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Dynamical fluctuations in ion conducting glasses: Slow and fast components in lithium metasilicate

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Molecular dynamics 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. 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 (fracton), while type B particles show fast dynamics related to cooperative jumps and a strong forward correlated motion (Lévy flight). Mutual changes of two kinds of dynamics with the relatively long time scale have been observed. The changes cause an extremely large fluctuation of the mean squared displacements as well as the squared displacement of each particle, which depends on the time window of observation. Localized jump motion (fracton) cannot contribute to the long-time-translational diffusion but it can contribute to the rotational diffusion. On the other hand, forward correlated jump motion mainly contributes to long-time-translational diffusion and not to the short-time-rotational diffusion, although this can be a slower part of the rotational diffusion. These results have been compared with those of simple glass-forming liquids exhibiting the dynamic heterogeneity near T_g. The translation-rotation paradox can be explained by the characteristics of slow and fast dynamics.

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I. INTRODUCTION

The existence of slow and fast dynamics was observed in many glass-forming liquids [1–6] and discussed in relation to the heterogeneity near the glass transition regime, although the definitions of ‘‘slow’’ and ‘‘fast’’ dynamics and ‘‘heterogeneity’’ seem to be different in each work. For example, Richert [7] used the terms ‘‘heterogeneous scenario’’ and ‘‘homogeneous scenario’’ to classify the type of nonexponential relaxation near the glass transition region, in which ‘‘heterogeneous’’ was used for the superposition of the exponential relaxation process with different rates, while ‘‘homogeneous’’ was used for the identical intrinsically nonexponential relaxation processes. In the present work, heterogeneity comes from the existence of some distinguishable types of dynamics and there are fluctuations among them. This concept does not directly involve the origin of a stretched exponential form, as discussed later. In our previous works based on the molecular dynamics (MD) simulations, the coexistence of slow and fast dynamics and changes between them were found in ionics for the glassy lithium silicate [8–11]. In the lithium metasilicate glass, the lithium ion plays the role of a probe reflecting the landscape of the glass structure. A similarity between ionic motions in glasses and residual diffusion near T_g in simple glass-forming liquids may be expected, although there are some remarkable differences between them.

Blumen *et al.* have extended the continuous time random walk (CTRW) to the dynamics on fractal structures [12]. The mean squared displacement (MSD) exhibits the power law behavior, in which spatial (geometrical) and temporal terms are α and γ values, respectively. That is,

$$\langle r_i^2(t)\rangle \sim t^{\alpha\gamma}. \tag{1}$$

$\alpha(=2/d_w)$, where d_w is a fractal dimension of random walk, depends on the geometrical correlation of successive jumps and γ depends on the waiting time distribution of the jump motions. Both fast and slow dynamics in motions of lithium ions are explained by a combination of different exponents. On the other hand, slow dynamics near the glass transition temperature for a simple liquid is usually characterized by a stretched exponential form of density-density correlation, $F(t)$ in α relaxation (long time) region,

$$F(t) \sim \mathrm{A}\exp[-(t/\tau)^{\beta}], \tag{2}$$

with $\beta<1$. Such behavior is also observed for the lithium motion, although the contribution of a fast component overlaps. Therefore, β also contains both spatial and temporal origins. Each origin was separately evaluated using the MD simulation [9–11,13]. In the long time limit, a slope of MSD with t linear dependence is determined by the mean behavior of slow and fast processes (after coarse grained). Thus CTRW approach is expected to be valid for both a simple glass-forming liquid near T_g and ion dynamics in realistic glasses, although the former is dominated by the slow component while the fast component contributes considerably for the latter.

It is necessary to take a general view of each fast and slow dynamics so far studied to discuss the heterogeneity and fluctuations between these dynamics. Characteristics of the fast and slow dynamics were summarized as follows. Stretched exponential behavior of the slow component (type A) is caused by a waiting time distribution with a long tail and localized jumps within neighboring sites (fracton).

Namely, both temporal and spatial terms contributed to the slow dynamics. On the other hand, type B particles in the stretched exponential region (correspond to α relaxation regime) show faster relaxation than that of the Debye type one. The accelerated dynamics with $\alpha>1$ and $\gamma>1$ has been caused by the cooperative jumps, because the backward jump of the first ion after a cooperative jump is prevented by the following second ion [10,13]. Power law distributions of the displacement and number of atoms contributed to the cooperative jumps were observed for the fast particles [10,13], the fast dynamics has been characterized as Lévy flight [14] and is a main mechanism of the diffusion (and to the DC conduction) [8,9,11,13]. The time interval between jumps has been shortened by the cooperative jumps. Namely, fast dynamics is related with the acceleration in both temporal and spatial terms. Coexistence of fast and slow dynamics explain the experimentally observed ''universal dynamic response'' [15] for frequency dependences of conductivity in many conducting materials.

