New analysis characterizing the dynamics heterogeneity and microstructure in liquid silicates

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Abstract.

We use molecular dynamics simulation to study liquid silicates at ambient pressure and temperature of 3500 K. New analysis on structure and dynamics is carried out using such characteristics as the rate of bond-breaking events, link-cluster function and different subnet types. We found that the structural heterogeneity exists in short and medium length scales. Namely, the local environments of cations are quite different. The parking of $\text{SiO}_x$ in the silicate systems is also very different. Further, the simulation shows that during a moderate long time the melt has a two-domain structure consisting of separate immobile domains and a mobile domain. These domain types differ strongly in the atomic mobility and chemical composition. The simulation also gives clear evidences for dynamics heterogeneity (DH) in the melt and that the non-uniform spatial distribution of bond-breaking events is responsible for the DH.

1. Introduction

Structure of silicate glasses and melts has been investigated by different techniques such as nuclear magnetic resonance, X-ray scattering as well as IR and Raman spectroscopy [1-5]. For sodium silicate, the sodium ion is much more mobile than Si and O ions which leads to the ion conductance at low temperature and very high mobility of sodium is assumed due to sodium-rich channels. In aluminium silicates, $\text{Al}^{3+}$ ions include four-, five- and six-fold aluminum that do not found in pure silica even at very high temperature. Moreover, the presence of high-coordinated units is accompanied with so-called tri-clusters, where oxygen is surrounded by three cations [6,7]. The appearance of high-coordinated aluminum and tri-clusters is an evidence of different local ordering of Si and Al which results in the structural ordering on length scale of $1 \text{ nm}$. This intermediate range order (IRO) can be described by a micro-phase separation where rich-Al network structure percolates through the Si-O network. As shown from previous experiments [8-10], certain silicates exhibit the similar IRO. Recently, many simulations have been successfully used to study the influence of network modifier on unique properties of silicates [11-14]. In particular, the simulation allows to study at the same time the structure on local and medium length scales in conjunction with dynamics properties. The simulation on various sodium aluminium-silicate melts showed that $\text{Al}^{3+}$ in Al-rich system will go into high-coordinated states and the environment of $\text{Na}^+$ varies strongly. This is used to interpret the anomaly observed experimentally that the viscosity reaches a maximum when $\text{Al}/(\text{Al}+\text{Na})$ ratio is around 0.5. Using molecular dynamics (MD) simulation, the dynamics heterogeneity (DH) can be clarified through variables such as trajectory patterns, non-Gaussian parameter, bond-lifetime patterns and multi-point dynamic susceptibilities [15-19]. Despite a great progress.
in our understanding of liquid silicates, many aspects about structure and dynamics of liquid silicates are still poorly understood [22-24]. Therefore, the goal of present paper is to shed some lights on this matter. Firstly, we built an accurate MD model of $Al_2O_3\cdot2SiO_2$ and make analysis of its microstructure on base of SiO- and AlO-subnets. Secondly, we calculate the link-cluster function and rate of bond-breaking events to clarify the dynamics and structure characteristics. Our calculation is general and can be applied to other liquid silicates.

2. Computational method
The model silicate $Al_2O_3\cdot2SiO_2$ consists of 5500 atoms (1000 Si, 3500 O and 1000 Al) have been constructed by MD simulation at ambient pressure and temperature of 3000 K. The Born–Mayer potential was used, and the Coulomb interactions were taken into account by means of Ewald method. All atoms moved by applying Verlet algorithm with MD step of 1 fs. Initial configuration is generated by randomly placing all atoms in a simulation cell and equilibrated at 5000 K. Then the sample was cooled down to 3000 K and relaxed for 30 ns. The obtained sample acquires structural characteristics that are in good agreement with experiment (see ref. [14]). We also performed an additional run of 10 ns. Within this period the dynamics and structure data were collected for further analysis. We calculate the link-cluster and ”commuting” linkage for sets of N specified atoms. The ”commuting” linkage called linkage for short is a geometrical characteristic and differs from the chemical bond. Two atoms form a linkage if the distance between them is smaller than particular distance $r_{linkage}$. A link-cluster consists of atoms connected to each other through a path of linkages. The link-cluster function $F_{link}(r,t)$ is defined as the number of link-clusters which are formed by specified atoms at the time t and $r_{linkage} = r$. Obviously, for a set of N atoms $F_{link}(r,t)$ varies from 1 to N. The calculation of link-clusters is performed by several stages. Firstly, we assign every atom to a cluster label k, where $k = 1, 2, ..., N$. Next, we reassign labels of atoms. If $r_{ij} < r_{linkage}$ and $k_i > k_j$, then the label of $i$th atom is reassigned to $k_i$. Here $k_i$, $k_j$ is the label of $i$th and $j$th atom, respectively; $r_{ij}$ is the distance between them. The reassigning is repeated until all pairs of atoms forming a linkage have the same label. Finally, we obtain two lists: $[k_1, k_2, ..., k_m]$ for labels and $[Cl_1, Cl_2, ..., Cl_m]$ for link-clusters, where m is the number of link-cluster; $F_{link}(r,t) = m$; the cluster $Cl_i$ consists of atoms having the label $k_i$.

