Dynamics heterogeneity and diffusion mechanism in sodium-silicate melts: Molecular dynamics simulation

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Abstract. In the present study, molecular dynamics simulation of sodium-silicate has been carried out to investigate microstructure and diffusion. The statistical and dynamical distribution of sodium in sodium-silicate melts with various compositions at 1873 K and ambient pressure has been studied via simplex method. The result shows that the spatial distribution of sodium is non-uniform. There is the simplex contains up to 6 Na and the radius of simplexes varies from 1.4 to 4.5 Å. We find that sodium tends to be in the non-bridging oxygen-simplexes and in larger-radius simplex. The temporal number density of Na around non-bridging oxygen and free oxygens is significantly higher than the one for others region. The static structure is heterogeneous and comprises Na-poor and Na-rich regions. Moreover, the "pockets for sodium" where network atoms having large number density of Na gather is observed. The structure comprises consists of separate micro-regions where immobile or mobile network atoms reside. It turns out that the dynamics is spatially heterogeneous. The Na atoms tend to move along diffusion pathways comprising simplex-regions of networks forming atoms having high number density of Na. The diffusion pathways for sodium consist of simplex-regions of solid-like non-bridging oxygen, free oxygens.

1. Introduction
The multicomponent oxide glasses have been widely applied in microelectronics, medicine (biomaterial), high technology materials. Therefore, understanding their structure and dynamical properties are fundamentally necessary. In the case of sodium-silicates the physical properties were intensively investigated via experimental techniques such as x-ray diffraction, photoelectron spectroscopy, in-situ Raman spectroscopy and elastic neutron scattering [1-4], and simulations [5-6]. According to X-ray photoelectron spectroscopy study [3], two types of bridging oxygen (BO) were found in sodium-silicate glass: one of which is two-fold coordinated to two Si and another of which is three-fold coordinated to two Si and one Na. The degree of polymerization quantified via Q(n) species characterizes the number density of Si-O-Si bonds, where Q represents SiO₄ and n is the number of BO [4]. Usually, the high de-polymerization offers specific properties that are changed by effect of alkali modifier. The sodium-silicate melts the degree of polymerization drops from pure SiO₂ to 2Na₂O.SiO₂ [5]. The addition of alkali oxides into pure silica SiO₂ disrupts the basic silica network by breaking part of the Si-O bonds, generating non-bridging oxygen (NBO) [7-8]. But there is not this phenomenon at high pressure. The Na₂O concentration in sodium-silicate increases, it will result in increasing [NBO]⁻ concentration, reducing melting temperature and viscosity... [9-10]. At low Na₂O concentration, Na⁺ cations tend to be close to the [BO₄]⁻ , [AlO₄]⁻ units and they have role of charge-balance. Conversely, at higher Na₂O
concentrations, the Na$^+$ cation tend to be closer to the [NBO]$^-$ and they act as the network-modifier \cite{11-12}. Alkali-silicate melt and glass are featured by very high mobility of alkali ions \cite{13}. The existence of preferential diffusion pathways is thought to be the origin of fast mobility of alkali ion. Meyer et al. showed that the pre-peak around 0.95 Å$^{-1}$ of the structure factor for silicate glass has its origin from sodium rich channels \cite{14}. Molecular dynamics (MD) simulations provided more details about dynamics in alkali-silicates \cite{14}. Many studies show that the space regions most visited by sodium atoms form a network of pockets and channels which have high density of sodium compared to the rest area of the system \cite{15,16}. Moreover, as shown from previous studies \cite{17,18}, the dynamics in silicate melt is heterogeneous, i.e. the system comprises distinct regions where the mobility of network forming is significantly higher than in the rest area of the system. The behavior of Na around network of such regions differs from that around other network. Therefore, in the present work we conduct a topological analysis based on simplexes to clarify the mentioned problems. Especially, we focus on simplex-region and clustering of specified network forming. The pockets, diffusion pathways for sodium and structural heterogeneity are studied.

