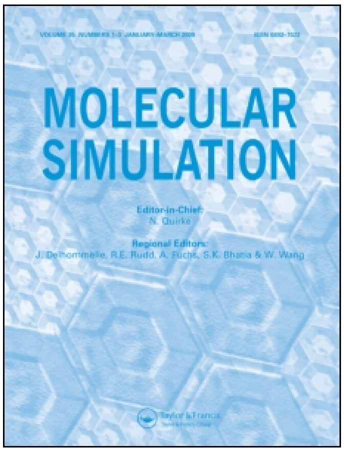

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A Molecular Dynamics Study for Lithium Metasilicate: Liquid and Quenched Supercooled States

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A MOLECULAR DYNAMICS STUDY FOR LITHIUM METASILICATE: LIQUID AND QUENCHED SUPERCOOLED STATES

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A molecular dynamics (MD) simulation of the lithium metasilicate (Li_2SiO_3) system has been performed to study the dynamics and geometrical structure of a liquid state at 1673 K and a glassy state at 700 K. The long term dynamics of the glassy state is shown for the self-part of the van Hove correlation functions. In the glassy state, diffusion of lithium ion was found to occur mainly through jump motions among equilibrium sites surrounded by oxygen atoms. A geometric structural analysis with polyhedra made of oxygen atoms around lithium was applied to characterize the structure and dynamical behavior.

KEY WORDS: Lithium metasilicate, liquid and glass, structure and dynamics, MD simulation

1 INTRODUCTION

The glass transition seems to occur in all classical liquids as a universal phenomenon, when crystallization is bypassed. In the present study, lithium metasilicate, a typical alkali silicate glass, was chosen to study the liquid and glassy states of an ionic system and the results were compared with those of soft-core, uncharged systems, which have been extensively studied by molecular dynamics simulations. The present system consists of chain structures formed by SiO_4 units and mobile lithium ions surrounded by oxygen atoms.

Some diagnostic of the structural slowing-down near the liquid–glass transition has been studied [1, 2] for uncharged classical systems by molecular dynamics simulation. However, the relationship with the characteristic structure of the glass has been little examined, though some characteristic features of the structures have been found by using a geometrical structural analysis such as Voronoi polyhedron analysis or the Delaunay tetrahedron analysis for some systems [3, 4].

In a previous paper for the study of lithium metasilicate [5], the number of vertices, V, of a polyedron within the distance R_L centred at each lithium ion was analyzed in relation to the number of the O–O pairs (N), shorter than R_O; R_L is the distance at which the running coordination number $n_{Li\text{-}O}(r)$ begins to increase more rapidly due to contributions of the second coordination shell, and R_O is the distance where the

Table 1 Parameters of the potential used in this work.

Ion	*z*	$c/\text{Å}^3\,kJ^{1/2}\,mol^{-1/2}$	$a/\text{Å}$	$b/\text{Å}$
O	−1.40	54.0	1.81	0.142
Si	2.60	0	0.75	0.036
Li	0.80	0	0.85	0.040

running coordination number $n_{O-O}(r)$ begins to increase more rapidly due to contributions of the second neighbours. The N corresponds to the number of the O–O contact pairs of a polyhedron around a lithium ion. In the liquid state, the structures with $N = 3V - 7$ are found frequently for $V = 3$, 4, and 5. The distribution of N at $N = 3V - 7$ decreases with decreasing temperature and is found to have the peak maxima at $N = 3V - 6$ below the glass transition region; the internal geometrical degree of freedom of a polyhedron is $3V - 6$. The position of the maxima at $N = 3V - 6$ does not change any more on lowering the temperature. This suggests that the saturation of packing of oxygen atoms occurs at the glass transition temperature. The life time of the structure with $N = 3V - 6$ was found to be much longer than other polyhedra with other N-values. Thus N values as a function of V are good measures of packing of oxygen atoms.

The glass transition temperature (T_g) may be obtained as the narrow temperature range in which the heat capacity C_p changes drastically or the transport properties exhibit a drastic change. The T_g for a frozen polyhedral structure with the geometrical degree of freedom outlined above was found to be about 900 K for the lithium metasilicate system [5]. In this work, the atomic dynamics is also investigated in relation to the geometrical structure and it will be shown how the geometrical structural change is responsible for the diffusion of lithium ions in the highly supercooled state. The trapping diffusion model for the glass transition recently developed by Odagaki and Hiwatari [6, 7] is also tested with the present system.

2 METHOD

2.1 *MD simulation*

The MD calculation was performed with the same method as in the previous studies [5, 8]. The periodic cube contained 144 Li, 72 Si and 216 oxygen particles. A Gilbert-Ida type potential function [9] plus an r^{-6} term was used:

$$\Phi_{ij} = z_i z_j e^2/r + f_0(b_i + b_j)\exp\{(a_i + a_j - r)/(b_i + b_j)\} - c_i c_j/r^6, \qquad (1)$$

where z is the effective charge number, e the elementary charge; a, b and c are the parameters characteristic of each atom and f_0 is a normalization constant (4.184 kJ Å^{-1}mol^{-1}). The potential parameters are summarized in Table 1, which effectively reproduce the interference functions, s.i(s), obtained by X-ray diffraction [10] for a molten state and the crystal structure of lithium metasilicate at room tempeature. The system was equilibrated at 4000 K for more than 10 000 time-steps, starting from a random configuration, then the system was cooled down to lower temperatures. Simulations were carried out at 3000, 2000, 1673, 1173, 973, 700 and 500 K. A time step was 1 fs from 4000 to 2000 K and 4 fs from 1673 K to 500 K. The velocities of all particles were initially set to zero at each temperature, and 200 steps were simulated at constant temperature. In the present work the most detailed analysis was made for

1673 K (melt) and 700 K (glass), during which the molecular dynamics run was carried out over 6000 steps and 100 000 steps, respectively. The volume at the respective temperature was taken from available data [11, 12] on the density of the melt and the glass.