In the present work, fluctuations between fast and slow components in a longer time region have been examined in detail. We have compared the dynamic heterogeneity in ionic motion with that of the simple glass-forming liquids. In both cases, cooperative jumps (simultaneous jumps of neighboring ions or those occurring within several picoseconds before the relaxation of the jump sites [16,17]) play important roles in dynamics. The role of such motions in translation-rotation paradox has been also discussed.

II. MD SIMULATION

MD simulations in Li_2SiO_3 were performed in the same way as in previous studies [8–11,13,17–20]. 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 [21] 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 [20], 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 for the Li_2SiO_3 system [10,13] at 700 K.

Definition of the jump motion and type A and B particles

The number of jumps for each ion was counted in a similar manner to that in the previous works [8,9,11,13,22,23]. The displacement greater than 1/2 of the distance of the first maximum of the pair correlation function, $g(r)^{M-M}_{max}$, was judged as the jump, where the positions of atoms were averaged for several ps to remove the effect of small displacement due to thermal vibration, near constant loss (β-relaxation) and low energy excitation. Particles showing a displacement less than the distance at the first minimum of $g(r)_{Li-Li}$ during a given time (T) was defined as type A. Namely, the ion is located within neighboring sites during T. Particles showing a displacement greater than the distance of the first minimum of $g(r)_{Li-Li}$ during T were defined as type B. Type A and B depend on the time windows selected [9,11]. In the present work, T was set to be 920 ps and the time window was set to be 80 ps (including 100 points of initial t) as II in [11] in each 1 ns time region, unless otherwise stated.

III. RESULTS AND DISCUSSIONS

A. Change of fast and slow dynamics and time resolution of observation

In previous works on Li_2SiO_3 [10,11,13], the coexistence of fast and slow dynamics in translational diffusion of the lithium ions has been found in the glassy state. Since many particles keep either 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. These two kinds of dynamics are clearly distinguishable and not parts of one distribution function being that belongs to the same kind of dynamics [11], since plots of displacements of Li ions against jump angles between successive jumps (measured using a fixed scale during 1 ns at 700 K) showed two regions clearly (cf. Fig. 6 in [10] in the glassy state).

In a study of dynamic heterogeneities in a supercooled Lennard-Jones liquid, Kob *et al.* [3] have defined ''mobile particles'' (Am) as A (where A is a name of species) particles that have moved farther than a distance r^* within a time t^*, where r^* is the value of r at which the normalized difference from the Gaussian approximation starts to become positive and very large. Our definition of type B [9,10,13] particles may be quite similar to that by them, because the coexistence of slow and fast dynamics resulted in an enhancement of non-Gaussian behavior [24]. However, caution may be necessary in characterizing the dynamics by non-Gaussian parameters, which have nonadditive characters in nature. Definition II [11], which depends on the time window, was introduced by taking account of the time resolution, since the difference of type A and B particles can be observed only when the time scale of the change between A and B is longer than that of observation.

Typical examples of time evolution of displacements of several Li ions at 700 K in Li_2SiO_3 glass are shown in Fig. 1. Particles with a long waiting time of jump motions and those localized between neighboring sites were observed. Arrows in Fig. 1 mean the cooperative motions of some particles, where the jump events occur almost at the same time and in almost the same direction. The cooperative jumps tend to repeat several times with relatively short intervals. Although these particles tend to hold their characteristics for fairly long times, several particles exhibited the mixing of slow and fast dynamics.