### 2. Calculation method

MD simulation of sodium-silicate is studied by the MXDORTO code \cite{19}. The model of \(Na_2O.SiO_2\) (NS1), \(Na_2O.2SiO_2\) (NS2), \(Na_2O.3SiO_2\) (NS3) and \(Na_2O.4SiO_2\) (NS4) melts at pressure of 0.1 MPa and temperature of 1873 K is constructed. These models consist approximately 8000 atoms. We simulate sodium silicate with the pair potentials and three-body potential that has the form:

\[
U(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{Z_i Z_j e^2}{r_{ij}} + f_0(b_i + b_j) \exp \left( \frac{a_i + a_j - r_{ij}}{b_i + b_j} \right) + \frac{c_i c_j}{r_{ij}^6} + D_{1ij} \exp (-B_{1ij} r_{ij})
\]

The three-body part that relates to O-Si-O angle has the form:

\[
U_{ijk}(\theta_{ijk}, r_{ij}, r_{jk}) = -f \left\{ \cos[2(\theta_{ijk} - \theta_0)] - 1 \right\}(k_1 k_2),
\]

\[
k_1 = \exp[r_{ij} - r_{ij} - r_{jk} + \Pi],
\]

\[
k_2 = \exp[r_{ij} - r_{ij} - r_{jk} + \Pi].
\]

This potential provided the reproduction of structure of silicate crystals and pressure dependence of transport properties of silicate liquid. More details about the applied potential can be found elsewhere \cite{20}. The constructed models have been relaxed for long times until reach the equilibrium. Afterward we perform additional runs of 150 ps to produce a series of configurations separated by 10 ps. The dynamical and structural data are collected from these configurations. The melt also contains free oxygens (FO) which are not connected with any Si. For the convenience both FO and NBO are denoted to FNB. The Si-O bond, basic unit and Si-O subnet is figured out as follows. Si and O form a Si-O bond if the distance between them is smaller than a cutoff distance \(r_{cutoff} = 2.45\) Å. Here \(r_{cutoff}\) is taken from first minimum of the pair radial distribution function (PRDF). The basic unit such as \(SiO_x\) and \(OSi_y\) consists of a central atom and coordinated atoms. We determine spheres passing four networks forming atoms (NF). If the determined sphere does not contain any NF inside, it is a simplex (see Fig.1). Four NF lying on the surface of simplex are denoted to the simplex-forming NF (SNF). The simplex therefore is a sphere in which a number of Na and not any NF reside. The simplex is characterized by radius RS and number of Na located inside \(n_{NaSR}\). For the case when \(n_{NaSR} = 0\) the simplex represents a void-simplex. All simplexes having one common SNF occupy a close percolated region (simplex-region) as shown in Fig.1. The simplex-region contains a number of Na and one NF inside. Other SNF of those simplexes lie on the outer surface of simplex-region. The number of Na located in the simplex-region \(n_{NaSR}\) represents the number density of Na around NF. Cluster of simplexes consists of NF atoms belonging to simplexes which overlap with each other.
3. Results and discussion

3.1. The structural characteristics and distribution of sodium atoms in sodium-silicate

The structural characteristics of liquid sodium-silicate are presented in Table 1, 2. These inter-atomic distances are calculated from PRDF of sodium silicate. The results are closed to those reported in [1, 21] (see Table 1).

