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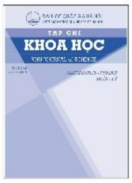

Original Article

Structural and Dynamics Heterogeneity in Sodium Silicate Liquid

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Abstract: Liquid Na_2O-$4SiO_2$ has been constructed by molecular dynamics simulation at 1873 K, ambient pressure with periodic boundary conditions. To clarify the local environment of atoms, we apply the oxygen simplex (OS) which is characterized by the size, forming oxygen atom types and the number of sodium atoms located inside the OS. The simulation shows that the liquid comprises the Si-O network and sodium atoms are distributed through different OS types forming by four O atoms. The number of sodium in particular simplex depends on the size and types of OS. There are five types of OS corresponding to values of n=0÷4. Here *n* is number of bridge oxygens which an OS passed through. We also found that the OSs are connected to each other form a long channel where hundreds of sodium atoms move. The observed distribution of sodium through Si-O network clearly indicates the structural and dynamics heterogeneity in sodium silicate liquid.

Keywords: Simulation, oxygen simplex, sodium silicate, structural heterogeneity.

1. Introduction

Network-forming liquid of SiO_2 with an alkali oxide such as Na_2O, Li_2O or K_2O are of general interest for the study of ion transport mechanisms in silicates [1-21]. It is related to the ionic conductivity capable, viscosity and diffusivity of material. The Si and O atoms form a disorder tetrahedral network and sodium atoms fill into this network and to be network modifier atoms [1, 2]. The diffusion coefficient of Si and O atom is very small (about 10^{-5} cm^2/s), and the one of Na is larger [3, 4]. Thus, Si and O atoms are immobility atoms and Na atoms are mobility atoms. The distribution of atoms Na in space is main cause of structural and dynamics heterogeneity of sodium silicate. The Na atoms locate

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nearly non-bridge oxygens and form a network of pockets and channels [5, 6]. The Na channel is recognized through pre-peak in structural factor function S(q) [7]. The height of prepeak depends on Na concentration in system. The structural and dynamics heterogeneity in sodium silicate is proposed by a simulation study [8]. In this study, simulation box is divided into small cubes with a volume of about 1Å^3 and obtain more than 50% of the cubes has not been visited yet by Na atoms after investigating time 2.5 ns. Thus, we suggest that Na atoms carry out selective jumps, the Na atoms being attractive by the negative charge regions. The diffusion of Na is characterized by an activation hopping through the Si-O matrix [9], or the jump processes of Na atoms are appropriately considered to be vacancy-like [10]. In addition, Angell [11] and others [7, 12] suggest that there are “preferential pathway” through which the Na atoms can easily move. Thus, diffusion mechanism of Na atoms can be the vacancy or free movement. It depends on disorder degree of structural network and local environment of Na atoms in sodium silicate liquid.

To clarify the local environment of atoms, we use simplex analytic method which presented detail in a recent public [13] with three simplex types: void simplex (VS), oxygen simplex (OS) and cation simplex (CS). However, in this research we only use OS which can indicate the structural and dynamical heterogeneity in liquid silicate.

2. Calculation Method

The liquid $Na_2O.4SiO_2$ (NS4) model consists of 7995 atoms (4797 Oxygen, 2132 Silicon and 1066 Sodium atoms) built at temperature of 1873 K and under ambient pressure with periodic boundary conditions. The molecular dynamics program is performed by using MXDORTO code [14]. The Verlet algorithm is used to integrate motion equation of atoms with time step of 1.0 fs. Details of the interactions used to construct the model are presented in [15]. First, the all atoms were randomly placed in a simulation box of size of 5.1 nm. The model is relaxed to equilibrium state after 4x 10^6 MD steps and at 1873 K and pressure of 0.1 MPa. The structural characteristics are calculated and compared with the experimental data that show a good agreement with results from works [9, 16].

To study local environment of atoms, we divide model into two space parts: one contains O and Na atoms and other only contains Si atoms. OS is a sphere passing center of four oxygen atoms and give the space regions where only O and Na atoms present. The OSs contain Na atoms provide the spatial distribution of Na for the liquid. The OS is characterized by the size, forming oxygen atom types and the number of sodium located inside the OS. Let n and h be the number of bridge oxygen (BO) and of Na atom located in an OS, respectively. The Na channel is studied by forming cluster of OSs which contain Na atoms. If two OSs share a Na atom, they are formed a cluster. The smallest cluster contain one Na atom.

3. Result Discussions

The structural characteristics of liquid NS4 model are analyzed via the first peak position of partial pair correlation function and coordination number distribution are listed in Table 1.

