Molecular Dynamics Study of Microscopic Mechanism of Diffusion in Li_2SiO_3 System

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MD simulation has been performed to learn the microscopic mechanism of diffusion of ions in the Li_2SiO_3 system.

The motion of lithium ions can be explained by the trapping model, where lithium is trapped in the polyhedron and moves with fluctuation of the coordination number. The mean square displacement of lithium was found to correlate well with the net changes in coordination number.

I. Introduction

In molten and glassy SiO_2, each oxygen is shared by two tetrahedral SiO_4 units. The addition of Li_2O results in a breakdown of this framework. The order of the diffusion coefficients in Li_2SiO_3 is $D_{Li} \gg D_O \gtrsim D_{Si}$ both in the molten and glassy states [1].

Adams et al. [2] pointed out that binary collisions cause the rapid decay in the memory function, i.e. the autocorrelation function of the random forces acting on the particles, whereas the long lived quasiexponential decay arises from dynamic events involving large numbers of ions. Lantelme and Turq examined the ionic dynamics of liquid eutectic LiCl–KCl [3] and proposed two main mechanisms resulting in the memory function: oscillations in the force field of the surrounding particles and a collective motion of the ion and its neighbours.

In the present article, we have applied polyhedral analysis to investigate the geometrical characteristics and the changes in the short-range order in molten and glassy Li_2SiO_3. The treatment is similar in principle to other types of topological analysis such as Voronoi polyhedral analysis. The momentary number V of oxygens around a lithium within the distance R_L and the corresponding number N of O–O pairs with distances shorter than R_O ($N \leq \frac{1}{2}(V-1)V$) were taken to be the characteristics of a polyhedron. R_L is the distance where the running coordination number $n_{Li-O}(r)$ begins to increase more rapidly due to contributions of the second coordination shell, and R_O is the distance where the running coordination number $n_{O-O}(r)$ begins to increase more rapidly due to contributions of second neighbours. This treatment enables one to examine the behaviour of neighbouring oxygens around lithium.

In the trapping model, Li is trapped within a polyhedron and can not be displaced unless a transformation of polyhedra occurs. To verify this mechanism, we examined the following:

1. The relationship between the evolution of the Li position and that of V and N for each Li. Since a change of V is accompanied by a change of the position of the center of gravity (C.G.) of the polyhedron, the squared displacement of the C.G. was also examined.

2. The relationship between mean squared displacement of Li and net changes in coordination number.

Additionally, the probability of changes of the polyhedron was analyzed, because the diffusion of lithium in this model is restricted by this probability.

For other aspects of the dynamics in the glassy state in longer time scale see [4].

II. Method

The MD calculation was performed in a manner similar to that in a previous study [1]. The periodic cube contains 144 Li, 72 Si and 216 O particles. A Gilbert-Ida type potential function [5] with r^{-6} terms was used:

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

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where z is the effective charge number, e the elementary charge, a, b, and c are the parameters characteristic of the atoms and f_0 is a normalization constant (4.184 kJ $Å^{-1}$ mol^{-1}). The potential parameters, which are given in Table 1, were chosen to reproduce the interference functions, si(s), obtained by X-ray diffraction [6].

Since the periodic cube contains 144 Li particles, the result for 144 polyhedra in each step was used for the statistical analysis.

The system was equilibrated at 4000 K during a run of more than 10 000 time-steps, starting from a random configuration. Then the system was cooled down in the following way: The chosen temperatures were 3000, 2000, 1673, 1173, 973, 700 and 500 K. Time steps of 1 fs (from 4000 to 2000 K) and 4 fs (from 1673 K to 500 K) were used. The velocities of the particles were set to be 0 at the beginning of the equilibration, and 200 steps runs at constant temperature were carried out at each temperature. Following this, the results of 6000 step runs and 20 000 step runs under constant energy conditions were analyzed for the melt (1673 K, 1173 K) and the glass (700 K), respectively. The volume at each temperature was obtained from data [7, 8] on the density of the melt and the glass.

III. Results

In Fig. 1 the evolution of square displacements of some arbitrarily chosen lithium ions and of the C.G. are plotted along with the changes in V and N for melt (1173 K) and glass (700 K).

From Fig. 1 we find that the lithium ion moves synchronously with the C.G. of the polyhedron. This is quite natural because the C.G. can be regarded as the potential minimum made by the oxygens around lithium if we neglect the contribution of forces from the further coordination shells.

In the case shown in Fig. 1 c, the polyhedron around a lithium ion has the typical structure found in glass [9], namely, V is almost 5 and N fluctuates around 9 ($N=3V-6$ for $V=5$). In this case, the lithium ion is trapped in the polyhedron having a close packed structure. When the fluctuation of the structure is large, the lithium ion moves largely and sometimes jumps as shown in Figure 1 d. The deviation of the position of lithium from the C.G. was found to decrease with decreasing temperature.