Table 1. Inter-atomic distances (Å).

| Models/References | r_{OO} | r_{SiO} | r_{ONa} | r_{SiSi} | r_{SiNa} | r_{NaNa} |
|-------------------|--------|---------|---------|---------|---------|---------|
| NS1               | 2.62   | 1.62    | 2.17    | 3.12    | 3.12    | 3.1     |
| NS2               | 2.62   | 1.62    | 2.2     | 3.12    | 3.15    | 3.1     |
| NS3               | 2.62   | 1.62    | 2.2     | 3.12    | 3.30    | 3.35    |
| NS4               | 2.62   | 1.62    | 2.15    | 3.12    | 3.20    | 3.32    |
| [21]              | 2.62   | 1.62    | 2.29    | 3.05    | 3.5     | 2.6-3.05|
| [1]               | 2.35   | 1.65    | -       | 3.12    | -       | -       |

As seen, although r_{SiNa} and r_{NaNa} show some discrepancies, the constructed models are well consistent with experiments. In particular, the simulation reproduces the experimental data for r_{OO}, r_{SiO}, r_{SiSi} and r_{NaO}. The fraction of SiO_x and different oxygen types is shown in Table 2. The structure comprises SiO_4 tetrahedrons and a small amount of SiO_3. With increasing Na_2O content the silica network is altered by increasing NBO and FO. In contrast, the fraction of BO decreases.
Table 2. Fraction of SiO\textsubscript{x} and different oxygen types.

| System | SiO\textsubscript{3} | SiO\textsubscript{4} | SiO\textsubscript{5} | FO | NBO | BO | OSi\textsubscript{3} |
|--------|----------------|----------------|----------------|----|-----|----|----------------|
| NS1    | 0.0409         | 0.9591         | 0.0001        | 0.0245 | 0.6314 | 0.3441 | 0.0001 |
| NS2    | 0.0116         | 0.9883         | -             | 0.0019 | 0.4008 | 0.5972 | -     |
| NS3    | 0.0058         | 0.9941         | 0.0001        | 0.0007 | 0.2868 | 0.7124 | 0.0001 |
| NS4    | 0.0041         | 0.9958         | 0.0001        | 0.0007 | 0.2225 | 0.7767 | -     |

Table 3. Fraction of simplexes containing different \(n_{NaS}\).

| System | \(n_{NaS}=0\) | \(n_{NaS}=1\) | \(n_{NaS}=2\) | \(n_{NaS}=3\) | \(n_{NaS}=4\) | \(n_{NaS}=5\) | \(n_{NaS}=6\) |
|--------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| NS1    | 0.0882        | 0.5168        | 0.2969        | 0.0844        | 0.0126        | 0.0011        | 0             |
| NS2    | 0.2719        | 0.5459        | 0.1574        | 0.0225        | 0.0022        | 0.0001        | 0.0001        |
| NS3    | 0.4149        | 0.4839        | 0.0906        | 0.0100        | 0.0006        | 0             | 0             |
| NS4    | 0.5134        | 0.4213        | 0.0599        | 0.0050        | 0.0004        | 0             | 0             |

As shown in Table 3, the simplex contains up to 6 Na and the fraction of simplexes with \(n_{NaS} = 2, 3\) and 4 decreases from NS1 to NS4. Meanwhile the void-simplexes show the opposite trend. Fig.2 presents the radius distribution of simplexes and the one of simplexes having the same \(n_{NaS}\). For NS1 the graph shifts largely to the right with increasing \(n_{NaS}\). Similar trend is observed for NS2, NS3 and NS4. In contrast the distribution of simplexes having the same \(n_{NaS}\) is slightly changed.