The behaviour of atoms may differ in different time windows, which can be specified as long (~ several hundred ps), medium (~ several tens ps) and short (~ several ps) time regions.

3 RESULTS

3.1 *Long Time Behaviour*

3.1.1 *Mean squared displacements*

The mean squared displacements of each ion are shown in Figure 1 for both 1673 K and 700 K. Owing to the small number of jump motion in the low temperature state, initial 100 time origins over 20 000 steps (80 ps) were taken for 700 K.

The order of magnitude of the diffusion coefficients for the three species in this system is $D_{\mathrm{Li}} \gg D_{\mathrm{O}} \approx D_{\mathrm{Si}}$ both in the molten and glassy states. In Figure 2(a), the mean squared displacements for oxygen and silicon at 700 K were plotted. The difference between these values is shown in Figure 2(b), and can be ascribed mainly to the rotational motion of oxygen atoms around silicon in the glassy state, for which the exchange of oxygen atoms between SiO_4 units scarcely occurs. The rotational motion contributes less to the diffusion coefficient, since the curve in Figure 2(b) become nearly flat after about 120 ps. On the other hand, the difference at 1673 K may contain not only the rotational part but also the exchange motion of oxygen atoms among SiO_4 units. The diffusion coefficients obtained from the long time region are listed in Table 2.

3.1.2 *Self-parts of the van Hove correlation functions*

The self-parts of the van Hove functions of species α defined by Equation (2) were calculated to observe the behaviour of particle motion both in the liquid and glass:

$$G_s^{\alpha}(r, t) = (1/N_{\alpha}) \sum_{i=1}^{N_{\alpha}} \langle \delta(r_i(t) - r_i(0) - r) \rangle, \qquad (2)$$

where $r_i(t)$ denotes the position of species α at time t and N_{α} is the number of particles of species α.

The functions $4\pi r^2 G_s(r, t)$ at 1673 K and 700 K are shown in Figures 3 and 4 for (a) lithium and for (b) oxygen, respectively. In Figure 3(a) for the lithium ion at 1673 K, it is clearly seen that the position of the main peak shifts rapidly to greater distances and the peak height decreases with increasing time, while for the lower temperature in Figure 4(a) the position of the main peak for lithium ion is independent of time and its area decreases gradually with elapse of time. For oxygen in the liquid state (see Figure 3(b)), the position of the main peak of $4\pi r^2 G_s(r, t)$ shifts significantly toward a larger distance and the intensity decreases with increasing time. On the other hand, for oxygen atoms in the glassy state, the main peak is nearly frozen and no tail appears, at least in the time scales shown here. Thus, the chain structures formed by SiO_4 units are little changed during this period in the glassy state, and the lithium ion moves among quasi-equilibrium sites surrounded by the near-neighbour oxygen atoms.

The present result suggests that the dynamical behaviour of single particle motions

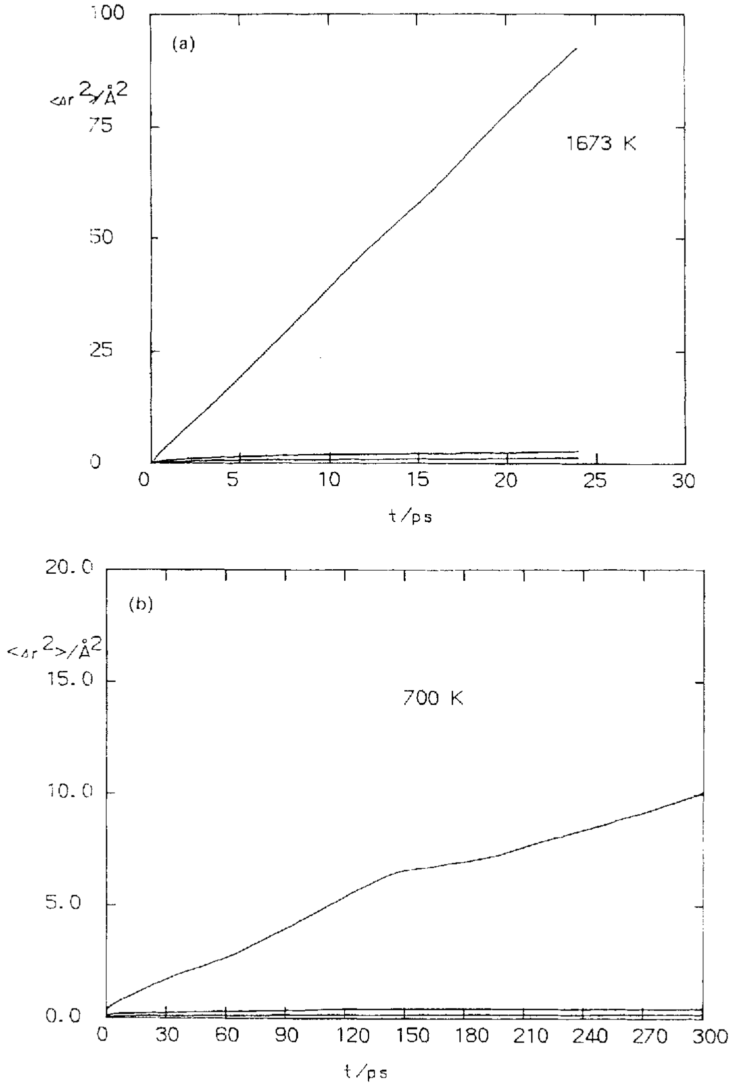

Figure 1 Mean squared displacements of lithium, oxygen and silicon at 1673 K(a) and at 700 K(b).

for lithium ions is similar to that for simple binary alloy systems reported by Roux *et al.* [1] where atoms diffuse *via* activated processes such as individual or correlated jump motions [3] in highly supercooled states. The jump motion of lithium will be discussed in detail later.