3. Results and discussion
Structure of the melt represents a TO network which consists of oxygen-shared $TO_x$, where T is the Si or Al. To determine this structural network, we use cutoff distances rcutoff which are chosen from pair radial distribution functions and equal to 2.45 and 2.55 Å for Si-O and Al-O pair, respectively. We employ following notations and definitions: O and T form a T-O bond if the distance between them is less than rcutoff; TO-subnet consists of atoms connected to each other through a path of linkages. The different subnet types are schematically illustrated in Figure 1.

In our analysis O are assorted into three groups: (i) $O_{Si}$ consists of O linked only to Si; (ii) $O_{Al}$ comprises O linked only to Al; (iii) $SiO_{Al}$ includes O linked to both Si and Al. This follows that SiO-subnets are formed by $O_{Si}$ and Si, while AlO-subnets are formed by Al and $O_{Al}$. Unlike those groups, $SiO_{Al}$ atoms are mediator connecting SiO- and AlO-subnets. Clearly, SiO- and AlO-subnets occupy separate domains of the TO network because of they do not share any common atoms. Table 1 provides characteristics of TO network as determined from the simulation. About 77 % of total O are twofold coordinated. The network also contains tri-clusters where O links to three T. Notably, most of Si is linked to four O, whilst the majority of Al is surrounded by three or four O. The number of $O_{Si}$ is larger by 1.7 times than that of $O_{Al}$. This shows that the local environment of Al strongly differs from that of Si.

In Table 2 we list characteristics of SiO- and AlO-subnets. Here the size of subnet is defined as the number of atoms in the subnet. It can be seen that the size distribution for both subnet
Figure 1. Schematic illustration of TO-, SiO- and AlO-subnets.

Table 1. Characteristics of TO network. \( mSiO_x \), \( mOT_y \) and \( mAIO_x \) is the fraction of \( SiO_x \), \( OT_y \) and \( AlO_x \) units, respectively; \( mO \) is the fraction of O for different groups.

| \( SiO_x \) | \( mSiO_x \) | \( OT_y \) | \( mOT_y \) | \( AlO_x \) | \( mAIO_x \) | Group | \( mO \) |
|-------------|-------------|-------------|-------------|-------------|-------------|-------|-------|
| \( SiO_4 \) | 0.976       | 0.771       | 0.289       | 0.339       |             | \( O_{Si} \) | 0.339 |
| \( SiO_5 \) | 0.023       | 0.224       | 0.634       | 0.199       |             | \( O_{Al} \) | 0.199 |
| \( SiO_6 \) | 0.001       | 0.005       | 0.072       | 0.461       |             | \( O_{Al} \) | 0.461 |
|             | –           | –           | –           | –           |             |       |       |

types is non-Gaussian. The parking of \( SiO_x \) and \( AlO_x \) in the TO network is quite different. Namely, about 92 % of total Si belong to a large SiO-subnet, while Al atoms are distributed though from 150 to 175 AlO-subnets. Largest AlO-subnet consists of about 45 % of total Al. In other words, the size distribution of AlO-subnet is much wider. We also observe that SiO- and AlO-subnets change in space and time and see that the size distribution of these subnets shows only subtle change with time. This means that the system’s dynamics comprises both splitting and merging of subnets into new ones, with quite similar intensity for the same subnet type. On the other hands, the splitting and merging occur heterogeneously in the space and time, because of the Si-O bond is stronger than Al-O bond. The link-cluster functions have been calculated for sets of atoms that belong to SiO- and AlO-subnets. The calculation result is graphed in Figure 2.
Table 2. Size distribution of SiO- and AlO-subnets. Here $[s_1 - s_2]$ is the range of subnet size; $N_{SiO}$, $N_{AlO}$ is the number of SiO- and AlO-subnet with corresponding size.