Details of fluctuations between fast and slow dynamics were examined in a longer time scale. A successive 4 ns simulation run at 700 K was divided into four regions and particle types were distinguished by the averaged squared displacement during 920 ps in each 1 ns region. Figure 2

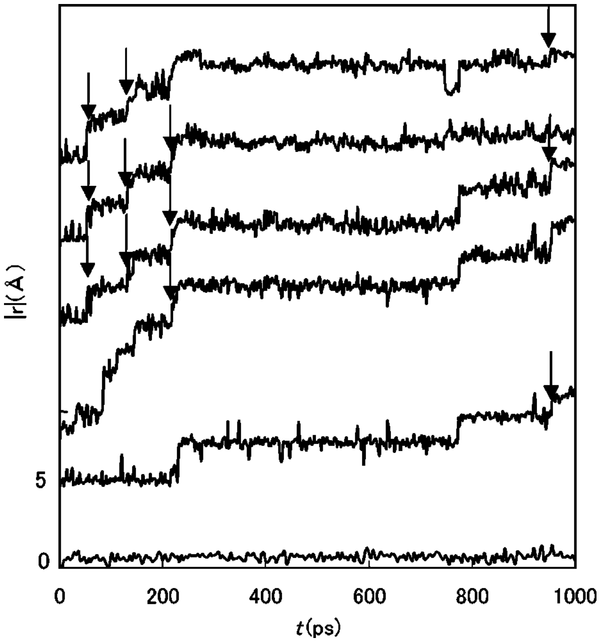

FIG. 1. Examples of displacements of several lithium ions during 1 ns. Arrows mean the cooperative jumps of the neighboring ions in almost the same direction.

shows a plot of the squared displacement of each lithium ion against the number of jumps in each time region. Mean squared displacement (MSD) of particles should be a linear function of an accumulated jump number, at least in a macroscopic point of view. However, we can find a wide distribution of points in Fig. 1 in a limited time scale. There are particles with a long waiting time and those repeating the jump motion within neighboring sites (fracton). Such a localized jump motion contributes to the slow dynamics. On the other hand, particles with large displacements, which show a medium jump frequency [11] were also observed. A pattern of the distribution is kept unchanged through four regions. Macroscopic behavior of MSD is obtained only when the dynamics of these particles having fairly different characters is averaged. MSDs at 700 K calculated using a different time window are shown in Fig. 3. In a simulation of glass, we have always encountered a large fluctuation of MSD. As shown in the figure, the irregularity is dependent on the time window used for the initial times and is smeared out in principle when we use an extremely large time window. This means that the fluctuation is not by poor statistics but depends on time resolution of the observation. The fluctuation is related to the following events.

(1) The discrete nature of the jump motion. This character of the jump diffusion is one of the causes of the fluctuation of the MSD. However, the relaxation of the jump site occurs within several picoseconds and the number of jump events is large enough to average such an effect even in the condition in the calculation of the MSD using a small time window in Fig. 3. Therefore, this is not a main cause of the large fluctuation.

(2) Jump motions taking place in cooperation of several particles. Since such a cooperative motion of several particles occurs almost at the same time, this enhances the discrete character of the displacement mentioned in (1). However, the time window of 80 ps seems to be large enough to average this effect, too.

(3) Characteristics of the Lévy flight dynamics. This effect seems to be one of the main causes. As shown in Fig. 2, there are several particles showing quite large square displacement (r_i^2). Particles participating in the cooperative jumps have large forward correlation probability. Namely, the effective jump length of the cooperative jumps, which tend to continue the jump in the same direction as the previous one, is larger than that of single jumps. In Lévy flight dynamics, even a smaller number of events with high n value (n is the number of particles participating in a cooperative jump) can considerably contribute to the MSD. Namely, dynamics is dominated by their largest terms, and thus by rare intermittent events [14]. Intermittent and sporadic nature of such dynamics has been discussed by Wang [25].

(4) Fluctuations between slow and fast dynamics. This effect is significant and a main reason to require the extremely large time window to average the diffusive motion. Multitime correlation functions used by Schmidt-Rohr and Spiess [6] and Heuer *et al.* [26] is a useful technique to characterize such fluctuations. Since the observation by