3.1.1 *The non-Gaussian parameters*

The non-Gaussian parameter $A(t)$ defined by Equation (3) for the respective species

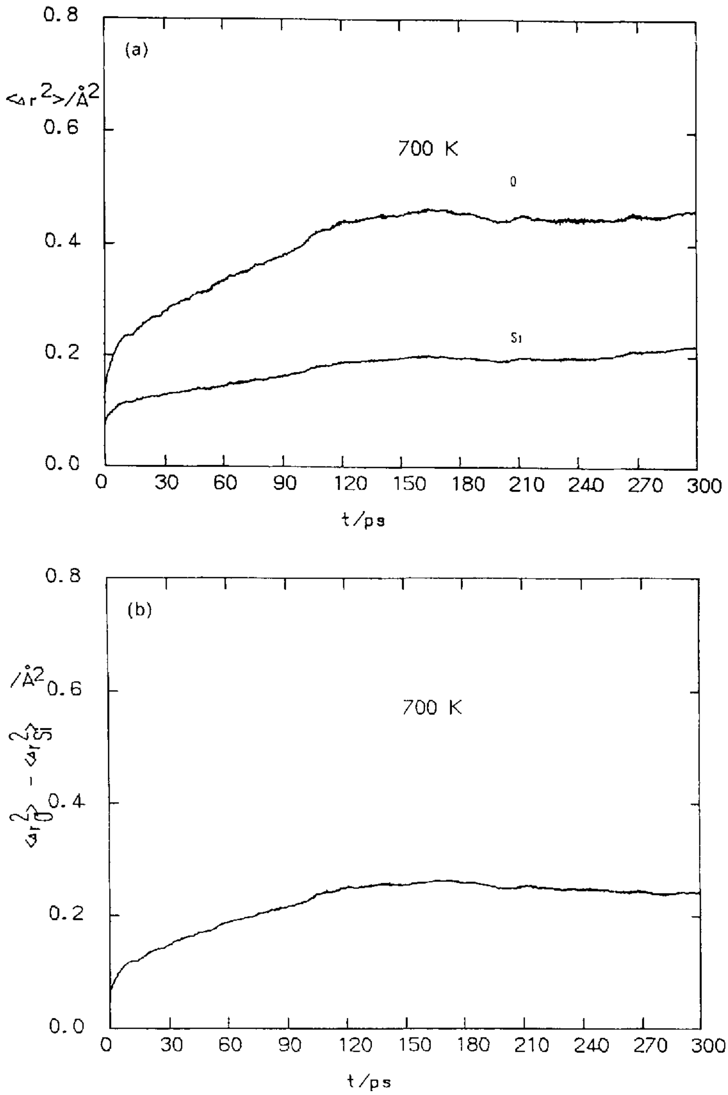

Figure 2 Mean squared displacements of silicon and oxygen at 700 K on an expanded scale (a) and the difference of these values (b).

Table 2 Diffusion coefficients of atoms (m^2s^{-1}).

T/K	*1673*	*700*
D_{Li}	6.5×10^{-9}	$\approx 1.1 \times 10^{-11}$
D_O	1.3×10^{-10}	$< 1.1 \times 10^{-13}$
D_{Si}	1.3×10^{-10}	$< 1.1 \times 10^{-13}$

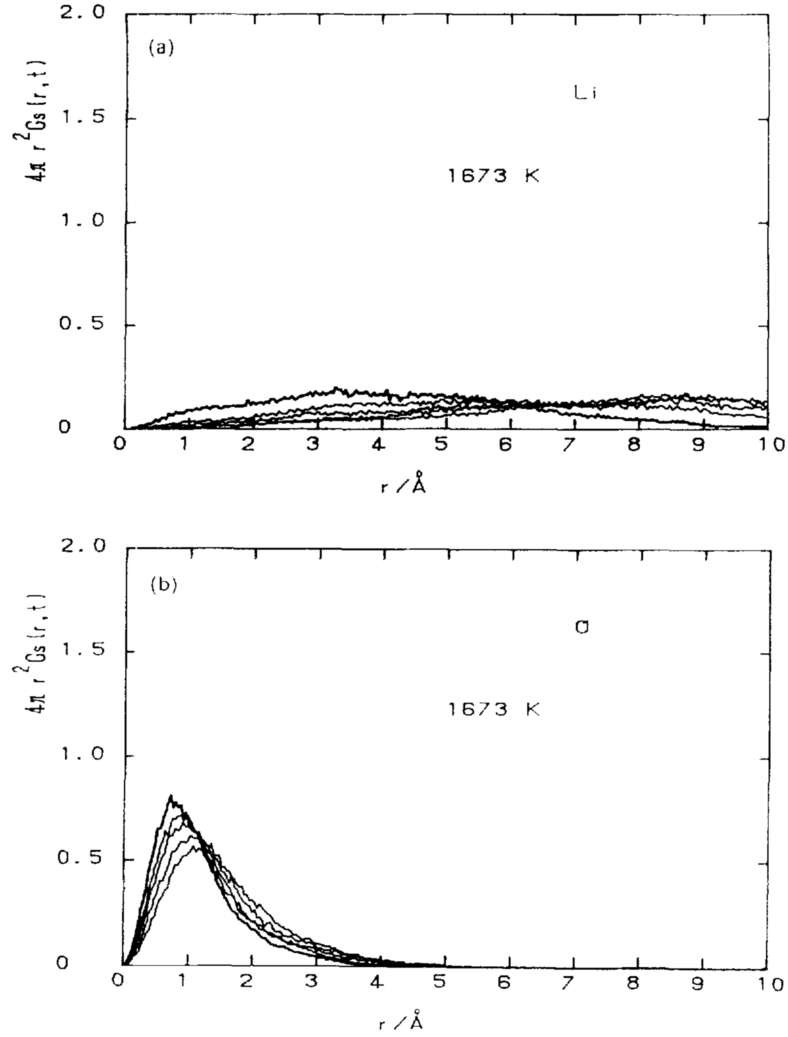

Figure 3 $4\pi r^2 G_s^{\mathrm{Li}}(r, t)$ (a) and $4\pi r^2 G_s^{\mathrm{O}}(r, t)$ (b) vs r at 1673 K. The curves from top to bottom for the first peak correspond to t = 6.4, 12.8, 19.2, 25.6 and 32.0 ps, respectively.

