longer timescales, $\text{Li}/\overline{\text{K}}$ and $\text{K}/\overline{\text{Li}}$ jumps occur accompanied by the changes in chain structure. This results in loosening of the frame structure in spite of the slowing down of the ion dynamics.

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