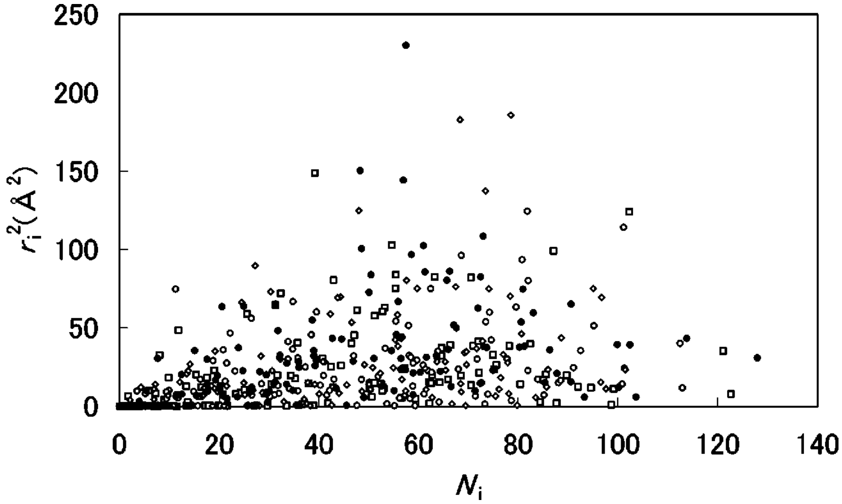

FIG. 2. Squared displacement of each lithium ion is plotted against the number of jumps in each (1 ns) time region. □, 0–1 ns; ○, 1–2 ns; ◇, 2–3 ns; ●, 3–4 ns region.

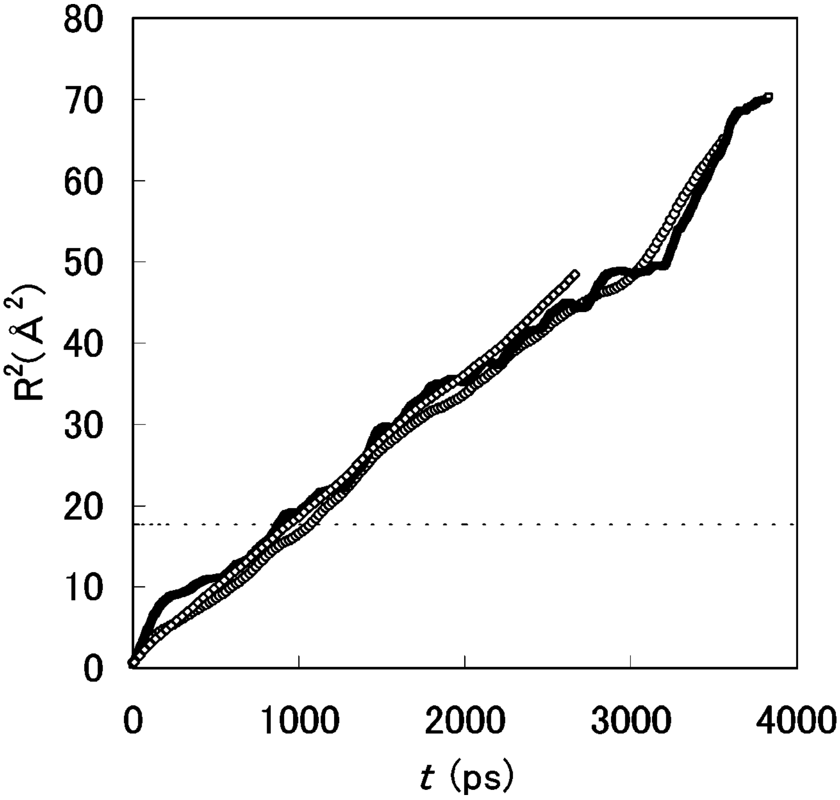

FIG. 3. MSD of lithium ion with a different time resolution at 700 K. Time windows, δt are □, 80; ○, 400; and ◇, 1200 ps, respectively. Since the same number of t_0 value was used in each case, irregularities in the curves with a small time window are not due to poor statistics, but are mainly due to fluctuations between slow and fast dynamics.

NMR is on a rotational diffusion, one must take into account the difference between rotational and translational diffusion for a detailed comparison.

In Fig. 4 squared displacements for arbitrary chosen ten lithium ions are shown for each time region. Large fluctuation of the square displacement means mutual change between fast and slow dynamics. For example, a Li ion (No.1) changed the type of motion during a 4 ns run as *A*-*B*-*B*-*A*. Some particles keep their characters through 4 ns. For example, a particle (No. 9) did not jump during 4 ns.

In Fig. 5 the number of jumps N_i for the same Li ions as in Fig. 4 is shown for each region. As naturally expected, particles showing a small number of jump events (e.g., No. 2) show small displacements. However, in other cases, the relation between r_i^2 and N_i is not simple due to the mixing of localized and diffusive jumps. For example, a motion of a particle (No. 4), changed from a localized jump to an accelerated one. Average and dispersion of the N_i and r_i^2 values are shown in Table I, where the data for 144 Li ions in four