is shown in Figure 5:

$$A(t) = \frac{3\langle[(r(t) - r(t_0)]^4\rangle}{5\langle[r(t) - r(t_0)]^2\rangle^2} - 1 \tag{3}$$

With the stochastic-trapping diffusion model [6, 7], it was shown that the non-Gaussian parameter at $t = \infty$ becomes nonzero in glassy states whereas it vanishes in fluid states. Although it is impossible to reach $t = \infty$ in computer simulation, the value for the oxygen atoms does tend to increase at 700 K in the longer time region. However, the value for lithium still tends to decrease, because lithium ions, having a

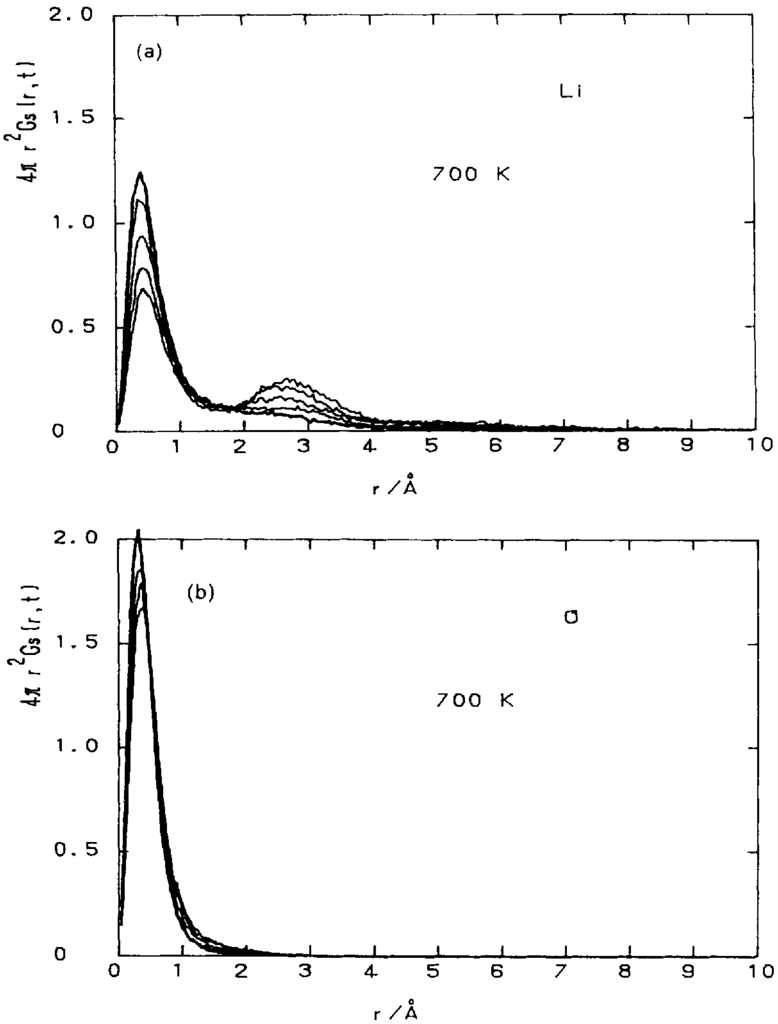

Figure 4 (b) $4\pi r^2 G_s^{\mathrm{Li}}(r, t)$ (a) and $4\pi r^2 G_s^{\mathrm{O}}(r, t)$ (b) vs r at 700 K. The curves from top to bottom for the first peak correspond to $t = 32, 64, 96, 128$ and 192 ps, respectively.

much small size, can more easily diffuse by jump motions. The time dependence of the parameter for silicon is nearly flat at 1673 K but slightly increases at 700 K.

These results are consistent with the predictions of the trapping-diffusion model for the glass transition by Odagaki and Hiwatari [6, 7].

3.2 *Behaviour in the Medium Time Range*

3.2.1 *Jump motion of atoms and the correlated jumps*

The behaviour of each atom in a time scale of ~ 10 ps was obtained by averaging the position of atoms over several vibrations. The squared displacements for arbitrarily