Figure 2 shows the distribution of squared displacements of the C.G. after 16 fs at 1673 K. The distribution on the left side is for the polyhedra without a change in V and that on the right side is for the polyhedra with changes in V. The motion of lithium observed in Fig. 1 is comparable to that of the C.G. Thus lithium moves with changes in V, and the contribution of the cooperative motion of the polyhedra to the diffusion of Li is relatively small in this system.

The relationship between the mean squared displacement of Li and the net change in coordination number was examined as follows.

The relation between ΔV and $\Delta r^2 = \sum^{n} r_i^2/n$ of lithium for an appropriate time interval at 1673 K and at 700 K is shown in Fig. 3, where ΔV is the mean change in V, r_i^2 is the squared displacement of Li and n is the number of Li ions contained in the range $\Delta V \pm 0.05$. The V and r_i^2 values are time-averaged over 0.2 ps for 1673 K and over 0.8 ps for 700 K to reduce the influence of vibrational motion. According to Fig. 3 b, changes in V of ± 1 correspond to displacement of about 0.3 $Å^2$ for lithium ion at 700 K and the displace-

Table 1. Parameters of the potentials used in this work.

Ions	z	c/Å^{3}kJ$^{1/2}$ · mol$^{-1/2}$	a/Å	b/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

Table 2. Matrix of transition probabilities (P_{ij} in %) for changes from V_i (at t_0) to V_j (at t_1) ($t_1 = t_0 + \Delta t$).

(a) at 1673 K ($\Delta t = 16$ fs)

j \ i	3	4	5	6	7
7				1	1
6		1	5	8	1
5	1	9	23	6	
4	3	21	9	1	
3	4	3	1		

(b) at 1673 K ($\Delta t = 4$ fs)

j \ i	3	4	5	6	7
7					1
6			2	16	1
5		3	34	2	
4	1	28	3		
3	6	1			

(c) at 700 K ($\Delta t = 16$ fs)