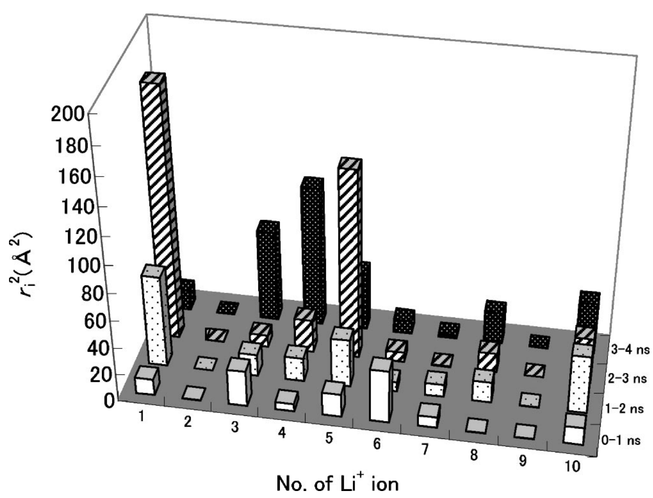

FIG. 4. Squared displacements r_i^2 for ten arbitrarily chosen Li ions in each time region.

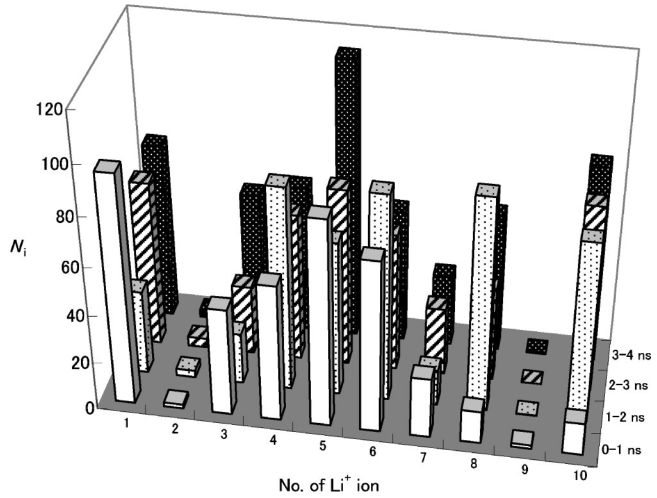

FIG. 5. Number of jumps N_i for ten arbitrarily chosen Li ions in each time region. (The number corresponds to that in Fig. 4.)

TABLE I. Average, dispersion, and standard deviation of the fluctuations in the number of jumps (N_i) and the square displacement (r_i^2) during 1 ns of lithium ions.

	N_i	r_i^2 (Å^2)
Average	38.74	22.53
Dispersion	918.67	882.36
Standard deviation	30.31	29.45

regions were used. There exists an extremely large fluctuation in each value, especially in r_i^2 values.

In Fig. 6 changes of characters of some particles (Nos. 1–6) in the $N_i - r^2$ phase through four time regions are plotted. Qian *et al.* [27] have argued that the intrinsic non exponential relaxation in the so-called homogeneous scenario is caused by the correlated back and forth jumps. This behavior is similar to the localized jumps observed in the large N_i and small r^2 regions in the present work; however, this motion can switch to that of type B with accelerated dynamics, which is characterized by a medium N_i and large r^2 values. This means that the fluctuations between localized (back-correlated) motion and accelerated (forward correlated) exist, where both dynamics is related with the spatial (geometrical) character of the jump motion. The change of the jump frequency was also observed, although some slow particles seem to keep their character for a fairly long time. Large displacements of B type particles cause large changes to their environment by themselves. Examples of the motion of A- and B- type particles and fluctuations between fast and slow dynamics in the r-θ phase have been shown in [23]. The difference of the peak heights (mainly for the second peak) between $g(r)_{Li(A)-Li(A)}$ and $g(r)_{Li(B)-Li(B)}$ was observed [22]. Such a difference in the medium range structure can be observed only when the structure is averaged for a suitable time region. Thus, the heterogeneity is consistent with the fluctuation of the local density of Li ions. Spatial heterogeneity of type-A and -B particles in this system was also shown [9]. We have explained the localized motion as a fracton (being dependent on the geometrical condition of the jump path and jump motion) unlike the fixed double well potential model. The mobile region and immobile region can change in time.

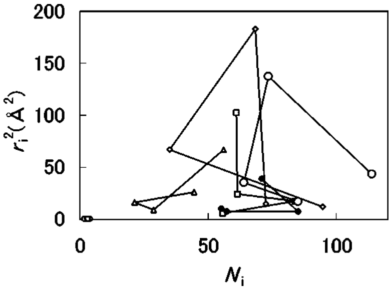

FIG. 6. Change of character of particles in the r_i^2-N_i plot of lithium ions during 4 ns (Nos. 1–6). The data in each 1 ns region are connected. (The number corresponds to that in Figs. 4 and 5.) (◇, No. 1; ∘, No. 2; △, No. 3; □, No. 4; ○, No. 5; and ●, No. 6.)