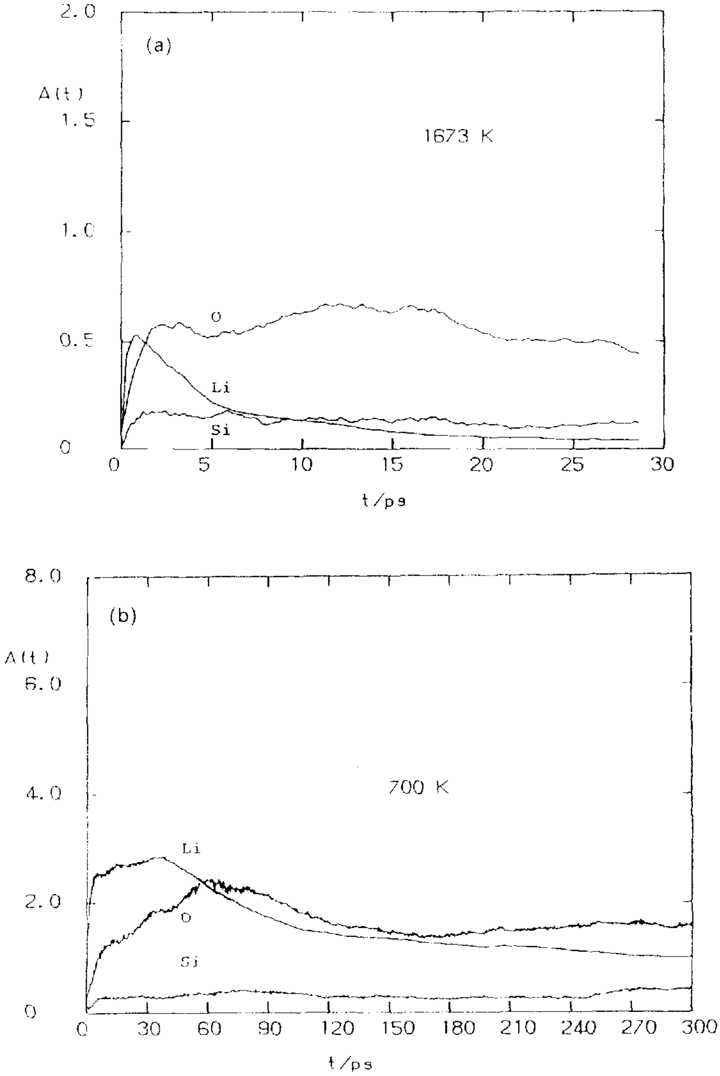

Figure 5 Non-Gaussian parameters $A(t)$ of atoms at 1673 K(a) and at 700 K(b).

chosen lithium ions in the glassy state are plotted *vs* time in Figure 6, where every position of lithium at time t is averaged over 0.8 ps around t. Clear jumps are observed in some cases from abrupt increases of the magnitude of the squared displacements.

Similar jump motions were also observed for the oxygen atoms, but occurred much less frequently than for lithium ions in the glassy state. Examples of such jumps are shown in Figure 7. The jump motion of oxygen in (a) was found to correlate with the motion of the oxygen atoms in (b) and (c); the position of the oxygen before the jump in (a) (from $X = 4.5$, $Y = 8.5$, $Z = 2.8$ Å to $X = 6.2$, $Y = 9.5$, $Z = 2.9$Å) is nearly the same as those of the end position after the jump in (b) (from $X = 4.3$, $Y = 6.0$,

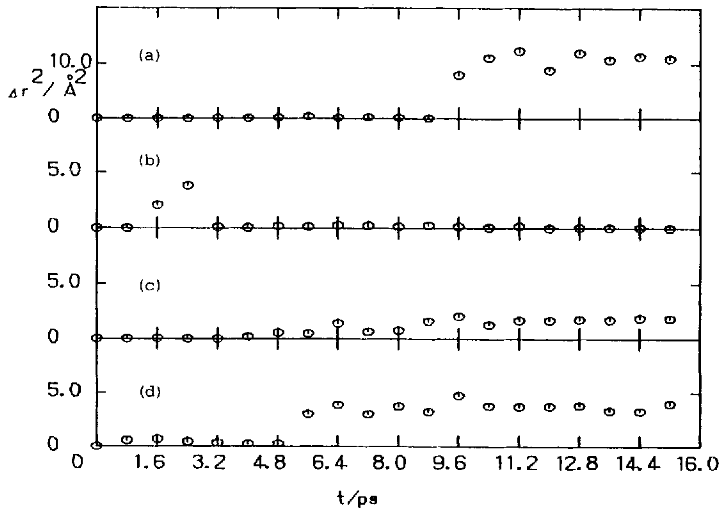

Figure 6 Squared displacements of some arbitrarily chosen lithium ions at 700 K. The position of the ions was averaged over every 0.8 ps.

$Z = 2.7$ Å to $X = 4.1$, $Y = 8.1$, $Z = 2.7$ Å). These correlated jump motions are similar to those observed for the binary soft-sphere glasses [13].

3.2.2 *Correlation of the geometrical structures and the dynamics*

The relationship between N and V [5] has been mentioned in Introduction. Some schematic structures with different V and N are depicted in Figure 8(a). The N-distributions at 1673 K and 700 K are shown in Figure 8(b). The N-distribution is found to have maxima at $N = 3V - 6$ in the glassy state, which is a tightly packed condition for the oxygen atoms. On the other hand, the less closely packed structures, for example $N = 3V - 7$, are observed frequently in the liquid state. The dynamics

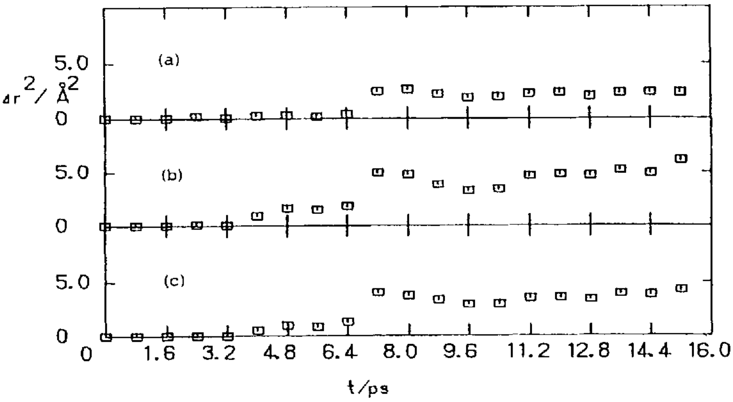

Figure 7 Squared displacements of some arbitrarily chosen oxygen atoms at 700 K. The position of ions was averaged over every 0.8 ps.