It can be seen that the positions of peaks of radial distribution functions are in good agreement with experiment [9, 17-20]. In Table 1 also shows that most Si atoms have four-coordination by O while the fraction of three coordination by O is very small, about 0.33%. Furthermore, the fraction of O atoms has one- and two-coordination by cations (Si or Na) are quite large (about 22.2 and 77.7%, respectively). The fraction of NBOs in NS4 is larger than the one in Silica and the tetrahedra network SiO_4 is broken when Na_2O added.

Table 1. Structural characteristics of liquid NS4 model. Here R_{ij} and Z_{ij} are the first peak position (in Å) for different atom pairs and coordination number for Si or O, *n* is number of bridge oxygen linked with an Si, f_{Si} and f_O are the fraction of Si and O atoms, respectively.

i-j	R_{ij}	Exp.	Z_{ij}	f_{Si}	f_O	n	f_{Si}
O-O	2.60	2.62 [5]	0	0	0.08	1	0.33
Si-O	1.60	1.617 [1]	1	0	22.2	2	7.41
O-Na	2.35	2.32 [2,3]	2	0	77.7	3	34.47
Si-Si	3.08	3.04 [4]	3	0.33	0	4	57.78
Si-Na	3.45		4	99.67	0		
Na-Na	3.25	3.20 [2,3]					

This shows the forming of paths what divided SiO_4 network into Si-O subnets. It means the number of Si atoms link with NBOs increases (the fraction of Si link with four BOs is 99% in pure SiO_2, but only is 57.78% in NS4). These results indicate that the network structure of constructed NS4 model consist of SiO_4 subnets (Si-rich region) and Na- and NBO-rich regions (the modifier network). This result also is in good agreement with experiment in [21]. We consider the distribution of OSs in system. It shows that most OSs locate in space region between SiO_4 units and do not contain Si atom. The OSs can contain or do not contain Na atom called VOS and NaOS, respectively. Table 2 lists the fraction of OSs. One can see that the fraction of NaOSs is 70% of the total OSs. It means that the 30% OSs are VOSs where attract Na atoms in diffusive process. For h=1, the fraction of NaOS is dominated (about 57.46%) and reduced with h increasing. We also find several NaOS with h=4 (about 0.05%). An OS, the smaller g, the higher the negative charge. This OS easy attracts Na atom to become a NaOS. If the OS has n=4, it is a neutral region and easy become a VOS. Thus, the electronegativity of OS depends on n value. Here, h depends on both charge value and size of OS. To clear this issue, we let k be ratio of number of NaOS and VOS with the same value of n (i.e. $k = f_{NaOS}/f_{VOS}$). The Table 2 also lists the fraction of VOS (f_{VOS}), of NaOS (f_{NaOS}) and k for all values g consider. These results indicate that as n increases, the number of VOS increase and k decrease quickly. Meanwhile, the f_{NaOS} receives maximum values for g=3. It means that the majority of VOS is made by four and three BOs.

Table 2. Statistic data the fraction of OS *vs h* and the fraction of VOS, NaOS and k *vs* n.

h	f_{OS}
0	30.59
1	57.46
2	10.97
3	0.92
4	0.05

n	f_{VOS}	f_{NaOS}	k
0	0.17	4.41	60.00
1	1.73	13.17	17.14
2	9.25	29.00	7.06
3	32.66	36.20	2.49
4	56.20	17.23	0.69

It can be seen that with n=0 then k equals 60 and It decreases strongly as *n* increases. It is interesting to note that OSs with n small are always more attractive Na atoms than the one with n large. Therefore, the distribution of Na depends on n and locates in rich-NBOs regions. Figure 1 shows the mean radius distribution of OS in NS4 liquid. We can see that the radius of OSs varies from 1.6 to 3.9 Å and has a peak at 2.7 Å. The result is showed that the radius of about 70% OSs is smaller than 2.7 Å. The number of Na atoms in an OS versus the radii is plotted in Figure 2 One can see that as h increases, the Na atoms can locate in all these OSs which have the radius around the range 1.8÷3.9 Å. Meanwhile, the radius of VOSs also is similar of NaOSs. As h increase, the distribution function of h shifts from left to right. The position of peaks is found to be 2.3, 2.6, 2.7, and 3.0 Å with h=0, 1, 2, 3 respectively. The NaOSs with h=4 are only 0.07 % of total OSs and not data enough to display on this figure. Hence, the location of

Na atoms is described not only by the number of NBOs but also depends on size of OSs. This implies that the VOSs belong to five OSs with n=0÷4 and become attractive positions on the mobility Na atoms carry out selective jumps in diffusion process.