B. Comparison with simple-glass forming liquids

In MD simulations of the soft core system, cooperative motions were visualized [1]. The existence of stringlike cooperative motions was also observed in some other systems [4], including the loop structure. (The loop structure seems to be a special case of stringlike motion, where the particles have a strong memory of the jump angle.) The cooperative motion also plays an important role in ion-conducting glasses. In a lithium metasilicate glass, each lithium ion is surrounded by oxygen atoms (3–7), and each silicon is surrounded by four oxygen atoms. Namely, the system is intricate combinations of chains made of SiO_4 and LiO_x units. The behavior of the lithium ion is more fragile compared to the chain structures with strong connections [8]. In such a case, the jump path made of chains has a longer relaxation time compared to the ionic motion [28]. The motion of the lithium ion is triggered by the change in shape of the coordination polyhedron [29]; nevertheless, ionic motion is decoupled with the whole structure relaxation. A lithium ion can move in its own path even in a glassy state, but is affected by the potential surface made of closely packed oxygen atoms. On the other hand, in a simple glass-forming liquid, the particle within a cage is also forming the cage of other particles. Due to such a dual character, each jump motion in a simple glass-forming liquid near T_g is coupled with the structural relaxation. As a result, the size of the cooperative region and its temperature dependence in the simple glass-forming liquid differs from that in the ion-conductive glasses. The difference may be enhanced in the two-dimensional (2D) case, where the particles have smaller degree of freedom. Except for the above differences, the following common features of the dynamics between simple glass-forming liquids and ionics in lithium metasilicate have been observed:

(1) The transport process occurs through jump motions.
(2) The cooperative motion of some or many particles exists.
(3) Coexistence of fast and slow dynamics.
(4) Existence of dynamic heterogeneity.
(5) Existence of spatial heterogeneity.
(6) Each type of dynamics can be represented by the extended CTRW.

When we consider the difference in the contribution of fast and slow dynamics and the spatial and temporal terms, many systems seem to be explained by a general concept.

C. Translation-rotation paradox for diffusion

In Fig. 7, the function $C(t)$, for each type of particles at 700 K, is shown,

$$C(t) = \langle \mathrm{V_i}(1) \cdot \mathrm{X_i}(t) / \mathrm{V_i}(1)^2 \rangle, \tag{3}$$

where the position vector $X_i(t)$ of a lithium ion is projected onto the first jump vector $V_i(1)$, and the type of the particles was determined in the first 1 ns region. $C(t)$ functions of types A and B consist of jump motions and fluctuations. $C(t)$ becomes 1 if every A particle performs the first jump. As