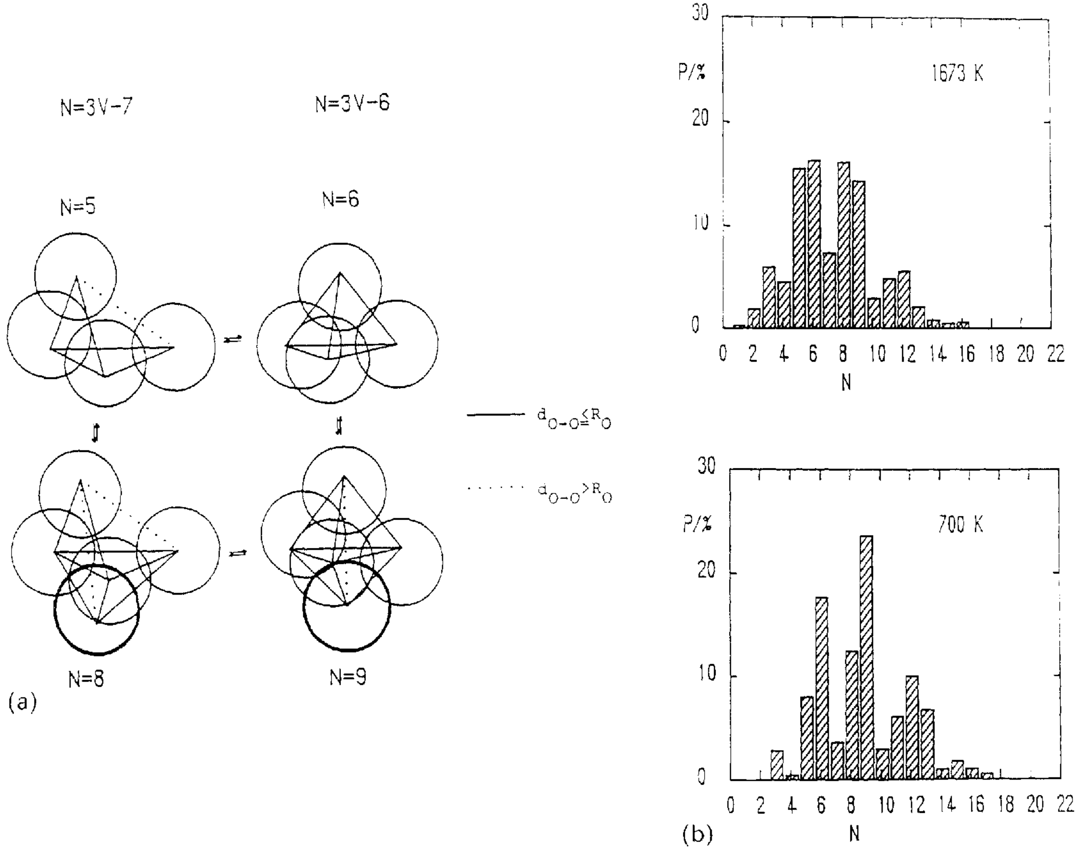

Figure 8 (a) Schematic drawing of some structures of the polyhedra with several values of N and V. The arrows in the figure show the main routes of structural changes in a short time interval. The circles represent oxygen atoms. The bold ones refer to oxygen atoms entering or leaving the polyhedra considered. (b) Distributions of N values at 1673 K and 700 K. ($N = 2 \sim 3$ for $V = 3$, $N = 4 \sim 6$, for $V = 4$, $N = 7 \sim 10$ for $V = 5$, $N = 11 \sim 13$ for $V = 6$, $N = 14 \sim 17$ for $V = 7$).

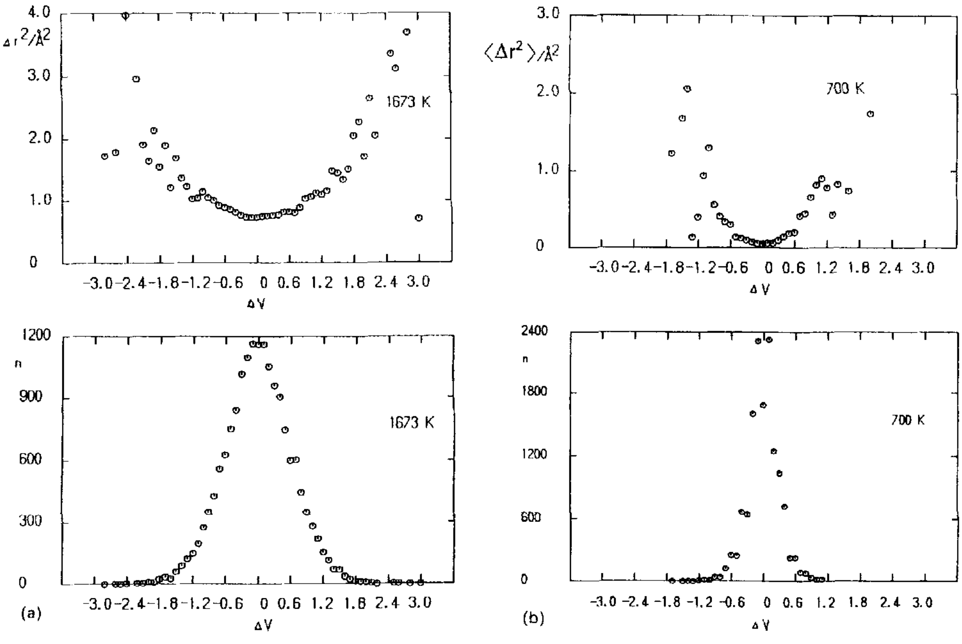

Figure 9 Relation between changes in V and mean square displacements for lithium trapped in the polyhedron (a) at 1673 K and (b) at 700 K. Each value is calculated with the time averaged structures over 0.2 ps (1673 K) and 0.8 ps (700 K). The corresponding distribution of n is also shown.

of lithium ions has been studied in relation to ΔV, that is, change in shape of the polyhedron.