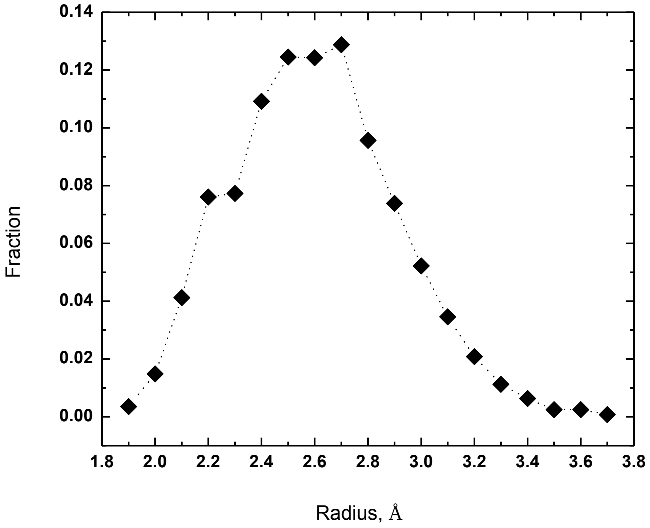

Figure 1. Mean radius distribution of OS in NS4 model.

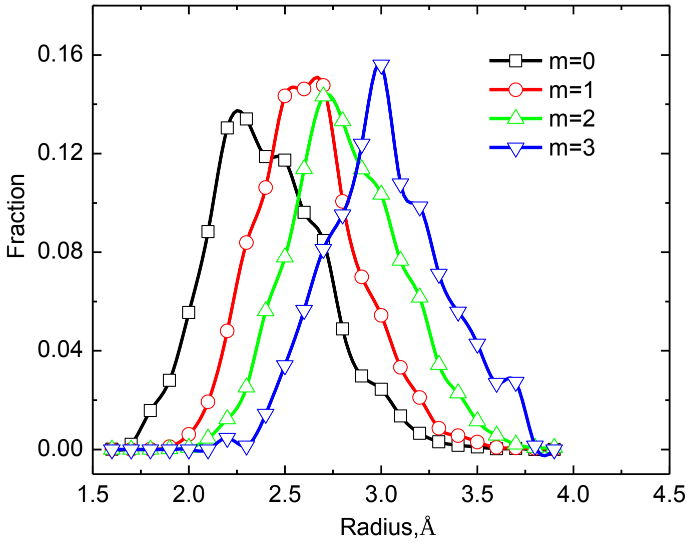

Figure 2. Radius distribution of OS vs number of Na atoms in NS4 model.

We also consider rich- Na regions by overlapping of NaOSs. Only 935 OSs in total 21619 OSs form 233 clusters. All NBOs in the model is present at these clusters. Table 3 lists cluster characteristics as number of Na atoms, ratio of volume of and of atom. One can see that the smallest cluster (137 clusters) only contains one Na atom. As number of Na atoms in a cluster increase from two to tens of atoms, the number of clusters decreases to one. Addition to, ratio of volume of cluster and of model also decreases. Especially, we find a largest cluster contains 433 Na atoms with volume equals 20% of model volume.

Table 3. The distribution of cluster in NS4; Where N_a is the number of N_a atoms tin a cluster; N_c is the number of clusters.

Na	1	2	3	4	5	6	7	10	11	12	15	26	32	35	46	433
Nc	137	41	21	8	4	5	2	3	2	1	1	1	1	1	1	1

Thus, the clusters containing from tens to hundreds Na atoms are channels. The small clusters are pockets. However, the mobility of Na atom in large and small clusters is different. To prove this thing, we investigate the modification of cluster versus simulation time. Three investigation periods are 10^4 (t_1), 10.10^4 (t_2) and 15.10^4 (t_3) MD steps. Obtained data shows that the number of BOs, NBOs, OS and Na atoms in one simplex change slightly over time (see Table 4 and 5). The Na atoms break the BOs linkages to create new NBOs and BOs linkages. The Na atoms can jump from one NaOS to nearest VOS to form a new NaOS. Note that VOS and NaOS are formed at the same time, but number of VOS and NaOS change very little over time. However, when investigating the number of NaOS and VOS with h, we obtained interesting result as shown in Figure 4.