| t=0 | t=1 ns |
|-----|--------|
| $[s_1 - s_2]$ | $N_{SiO}$ | $[s_1 - s_2]$ | $N_{AlO}$ | $[s_1 - s_2]$ | $N_{SiO}$ | $[s_1 - s_2]$ | $N_{AlO}$ |
| 1 | 45 | 1 | 117 | 1 | 46 | 1 | 136 |
| 2 | 11 | 3 | 13 | 3 | 11 | 3 | 20 |
| 3 | 10 | 4-6 | 8 | 5 | 2 | 5-6 | 5 |
| 5 | 2 | 7-9 | 5 | 7 | 4 | 8-11 | 4 |
| 9 | 1 | 10 | 2 | 2069 | 1 | 13 | 2 |
| 2092 | 1 | 15 | 2 | -- | -- | 21 | 1 |
| -- | -- | 17 | 1 | -- | -- | 27 | 1 |
| -- | -- | 30 | 1 | -- | -- | 86 | 1 |
| -- | -- | 1367 | 1 | -- | -- | 1286 | 1 |

Figure 2. Link-cluster function for atoms belonging to SiO- and AlO-subnets.

For the case of SiO-subnet $F_{link}(r, t)$ drops drastically as $r$ varies from 1.3 to 1.95 Å. This is originated from the fact that the system contains a large SiO-subnet consisting of about 90% of total Si, most of Si-O bond length is smaller than 1.95 Å. With further increasing $r$, $F_{link}(r, t)$ has a long flat tail which means that the distances between nearest neighboring SiO-subnets varies from 2 to 6 Å. Here the distance between two subnets is defined as a shortest distance between two atoms: each atom of which belongs to its own subnet. In the case of AlO-subnet $F_{link}(r, t)$ at $r = 2.05$ Å drops to the value that significantly larger than that of SiO-subnet. This is due to that the size distribution of AlO-subnets is much wider than that of SiO-subnets (see Table 2), then Al-O bond length is larger than Si-O bond length. From the behavior of $F_{link}(r, t)$ it follows that the SiO- and AlO-subnets are built in TO network. As a result, the melt will possess micro-regions with different atomic mobility and chemical composition. To detect such micro-regions, we consider the sets of fast, slow and random atoms denoted respectively as SFA, SSA and SRA. Each set contains 1100 atoms, i.e. 20% of total atoms. SFA and SSA are
determined by the square displacement of atom $q(t)^2$ and observation time $t_{\text{obs}}$. Here $t_{\text{obs}}$ is set from 1 to 5 ns. The atom belongs to SFA or SSA if its $q(t_{\text{obs}})^2$ is larger or smaller than that of remaining atoms. The atoms of SRA are randomly taken from the system.

**Table 3.** Characteristics of SRA, SFA and SSA. Here $N_O$, $N_{Si}$ and $N_{Al}$ is the number of O, Si and Al, respectively; $t_{\text{obs}}$ is equal to 1 ns; MSD is the mean square displacement per atom for the time $t_{\text{obs}}$.

| Set  | $N_O$ | $N_{Si}$ | $N_{Al}$ | $(N_{Si} + N_{Al})/N_O$ | $N_{Si}/N_{Al}$ | MSD, Å² |
|------|-------|----------|----------|------------------------|-----------------|---------|
| SFA  | 678   | 24       | 398      | 0.62                   | 0.06            | 335.13  |
| SSA  | 697   | 376      | 27       | 0.58                   | 13.93           | 3.14    |
| SRA  | 697   | 199      | 204      | 0.58                   | 0.98            | 106.46  |