The $\langle \Delta r^2 \rangle$ for lithium ions *vs* ΔV and the distribution of n *vs* ΔV are shown in Figure 9, where $\langle \Delta r^2 \rangle$ is the mean squared displacement of the lithium ions and n is the frequency of occurrence of ΔV. Both ΔV and $\langle \Delta r^2 \rangle$ were averaged over 0.2 ps and 0.8 ps for 1673 K and 700 K, respectively. Figure 9 reveals that lithium ions do not diffuse without change in number of coordinated oxygen atoms (V). The larger $|\Delta V|$ leads to the larger $\langle \Delta r^2 \rangle$. Thus, the correlation of diffusion of lithium ions with the surrounding oxygen atoms is significant. However, the correlation appears to be obscured at the large ΔV region, partly because in this region the number of n is too small for good statistics and mainly because ΔV is not necessarily additive for displacement of the lithium ions. The sharp distribution of n around $\Delta V = 0$ indicates that transformation of the polyhedra scarcely occurs at 700 K (as expected from the distribution of N), and this results in small diffusion of lithium ions. Some examples of correlation between the motion of lithium ions and the surrounding oxygen atoms in glassy state will be shown later in more detail. A similar relation between ΔV and $\langle \Delta r^2 \rangle$ has been obtained at 1673 K, where the distribution of n is broader than that at 700 K and the squared displacement of lithium around $\Delta V = 0$ is non zero. Thus the diffusion of lithium ions in the liquid state is not described in terms of a clear jump among quasi-equilibrium sites, as already suggested by the van Hove correlation function. The polyhedra at 700 K may be classified into two groups of their ΔV values [Figure 9(b)]. The distribution of N for class 1, with small ΔV values ($|\Delta V| \leqslant 0.5$),

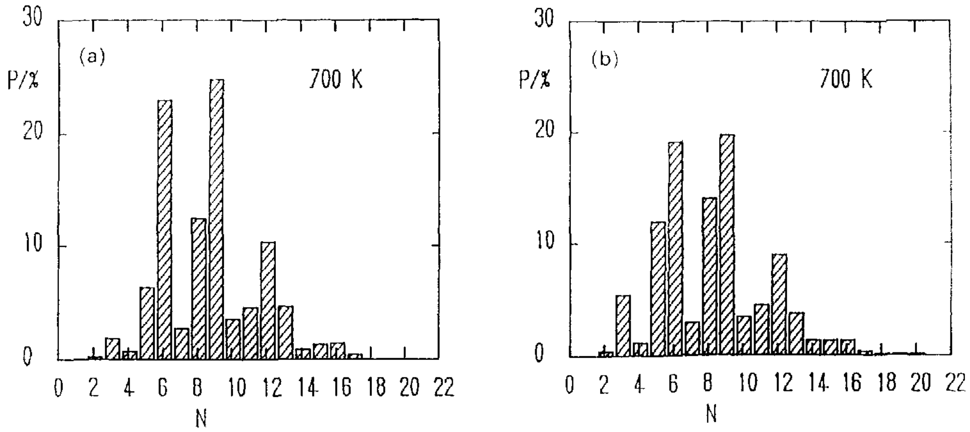

Figure 10 The distribution of N values for the polyhedra belonging to each class, specified by the ΔV values in Figure 9(b). (a) class 1 ($|\Delta V| \leqslant 0.5$) and (b) class 2 ($|\Delta V| > 0.5$).

which may be called "solid polyhedra", is shown in Figure 10(a). Similarly, the distribution of N for class 2, with large ΔV values ($|\Delta V| > 0.5$), which may be called "liquid polyhedra", is shown in Figure 10 (b). Polyhedra having the relation $N = 3V - 6$ are found more frequently for class 1 than for class 2. Thus, the interrelation of the geometrical structure and the diffusibility of lithium can be reasonably understood. The result also suggests that the jump rate depends on the amount of free space around mobile ions.

Figure 11(a) and 11(b) show the time evolution of the structural parameter N, V, and the squared displacement of lithium ions (corresponding to those in Figure 6(b) and 6(d), respectively, during the time range from 3.2 to 8.0 ps). The arrow in Figure 11(b) shows a clear jump event. In these figures, the position of atoms was averaged over 0.08 ps. The mean squared displacements of the centre of mass of each polyhedron are also shown. The corresponding motion of every oxygen atom around the lithium ions within distance 4 Å is shown in Figure 12(a) and 12(b). It follows that the larger motion of lithium correlates well with the motion of the centre of mass of the polyhedron but not with that of specific oxygen atoms. The lithium in the case of Figure 6(b) failed to jump to another site, but returned to the original site where the ion was trapped in the polyhedron $N = 6$ and $V = 4$ ($N = 3V - 6$). A clear gap is seen between the first coordination shell and the second shell in Figure 12(a). In contrast, the motions of oxygen atoms are much more complicated in Figure 12(b), where some oxygen atoms come into the first coordination sphere just before the jump. This suggests that fluctuation of the coordination number triggers the jump motions.

3.3 *Short Time Behaviour*

3.3.1 *Fluctuation of the geometrical structures*

The relationship between the structural fluctuation of the polyhedron and the motion of lithium ions in short time scale is shown in a separate paper [14], whose results will be briefly summarized as follows. By computing the transition probability of N values, two types of changes were often found, namely, (i) $\Delta N = \pm 1$, $\Delta V = 0$; (ii) $\Delta N = \pm 3$, $\Delta V = \pm 1$. (See the corresponding change in Figure 8). A time interval