j \ i	3	4	5	6	7
7				2	3
6		1	5	15	2
5		5	31	5	
4	1	20	5	1	
3	1	1			

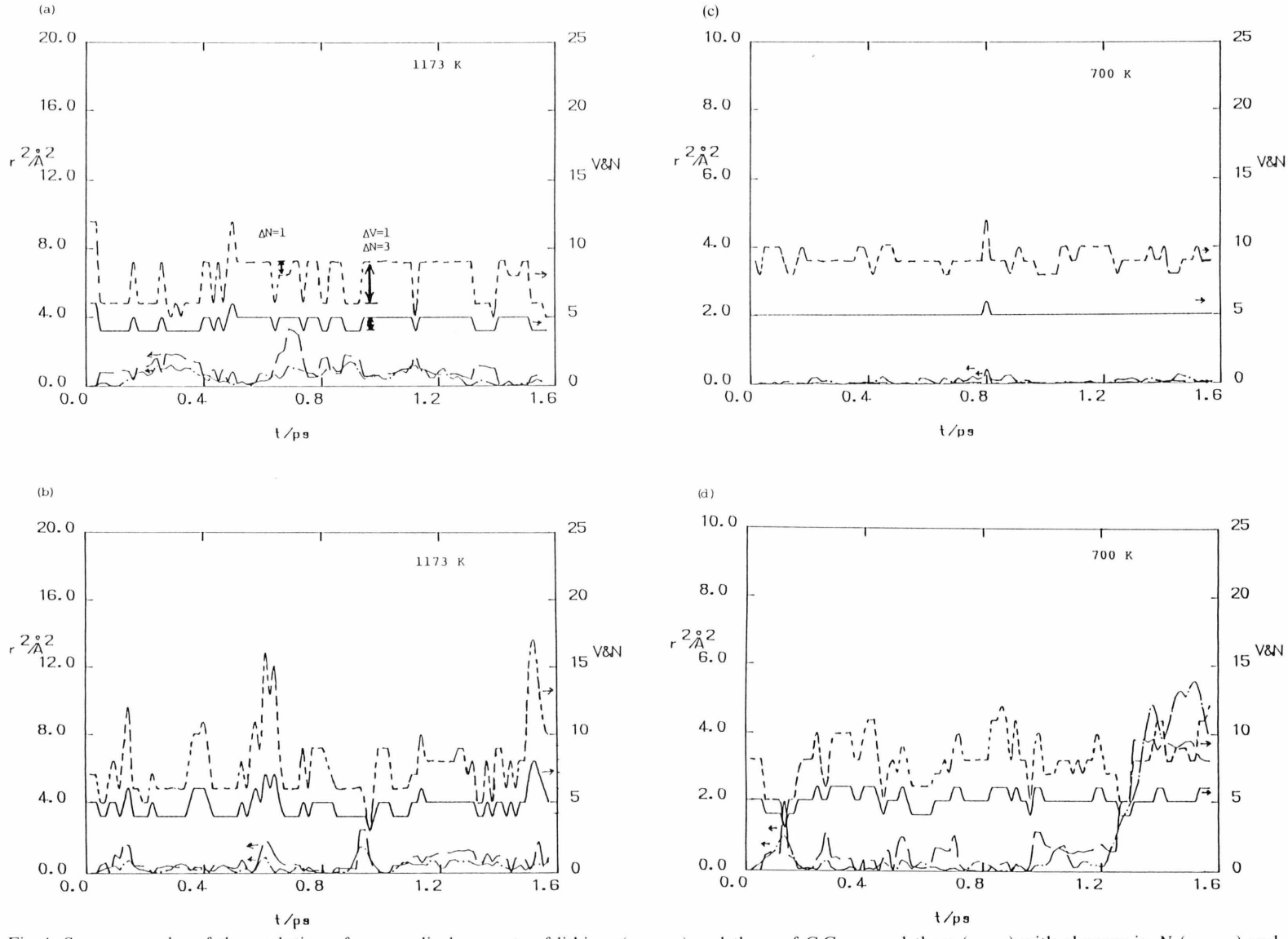

Fig. 1. Some examples of the evolution of square displacements of lithium (– – –) and those of C.G. around them (——) with changes in N (– – –) and V (——) values.

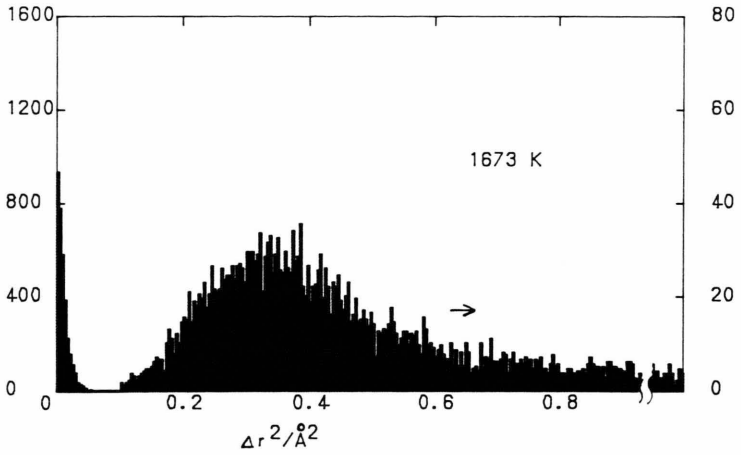

Fig. 2. Distribution (in arbitrary units) of square displacements of the C.G. after 16 fs at 1673 K without (left) and with (right) change of V.

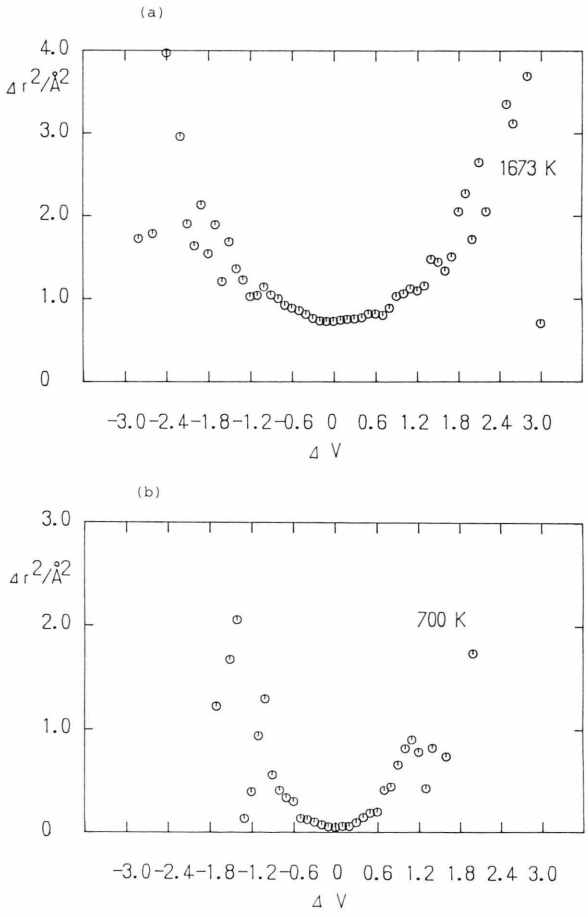

Fig. 3. Relationship between mean changes in V and mean square displacements for Li after 0.2 ps (1673 K) and 0.8 ps (700 K). (a) at 1673 K, (b) at 700 K.

ment nearly equals zero if $\Delta V = 0$. Although the relation is not clear for the melt (see Fig. 3 a) because of the larger thermal motions of lithium and oxygens around it, a similar tendency is obtained.