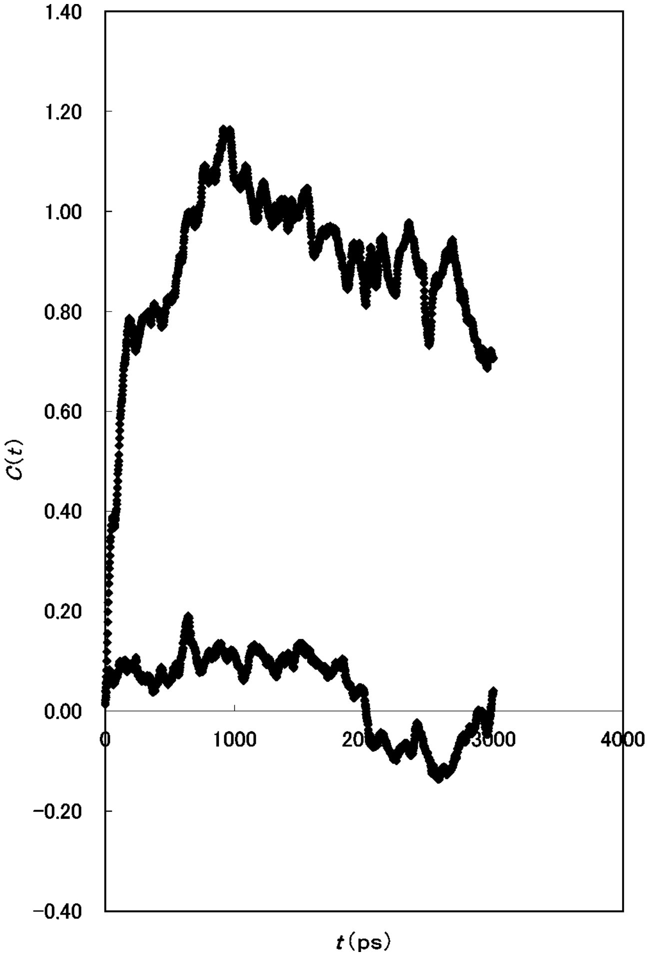

FIG. 7. Mean position vectors of Li ions projected onto the first jump vectors, $C(t)$. The lower curve is for type A and the upper curve is for type B particles. The mean direction of type A particles is reversed at 2 ns, while the type B particles show large forward correlation and have a long memory of the direction.

shown in Fig. 7, orientations of type A particles are reversed after about 2 ns. It turns out that the memory of the direction of the first jump angle was lost for A type particles much faster than B type particles. The localized motion of the type A is not a vibrational one in a cage but is a jump between neighboring sites, which leads to a stretched exponential decay of the relaxation. On the other hand, type B particles have a long memory of the direction of the first jump. $C(t)$ value becomes greater than 1 for the type B particle at around 600 ps, which indicates the existence of forward correlated motions overcoming the contribution from backward jumps. The function $C(t)$ is related with mean rotational angles of types A and B ions, while the definition of types A and B particles are based on the translational motion of the particles. Therefore, we can discuss relationships between the rotational and translational motion of types A and B particles as follows. Fast particles tend to show a small jump angle, while slow particles tend to show large jump angles. That is, the type A particle contributes less than the B type particle to translational diffusion but it contributes to rotational diffusion in a certain time regime. This trend was also observed in the plot of the displacement versus jump angles between successive jumps (r-θ plot) for some particles [10]. Particles with long time residences contribute to neither translational nor rotational diffusion. However, particles with localized motion can contribute to the rotational diffusion.

The diffusion constants D_{trans} and D_{rot} in fragile liquids are proportional to $T/\eta(T)$, where η is the shear viscosity when temperature T is not too low. The Stokes-Einstein-Debye relation holds well in such cases. D_{trans} and D_{rot}, respectively, measure the rates of increase with the time of mean-square positional and angular displacements of the particles. In fragile glass formers in the low T region, D_{trans} is known to be enhanced a hundred times. This phenomenon is called the "translation-rotation paradox" [32]. It is possible that the mean rotational correlation time is dominated by the slow environment, while the translational displacement occurs mostly when it is in a fast state [33]. The existence of accelerated dynamics due to the cooperative motion can reasonably explain the paradox when the number of localized jump is not remarkable. Qian *et al.* [27] have performed a MD simulation of propylene carbonate and considered different coupling cases of translational and rotational dynamics. They have pointed out that even in the D-coupling case, a molecule may display a large $\delta\ \theta(t)$ and a small $\delta\ r(t)$ or vice versa. The situation in the lithium silicate glass is similar to this case in some extent. Namely, localized jumps (fracton) show fast rotational dynamics, while the cooperative jumps with large forward correlation (Lévy flight) show slow rotational diffusion and fast translational diffusion. The ratio of the contribution of the localized motion to enhanced translational diffusion will be different system by system and depend on the temperature of the system. A NMR measurement for ionic glasses [30] shows that the activation energy for the local motions of alkali metal ions is about one-third of that for diffusion or conductivity. Therefore, localized motion can more easily occur in the conducting glasses. Such localized motion was enhanced in a mixed alkali-silicate glass system [11].

D. Relationship between heterogeneity and functional forms of decays

The existence of fast and slow dynamics sometimes has been discussed in connection with the heterogeneous scenario, where the stretched exponential behavior found for the relaxation is a result of the superposition of exponential distributions in both dynamics. For the present system, the wave-number-dependent density-density correlation function $F_s(k,t)$ can also be presented as a stretched exponential form

$$F_s(k,t)=A\exp[-C(t/\tau_k)^{\beta_k}], \tag{4}$$

where C is a constant and $\tau_k\sim k^{-n}$. In Fig. 8 partial $F_s(k,t)s$ for types A and B particles during 1 ns are shown. The stretched exponential region of $F_s(k,t)$ is about 20–300 ps judging from the slope of log{log[$F_{s(k,t)}$]}-log(t) plot. In such a time region, the decay of type A particles by localized motion is slower than the exponential because of the correlation. The waiting time distribution with a long tail can also cause the deviation from the exponential decay in the long