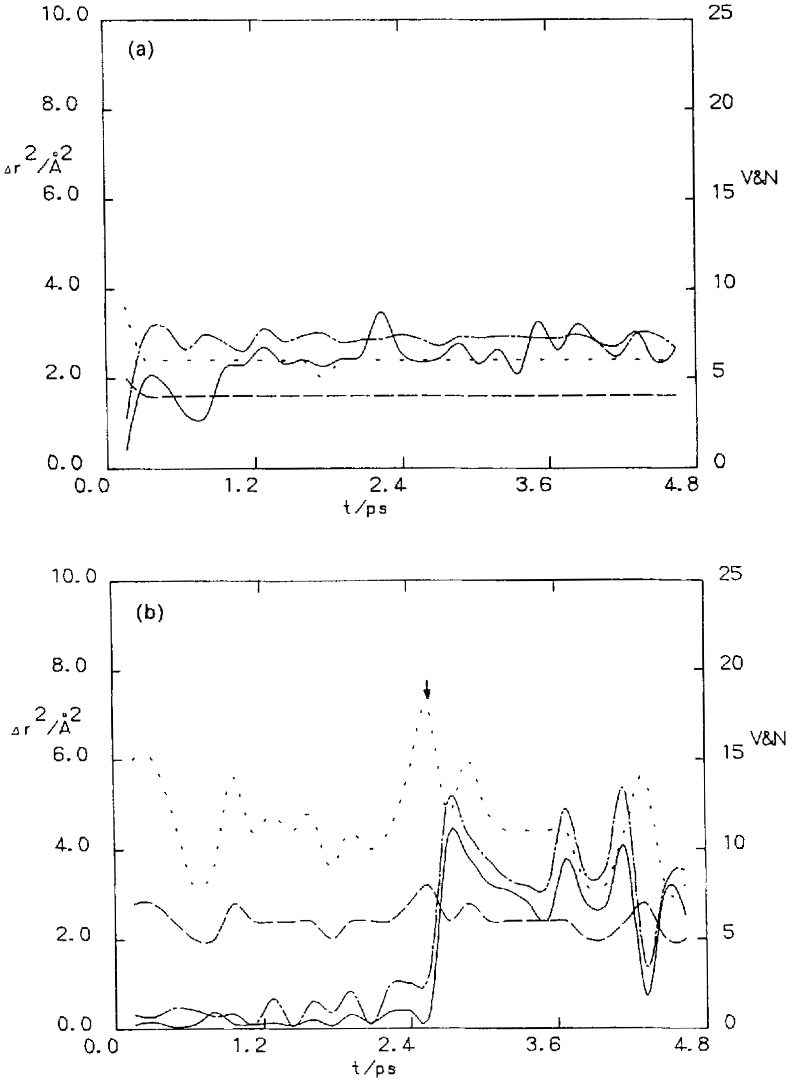

Figure 11 Evolution of the parameters N (····) and V (— —) together with the squared displacement of the lithium ions (a) and (b) (——), which correspond to those in Figure 6(b) and Figure 6(d), respectively, in the time region from 3.2 ps to 8.0 ps. The position of the atoms was time-averaged over every 0.08 ps. The positions of centre of mass of the polyhedra (–·–·–) are also plotted.

was taken during which N was changed for about half of the polyhydra, that is $\Delta t = 4$ fs at 1673 K and 16 fs at 700 K. Thus the structural fluctuation occurred according to a kind of selection of rule depending on the topological characteristics of the polyhedra.

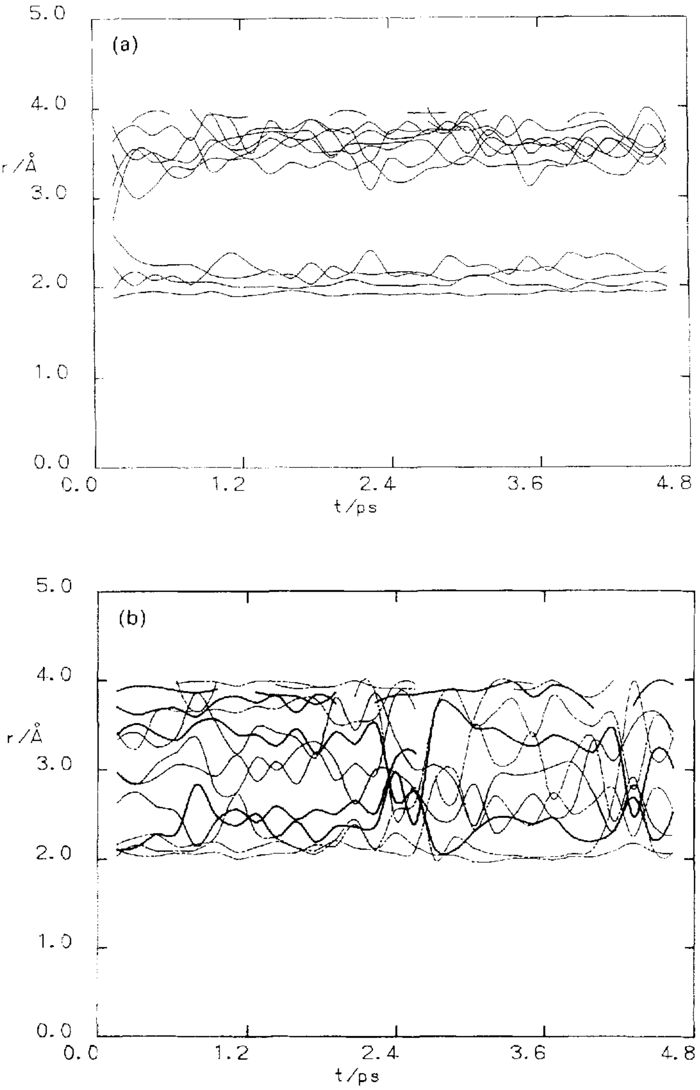

Figure 12 Evolution of Li–O distance for the reference lithium ions is shown ((a) and (b), which correspond to the ions in Figure 11(a) and Figure 11(b), respectively.) The oxygen atoms within 4 Å from the lithium ion are plotted.

4 CONCLUSION

The dynamics of atoms in liquid (1673 K) and glassy (700 K) states of lithium metasilicate was examined on different time scales. The self-parts of the van Hove correlation functions for oxygen and lithium decay differently in the liquid and glassy states. In the liquid state, the peaks of the function broaden and move to larger *r* values for both oxygen and lithium. On the other hand, the peak positions for lithium and oxygen are frozen in glassy state and a tail appears at larger r values resulting from jump motions of the lithium ion. Geometrical structural changes in the polyhedra of oxygen atoms centred on each lithium ion were found to correlate well with the diffusibility of the lithium ion both in the molten and glassy states. In the glassy sate, polyhedra with $N = 3V - 6$ are dominant and transformation of the polyhedra scarcely occurs, as expected from the N distribution. Thus, in turn, lithium ion tends to be trapped in the polyhedron. Thus, the diffusibility of the lithium is under control of the topology of polyhedron as well as that of oxygen.

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