In Fig.3 we display the fraction of networks forming atom against \(n_{NaSR}\). In the case of NS1 the curve for FNB shifts to the right compared to those for Si and BO. Similar trend is observed for NS2, NS3 and NS4. This means that Na atoms tend to concentrate around FNB instead of uniformly distributing around Si, BO and FNB. Regarding to SiO\textsubscript{2} content, the graph shifts to the left with increasing SiO\textsubscript{2} content. Therefore, the average number density of Na around NF decreases as the SiO\textsubscript{2} content of the melt increases. To clarify how NF atoms having high number density of Na are distributed in the space, we determine a subset of high sodium-density atoms (SHSDA) and another subset of random atoms (SRA) for comparison. SHSDA comprises 5 % of total NF which have most large \(n_{NaSR}\). SRA consists of NF randomly taken from the system and the number of NF in SRA is also 5 % of total NF. The calculation result for different configurations separated by 20 ps is shown in Fig.4. We observe that \(<n_{NaSR}>\) for SHSDA is larger by 1.5 - 6.1 times than that for SRA atoms, where \(<n_{NaSR}>\) is obtained by averaging \(n_{NaSR}\) over all NF of specified subset. The number of clusters of simplexes forming by SHSDA atoms is significantly smaller than the one by SRA atoms. Since the spatial distribution of SRA atoms is homogeneous, SHSDA atoms gather in large clusters of simplexes instead of uniformly distributing in the space. This result can be explained by that SHSDA atoms are concentrated in Na-rich regions, while SRA atoms spread over all regions occupied by Si-O subnets and clusters of simplexes. On the other hand, large clusters of simplexes of SHSDA atoms resemble the ”pocket for sodium”. This means that during specified time \(t_{sp}\) (the time simulation) the Na atoms are not uniformly distributed in the space, but instead they gather in separate pockets. Therefore, sodium atoms can easily move in “preferential pathways”. We can conclude that Na atoms tend to concentrate around NBO and FO which gather in clusters of simplexes. NF
Figure 2. Radius distributions of simplexes in NS1 and of simplexes having the same \( n_{NaSR} \). atoms having most large \( n_{NaSR} \) gather in clusters of simplexes instead of uniform distributing in space.

3.2. Diffusion mechanism of sodium atom in sodium-silicate

The diffusion constant of Na is significantly larger than that of NF. This means that fast Na move through simplex-regions of slow network forming. The Na atoms move from one to other simplex-regions and they tend to move along diffusion pathways comprising simplex-regions of NF having high number density of Na. The size of diffusion pathways decreases with increasing time \( t_{sp} \). Moreover, the diffusion pathways for sodium also modify strongly as the \( SiO_2 \) content of the melt changes. The flow of Na through simplex-regions is also explored through 15 configurations separated by 10 ps. Let \( m_{ij} \) be the number of Na in the simplex-
region of $i^{th}$ NF in $j^{th}$ configuration, where $i = 1, 2, .. N$; $j = 1, 2, .. 15$; $N$ is the total number of NF atoms. $m_{ij}$ is equal to $n_{NaSR}$ of $i^{th}$ NF in $j^{th}$ configuration. We denote $M_i$ to the number of Na atoms which visit simplex-regions of $i^{th}$ NF. $M_i$ is counted from Na atoms which are in the simplex-region of $i^{th}$ NF in 15 configurations. The ratio $\mu_i=M_i/\sum m_{ij}$ characterizes the average resident time for Na atoms which are present around $i^{th}$ NF. The smaller $\mu_i$ is the longer Na stays around $i^{th}$ NF. Furthermore, we denote $m_{i1}, m_{i2}$ to the number of Na which are in simplex-region of $i^{th}$ NF in two consecutive configurations separated by 10 ps.

The number of Na moving out and in is equal to $m_{i1} - m_{i3}$ and $m_{i2} - m_{i3}$, respectively, where $m_{i3}$ is the number of Na staying in the simplex-region of $i^{th}$ NF for 10 ps. The number of moving Na is given as $m_{i1} - m_{i2} - 2m_{i3}$. Due to exchange of neighbors between basic units the

Figure 3. Fraction of networks forming as function of number density of Na around network forming.
Figure 4. Upper panel shows the number of simplex-clusters forming by SHSDA and SRA atoms in different configurations. In lower panel we show the average number density of Na around a NF. Large difference in the number of spimplex-clusters indicates non-uniform spatial distribution of SHSDA atoms.

The system contains three types of O: $BO_{nsc}$, $FNB_{nsc}$ and $O_{cs}$. The status of first and second type for both configurations is the BO and FNB, respectively. Unlike $BO_{nsc}$ and $FNB_{nsc}$ the $O_{cs}$ changes its status, i.e. the status of $O_{ns}$ in the first configuration differs from that in the second configuration.