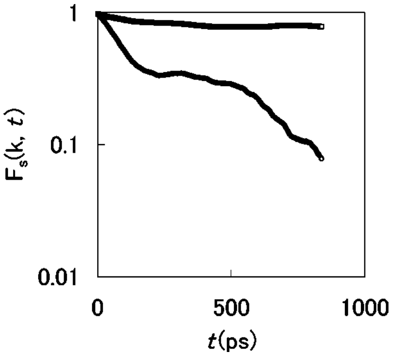

FIG. 8. Partial self part of the density-density correlation function, $F_s(k,t)$, for $k=2\pi/10$ at 700 K. The lower curve is for type B and the upper curve is for type A ions. Decay for type A is slower than the exponential type decay due to back-correlated jump motion (fracton). Decay for type B is faster than that for type A ions. Recovery of the decay curve observed for type B is caused by the mixing of slow dynamics. A relatively small time window (80 ps) was used here to distinguish types A and B clearly.

time region. On the other hand, type B particles show faster decay than type A particles and show recovery of the curve due to mixing of localized motion. The contribution of the $n<2$ component in the $F_s(k,t)$ [8] in the lithium motion can be attributed to such fast decay. Intervals of the jumps tend to be shortened in the fast dynamics [9] and this means that the fast dynamics of the type B particle is of the non-Debye and nonexponential type. Ion dynamics in the present system in both fast and slow components obeys nonexponential decay (and power law behavior in MSD). Therefore, heterogeneity in the present system is a superposition of two kinds of dynamics where both show nonexponential decay.

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 seem to be difficult to decompose into exponential functions due to contribution of backward jumps, while the latter can be decomposed into exponential contributions with different life times. The existence of such components is consistent with basic assumptions in the trapping diffusion model (TDM) [31], which was successfully proposed to deal with the glass transition in fragile liquids, such as soft core systems, based on the power law distribution of the waiting time of jump motions. We have previously shown that a lithium ion moves with the center of gravity of the coordination polyhedron made by oxygen atoms and 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 Ref. [29]. Thus to discuss the coexistence of the fast and slow dynamics and the origin of a stretched exponential form is independent and a separate problem.

The fast and slow parts of dynamics in the present system are well distinguishable by the restricted jump angles. Such restricted angles seem to be characteristics for the glass where the framework made by SiO_4 chains is stable and therefore the structure of the jump paths has a much longer lifetime compared with the time scale of the jump motion of the lithium ion. At higher temperatures (1673, 2000 K), there was no clear jump and a mutual change of fast and slow dynamics occurred with a high rate, where $F_s(k,t)$ was fitted well in an exponential form at a longer time region [8,10]. Namely, in liquid states, there is no distinguishable different component of dynamics [10]. In a supercooled liquid state (1200 K), the jump motion and the stretched exponential decay of $F_s(k,t)$ were observed, although the motion is not typical one [34]. In this case, both components may show nearly exponential decay and form a stretched exponential region, where the time scale of fluctuations is comparable to that of the jump motion. Such behavior leads to the so-called heterogeneous scenario. Therefore, it is not surprising that the heterogeneous scenario may hold well in a supercooled liquid state for the other glass-forming systems. Details for the motion of lithium ions in a supercooled liquid state will be examined in a separate paper.

Since jump paths of lithium and potassium ions in the $LiKSiO_3$ system are nearly independent in a relatively short time scale and the mixing of the jump paths occurs in a long time scale [28], the mixed alkali-metal system shows a kind of heterogeneity. Namely, heterogeneity can be realized only when the "memory" of characteristics of the dynamics is significantly longer than the relaxation time for the mixing. Observation of the heterogeneity is also dependent on the time (or spatial) resolution.

IV. CONCLUSION

Fast and slow dynamics of lithium ions in a metasilicate glass have been examined. A large forward correlation probability and short time intervals of the jumps accelerate the dynamics, where cooperative motion of like ions plays a role. By contrast, a large back correlation probability and the long time intervals of single jumps cause slow dynamics. Both spatial and temporal terms determine the characteristics of the dynamics. Large fluctuations between both dynamics were observed. The stretched exponential form of the decay is caused by the superposition of nonexponential forms of both dynamics. The translation-rotation paradox can be explained by the existence of fast dynamics, which mainly contributes to the translational diffusion but not to the local rotational diffusion.

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