**Figure 3.** Link-cluster function for SRA, SFA and SSA.

Table 3 presents characteristics of SRA, SFA and SSA. The number of O is close for these sets, but the number of Si and Al of SSA significantly differ from that of SFA. Obviously, this
is caused by large difference between Si and Al mobility. Figure 3 plots $F_{\text{link}}(r, t)$ for considered sets. We can see that $F_{\text{link}}(r, t)$ slightly changes with time, but is quite different for SRA, SFA and SSA. In particular, as $r$ increases to 2 Å, $F_{\text{link}}(r, t)$ drops to 825, 700 and 190 for SRA, SFA and SSA, respectively. This fast decrease is due to large TO-subnets formed by considered atoms. In particular, fast and slow atoms tend to locate nearby to forming large TO-subnets. The random atoms are distributed uniformly in the TO network so that they in contrast form only small TO-subnets. We note that the majority of $TO_x$ of SSA are $SiO_x$, whilst SFA mostly include $AlO_x$. The number of $OSi$ and $OAl$ in SFA is respectively smaller and larger than in SSA. With further increasing $r$ to 2.5 Å a shoulder appears and then $F_{\text{link}}(r, t)$ gradually decreases to 1 (see Figure 3). This means that the distances between nearest neighboring TO-subnets is larger than 2.5 Å.

Figure 4. MSD for fast, slow and random atoms as a function of time.

Figure 4 presents MSD for atoms of considered sets. We can see that slow atoms do not move far from their initial positions. This means that the size of immobile domains as well as positions of slow atoms is slightly changed during the time $t_{\text{obs}}$. Combined with the weak dependence of $F_{\text{link}}(r, t)$ with time we can conclude that the melt possesses a two-domain structure during $t_{\text{obs}}$ which clearly evidences the DH in the melt.

To give more details about immobile domains we calculate the size distribution of link-clusters with $r_{\text{linkage}} = 2$ Å. The calculation result is shown in Table 4. One can see that the number of clusters with size from 1 to 3 for SFA and SRA varies from 600 to 800 which is by four times larger than that for SSA. Moreover, the size of largest cluster of slow atoms reaches up to 650. This result confirms the mention remark that the immobile domains possess very high density of slow atoms.

We note that slow atoms of each immobile domain form a number of link-clusters during $t_{\text{obs}}$. For instance, initially a large cluster and some atoms are located separately, then these atoms and cluster merge into one large cluster at later moment. The immobile domain therefore can be determined by link-clusters detected at different moments during $t_{\text{obs}}$. We perform the calculation of immobile domains via 50 moments. Firstly, we determine link-clusters of slow atoms with $r_{\text{linkage}} = 2$ Å. Then for each moment $t_i$ we find domains and slow atoms belonging to them. Finally we determine the number of domains $N_D(t_i)$, where $i = 1, 2 .., 50$. The calculation result at several moments is listed in Table 5.
Table 4. Size distribution of link-cluster with $r_{\text{linkage}} = 2 \, \text{Å}$. $[s_1 - s_2]$ is the range of cluster size; $N_{\text{SFA}}$, $N_{\text{SSA}}$ and $N_{\text{SRA}}$ is the number of link-clusters with corresponding size for SFA, SSA and SRA, respectively.

| $[s_1 - s_2]$ | $N_{\text{SFA}}$ | $N_{\text{SSA}}$ | $N_{\text{SRA}}$ | $[s_1 - s_2]$ | $N_{\text{SFA}}$ | $N_{\text{SSA}}$ | $N_{\text{SRA}}$ |
|---------------|------------------|------------------|------------------|---------------|------------------|------------------|------------------|
| 1             | 500              | 141              | 634              | 1             | 475              | 137              | 603              |
| 2-3           | 165              | 33               | 163              | 2-3           | 169              | 35               | 187              |
| 4-5           | 27               | 5                | 16               | 4-5           | 25               | 5                | 13               |
| 6-10          | 14               | 4                | 4                | 6-15          | 17               | 4                | 3                |
| 11            | –                | 1                | –                | 17            | –                | 1                | –                |
| 45            | –                | 1                | –                | 46            | –                | 1                | –                |
| 129           | –                | 1                | –                | 114           | –                | 1                | –                |
| 650           | –                | 1                | –                | 648           | –                | 1                | –                |

Figure 5. Number $< N_{va}(t) >$ as a function of time.

small and we assume that they belong to a mobile domain. Thus for the case $t_{\text{obs}} = 1 \, \text{ns}$ the system contains 9 immobile domains with size from 5 to 719. We also observe that atoms make large displacements as $TO_x$ or $OT_y$ exchange their coordinated atoms. Accordingly, whenever a T-O bond is broken, then a new one is formed and causes atomic rearrangements in the TO network. For convenience of discussion, such diffusion mechanism is called bond-breaking mechanism. The atomic diffusivity depends on the rate of bond-breaking events (BBE), i.e. the breaking and reformation of T-O bonds. Because of BBE cause the atomic rearrangement in the TO network, the number $N_{va}(t)$ can be used to characterize the rate of BBE. To estimate the rate of BBE occurred in different domain types we determine $N_{va}(t)$ for every atom at 50 moments separated by 20 ps. Then we calculate $< N_{va}(t) >$ by averaging over all atoms in each considered set. The rate of BBE is approximately estimated by the slope of curve $< N_{va}(t) >$ vs. time $t$ (figure 5). We observe that the rate of BBE for SFA is by a factor of 7-8 larger than that for SSA. This result supports the bond-breaking mechanism by that the more BBE the
Table 5. Size distribution of immobile domains. $S_{1-2}$ is the range of domain; $N_D$ is the number of domains with corresponding size.