Fig.5 shows the fraction of NF as a function of $\mu_i$. The graph for Si shifts to the right indicating that the resident time for Na around Si is smaller than that around O. With increasing $SiO_2$ content the graph is spread over wider range and the height of peak is much lower. This result points out that the resident time for Na around NF strongly depends on the $SiO_2$ content.
Table 4. Diffusion constant for sodium-silicate melts.

|       | NS1        | NS2        | NS3        | NS4        |
|-------|------------|------------|------------|------------|
| \(D_O\), cm\(^2\)/s | 5.52x10\(^{-6}\) | 5.59x10\(^{-7}\) | 2.07x10\(^{-7}\) | 8.50x10\(^{-8}\) |
| \(D_{Si}\), cm\(^2\)/s | 4.27x10\(^{-6}\) | 4.36x10\(^{-7}\) | 1.62x10\(^{-7}\) | 6.50x10\(^{-8}\) |
| \(D_{Na}\), cm\(^2\)/s | 7.92x10\(^{-5}\) | 6.37x10\(^{-5}\) | 5.49x10\(^{-5}\) | 4.74x10\(^{-5}\) |

Figure 5. The fraction of NF as a function of \(\mu_i\).

In SiO\(_2\) -rich melt Na atoms stay around different NF for very different times. Fig.6 shows the number of moving Na for Si and three O types. The average number of moving Na increases
in the order: Si → BO_{nsc} → O_{sc} → FNB_{nsc}. In other word the number of Na atoms passing simplex-regions of FNB_{nsc} and O_{sc} significantly exceeds the one of Si and BO_{nsc}. So, Na atom pass intensively through simplex-regions of O having high number density of Na compared to the ones of NF having low number density of Na. Because NF atoms having large n_{NaSR} gather in large clusters of simplexes, so during t_{sp} the Na atoms do not move randomly between simplex-regions, but instead they tend to move along diffusion pathways comprising simplex-regions of NF having high number density of Na. Unlike glass state the diffusion pathways for sodium change in the time and space due to the movement of NF and change of status of O with time.
Thus, the Na atoms move from one to other simplex-regions and they tend to move along diffusion pathways comprising simplex-regions of NF having high number density of Na. The size of diffusion pathways decreases with increasing time $t_{sp}$. Moreover, the diffusion pathways for sodium also modify strongly as the $SiO_2$ content of the melt changes. Within a moderate time $t_{sp}$ the diffusion pathways for sodium observed in the $SiO_2$-rich melt resemble the sodium rich channels observed in silicate glass [2, 14]. This effect is due to the extremely slow mobility of NF compared to sodium compared to sodium (see Table 4).

3. Dynamic heterogeneity in sodium-silicate

![Figure 7. Distribution of Na atoms around solid-like and liquid type NF in NS2 (upper panel) and NS3 (lower panel).](image)

Due to exchange of neighbors between basic units the list of coordinated atoms for central NF may change with times. The basic unit is considered as solid-like type for a specified time $t_{sp}$ if its list of coordinated atoms is unchanged during $t_{sp}$. Otherwise it is the liquid type. Unlike solid-like type the liquid type O changes its status during $t_{sp}$. For the convenience the central
atom of such units is called the solid-like and liquid type atom, respectively. The distribution of Na around solid-like and liquid type NF is shown in Fig. 7. Here $t_{sp}$ is set to 150 ps. The curve for liquid type and solid-like Si differs slightly from each other. However, the graph for solid-like FNB moves largely to the right compared to solid-like BO and liquid type O. This indicates that the number density of Na around solid-like BO is significantly smaller than solid-like FNB. Furthermore, Na atoms are redistributed between simplex-regions of O when its status changes. Accordingly, the transformation from FNB to BO accompanies a migration of Na out from the simplex-region of this O. For $t_{sp}$ = 150 ps the structure contains a large number of solid-like BO atoms which form separate Si-O subnets. Because Si-O bonds between solid-like BO and Si are kept for whole time $t_{sp}$, Si-O subnets forming by solid-like BO and Si are rigid. The atoms of rigid Si-O subnets are immobile due to that these atoms move together as large molecules. Thus, the structure consists of separate micro-regions where immobile NF atoms reside. The number density of Na around solid-like BO and Si is significantly smaller than that of other type O. Therefore, rigid Si-O subnets occupy micro-regions (rigid micro-regions) in which NF atoms have low number density of Na. It turns out that the dynamics is spatially heterogeneous, and the structure comprises separate rigid micro-regions.