The probability of a transformation of the polyhedron was examined as follows. We defined a matrix whose elements $P_{ij}(\%)$ are the probability that the topology of the polyhedron will change from V_i (at t_0) to V_j (at t_1) (see Table 2). The results for more than 100 different t_0 values were averaged to each temperature. We counted 0.5 and higher fractions as a unit deleted the rest to clarify the pattern of distribution. Transformations of the polyhedra were found to occur mainly through modes $\Delta V = \pm 1$ at a time. The matrices are symmetrical, i.e. $P_{ij} = P_{ji}$. (An exception is due to insufficient statistics.) In vacancy jumps from sites i to j in a grain-boundary, Kwok et al. [10] pointed out that one can observe an asymmetry, $P_{ij} \neq P_{ji}$, which arises from the fact that sites i and j are at different levels of the potential energy surface. The symmetry in the present work suggests that the difference in levels for different V values is small and that the system is in local equilibrium.

The changes in N values were checked in a similar manner (see Table 3). The distribution matrices in N are also symmetrical. Two types of changes are often found:

I. $\Delta N = \pm 1$, $\Delta V = 0$; II. $\Delta N = \pm 3$, $\Delta V = \pm 1$.

The N values of the polyhedra change mainly among $N = 3V - 6$ and $N = 3V - 7$ in the former cases, while the changes occur among polyhedra with different V values ($V = 3 \rightleftarrows V = 4$ and $V = 4 \rightleftarrows V = 5$) in the latter cases. It is interesting to note that the changes of

Table 3. Matrix of transition probabilities (P_{ij}' in %) for changes from N_i (at t_0) to N_j (at t_1) ($t_1 = t_0 + \Delta t$).

(a) at 1673 K ($\Delta t = 16$ fs)

j \ i	3	4	5	6	7	8	9	10	11	12	13
13											1
12						1	1		1	2	
11						1			1	1	
10								1			
9			1	2		2	7			1	
8			2	1	1	6	2		1	1	
7		1	1	1	2	1	1				
6	1		2	9	1	2	2				
5	1	1	6	2	2	2	1				
4	1	1	1								
3	4		2								

(b) 1673 K ($\Delta t = 4$ fs)

j \ i	2	3	4	5	6	7	8	9	10	11	12	13
13											2	
12								1		1	5	
11										4	1	
10									3			
9					1		1	15			1	
8				1			10	1				
7				1		3	1					
6				1	14			1				
5		1		10	1		1					
4			3									
3		6		1								
2	1											

(c) 700 K ($\Delta t = 16$ fs)

j \ i	3	4	5	6	7	8	9	10	11	12	13	14	15	16
16														1
15														
14														
13							1			1	2			
12						1	2		1	4	1			
11						1	1		2	1				
10							1	2						
9				2		2	16	1		2	1			
8			1	1	1	6	2		1	1				
7					1	1								
6			1	13		1	2							
5	1		5	1		1								
4														
3	1		1											

type I occur at a location with a loose structure (with free volume), while the changes of type II occur with retention of the dense part of the structure. Other kinds of changes in Table 3 can be explained in terms of combinations of these modes, and changes between tight and loose structures are scarcely observed.

IV. Discussion

The diffusion of lithium in molten and glassy Li_2SiO_3 was examined in relation to the changes in the polyhedra made of oxygens. Analysis of the present MD simulation has revealed that the motion of lithium cannot be described in terms of simple vacancy jumps, whereas it can be described by the trapping model, where the motion of lithium is correlated with a change in the coordination number V. The fluctuation of V is considered to induce the motion of Li.

From analysis of the changes of the polyhedra, two types of modes were found, namely,

I. $\Delta N = \pm 1$, $\Delta V = 0$; II. $\Delta N = \pm 3$, $\Delta V = \pm 1$.

Changes of type II cause the movement of Li while changes of type I seem to be vibrational; however, the latter may be related to the frequency of the motion of type II.

Previously, we reported that the lifetimes of the polyhedron depended on the N and V values [9] and was related to the glass transition of this system. Since a longer lifetime means a smaller probability of transformation, we can conclude that the diffusion of Li is under the influence of the topology of the polyhedra.

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