Table 4. The distribution oxygen and simplex types in the NS4 model via time

MD steps	Oxygen types			NaOS				
	BO	NBO	FO	h=0 (VS)	h=1	h=2	h=3	h=4
t_1	77.72	22.20	0.08	30.76	56.59	11.55	1.03	0.07
t_2	77.63	22.31	0.06	31.54	57.57	10.64	1.00	0.08
t_3	77.57	22.35	0.06	30.64	57.57	10.99	0.93	0.06

Table 5. The time dependence of OS is created by different number of bridge oxygens

MD steps	OS				
	n=0	n=1	n=2	n=3	n=4
t_1	3.62	14.59	33.44	35.68	12.67
t_2	5.03	16.15	30.80	32.51	15.51
t_3	4.16	12.17	35.07	35.28	13.32

It can see that ratio of NaOSs and VOSs changes strongly with time for n=0. This change is reduced with n increases. For n=4, the ratio of NaOSs and VOSs is unchanged with time. It shows that, the Na atoms in NaOSs with n smaller are more mobility. Significantly, we observe the separation in the largest cluster into smaller clusters via time. Namely, the largest cluster at t_1 is separated into three smaller cluster at t_3 time (see Table 6)

This means that the Na atoms distribute in NBO-rich regions and move free. While, at BO-rich region, the Na atoms are scatered and their diffusion mechanism is vacancy. It jumps from one OS to other when it is excited. Thus, in the NS4 network, we also show two types of Na atoms: fast Na atom is located in the NBO rich region and slow Na atom is located in the rich BO region.

Table 6. The change number of Na+ ions in clusters via simulation time

t_1		t_2		t_3	
N_{NaC}	N_C	N_{NaC}	N_C	N_{NaC}	N_C
1	137	1	140	1	158
2	41	2	38	2	31
3	21	3	14	3	9
4	8	4	10	4	8
5	4	5	12	5	5
6	5	6	4	6	1
7	2	7	2	7	1
10	3	8	2	8	1
11	2	9	3	9	2
12	1	10	1	10	2
15	1	15	1	11	1
26	1	22	1	13	1
32	1	24	1	14	1
35	1	67	1	24	1
37	1	76	1	26	1
46	1	96	1	28	1
433	1	317	1	57	1
				75	1
				88	1
				112	1
				123	1
				132	1

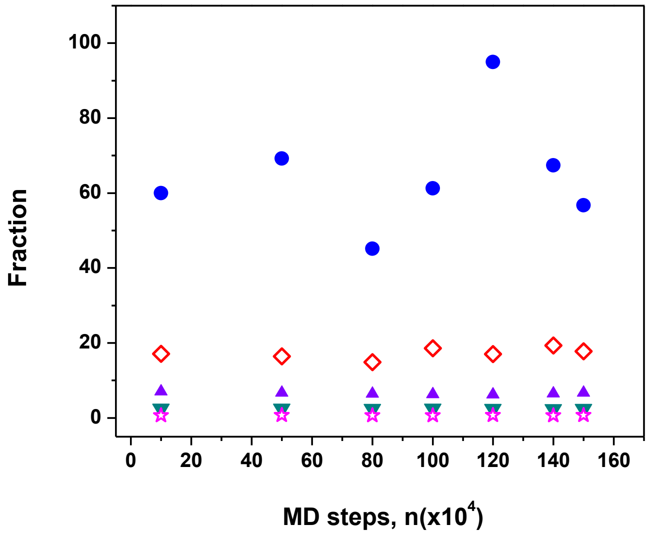

Figure 4. Time dependence on k in NS4 model. Here g=0,1,2,3,4 is circle, square, up-triangle, down-triangle, star symbols, respectively

4. Conclusion

By molecular dynamics simulation and OS analysis method, we investigate quantitatively the space and dynamics heterogeneity of Na atoms in NS4 liquid. The results show that, the OSs are distributed in space region only containing O and Na atoms. Each Na atom belongs to a certain OS. The OS can contain from 0 to 4 Na atoms. The number of Na atoms in an OS depends on charge and size of OS. It is shown that the NS4 liquid has a small amount of Na atoms (about 13%) which do not uniformly distribute over whole system and locate in small clusters. It means that the structure of NS4 liquid is heterogeneity. Furthermore, there is one cluster that only contains a Na atom. It is almost unchanged with time. This shows that the small clusters are inserted into SiO_4 units and the Na atoms become less mobile. Contrary to the small cluster, the large clusters are created by more NBOs, have larger size and contain from tens to hundreds Na atoms. The Na atoms in the largest and large clusters change strongly with time. It implies that the Na atoms have a quick displacement in large clusters. This is origin of dynamics heterogeneity in NS4 liquid.

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