Conclusion
MD simulation has been carried out for sodium-silicate melts with various compositions at 1873 K and ambient pressure. The simulation shows that the radius of simplexes varies from 1.4 to 4.5 Å and one simplex contains up to 6 Na. As the $\text{SiO}_2$ content of the melt decreases, the fraction of simplexes having 2, 3 and 4 Na monotonously increases. The simulation reveals that the number density of Na around FNB is significantly larger than the one around Si and BO. The static structure is heterogeneous and involves Na-rich and Na-poor regions occupied by Si-O subnets and simplex-clusters, respectively. During a moderate time, Na atoms are concentrated in micro-regions which resemble "pockets for sodium". The spatial distribution of Na is more heterogeneous as the $\text{SiO}_2$ content of the melt increases. The simulation also reveals that the Na atoms do not move randomly in the space, but instead they tend to move along diffusion pathways comprising simplex-regions of NF having high number density of Na.

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References
[1] Davidenko A O, Sokolskii V E, Roik A S, Goncharov I A 2014 Inorganic Material. 50 1375
[2] Meyer A, Horbach J, Kob W, Kargl F, Schober H 2004 Phys. Rev. Lett. 9 027801
[3] Nesbitt H W, Henderson G S, Bancroft G M, Ho R 2015 J. Non-Cryst. Sol 409 139
[4] Koroleva O N, Anfilogov V N 2013 J. Non-Cryst. Sol. 375 62
[5] Jabraoui H, Achhal E M, Hasnaoui A, Garden J L, Vaills Y, Ouaskit S 2016 J. Non-Cryst. Sol. 448 16
[6] Konstantinov K, Duffy D M, Shluge A L 2016 Phys. Rev. B. 94 174202
[7] Zhao Q, Guerette M, Scannell G, Huang L 2012 J. Non-Cryst. Sol. 358 3418
[8] Cormack A N, Cao Y 1996 Molecular Engineering. 6 183
[9] Jabraoui H, Vaills Y, Hasnaoui A, Badawi M, Ouaskit S 2016 J. Phys. Chem. B. 281 13193
[10] Bechgaard T K etal ... 2016 J. Non-Cryst. Sol. 441 49
[11] Mathieu H, Anne J F 2014 Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B. 53
[12] Cheng S 2015 Scientific Reports. 5 17526
[13] Sviridov S I 2013 Glass Phys. and Chem. 39 130
[14] Meyer A, Kargl F, Horbach J 2012 Scienc. Rev. 27 35
[15] Jund P, Kob W, Jullien R 2001 Phys. Rev. B. 64 134303
[16] Jund P, Kob W, Jullien R 2002 Phil. Mag. B. 82 59
[17] Shajahan M, Razul G, Matharoo G S, Poole P H 2011 *J. Phys. Condens. Matter* **23** 235103
[18] Appignanesi G A, Rodriguez Fris J A 2009 *J. Phys. Condens. Matter* **21** 203103
[19] H. Sakuma, K. Kawamura 2009 *Geochim. Cosmochim. Acta* **75** 4100
[20] Noritake F, Kawanura K, Yoshino T, Takahashi E 2012 *J. Non-Cryst. Sol.* **358** 3109
[21] Fabian M, Jovari P, Svab E, Meszaros G, Proffen T, Veress E 2007 *J. Phys. Cond. Matt.* **19** 335209