| $t$ (ps) | $S_{1-2}$ | $N_D$ | $S_{1-2}$ | $N_D$ | $S_{1-2}$ | $N_D$ | $S_{1-2}$ | $N_D$ | $S_{1-2}$ | $N_D$ |
|----------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|
| 200      | 1         | 114   | 1         | 103   | 1         | 100   | 1         | 90    | 1         | 82    |
| 400      | 2-4       | 33    | 2-4       | 33    | 2-4       | 32    | 2-4       | 29    | 2-4       | 28    |
| 600      | 5-10      | 8     | 5-10      | 7     | 5-10      | 5     | 5-10      | 3     | 5-10      | 6     |
| 800      | 11        | 11    | 11        | 11    | 11        | 11    | 11        | 11    | 11        | 11    |
| 1 ns     | 49        | 55    | 185       | 196   | 1         | 198   | 1         | 198   | 1         | 198   |
|          | 131       | 134   | 695       | 712   | 1         | 719   | 1         | 719   | 1         | 719   |
|          | 669       | 676   | –         | –     | –         | –     | –         | –     | –         | –     |

Figure 6. Link-cluster functions for different MD observation time $t_{obs}$.

atom undergoes, the faster it moves. This follows that BBE happen in the mobile domain more frequently than in immobile domains. In other words, BBE are non-uniformly distributed in the
TO network.

Figure 6 plots $F_{\text{link}}(r, t)$ for different observation time $t_{\text{obs}}$. One can see that $F_{\text{link}}(r, t)$ for SFA and SSA strongly changes with increasing $t_{\text{obs}}$ and it comes very closely to the curve for SRA at $t_{\text{obs}} = 4.4$ ns. The two-domain structure disappears when $t_{\text{obs}}$ is about 5 ns. This can be interpreted by that due to non-uniform spatial distribution of BBE and during a moderate time tobs, the TO network comprises separate domains where BBE happen so rarely that the atoms in them move not far from initial positions. Obviously, the atoms of these domains are immobile. On the other hands, most of BBE happen outside immobile domains so that the atoms of the mobile domain move fast. The size of immobile domains decreases with increasing tobs. Therefore, the non-uniform spatial distribution of BBE is responsible for DH in the melt.

4. Conclusion

MD simulation has been conducted to study structure and diffusion in the aluminum-silicate melt at ambient pressure and temperature of 3000 K. We found that the analysis based on AlO- and SiO-subnets could provide useful details about the structure heterogeneity on local and medium length scales. Furthermore, DH and diffusion mechanism can be successfully explored through the link-cluster function and rate of bond-breaking events. Our conclusions are summarized as follows:

(i) The network structure of the melt consists of separate SiO- and AlO-subnets. The size distribution of these subnets is non-Gaussian. The simulation shows that the melt exhibits the micro-segregation and structure heterogeneity on local and medium length scales. Namely, the local environment of Si differs strongly from that of Al. The parking of $SiO_x$ and $AlO_y$ in the TO network is quite different. About 90 % of total Si belong to one large SiO-subnet, whilst Al atoms are distributed throughout numerous small AlO-subnets.

(ii) It is found that during a moderate long time the melt has a two-domain structure consisting of separate immobile domains and a mobile domain. Most of slow atoms are concentrated in immobile domains. In contrast, the majority of fast atoms move inside the mobile domain. Different domain types differ strongly in the rate of bond-breaking events and chemical composition. The immobile and mobile domains represent respectively Si-rich and Al-rich regions. The two-domain structure disappears when the observation time is enough long. In the case when $t_{\text{obs}} = 1$ ns, we found immobile domains with size up to 719. The simulation also gives clear evidences for DH in the melt and that the non-uniform spatial distribution of bond-breaking events is responsible for DH.

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