The structural and dynamical properties of aluminosilicate melts: Insight via molecular dynamic simulation

Mai Van Dung\textsuperscript{1,2}\textsuperscript{*}, Tran Thanh Dung\textsuperscript{2}, Truong Duc Quynh\textsuperscript{3}, Nguyen Manh Tuan\textsuperscript{1}, Nguyen Van Yen\textsuperscript{4,5}, and Le The Vinh\textsuperscript{6}

\textsuperscript{1}Institute of Applied Materials Science, Vietnam Academy of Science and Technology, No. 1A TL29 Street, Thanh Loc Ward, District 12, Ho Chi Minh City, Vietnam.
\textsuperscript{2}Thu Dau Mot University, No. 6, Tran Van on Street, Phu Hoa Ward, Thu Dau Mot City, Binh Duong Province, Vietnam.
\textsuperscript{3}Ho Chi Minh city University of Transport, No. 2 Vo Oanh Str., Ward 25, Binh Thanh District, Ho Chi Minh City, Vietnam.
\textsuperscript{4}Institute of Theoretical and Applied Research, Duy Tan University, Hanoi, 100000, Vietnam.
\textsuperscript{5}Faculty of Natural Sciences, Duy Tan University, Da Nang, 550000, Vietnam.
\textsuperscript{6}School of Automobile Technology and Aviation Engineering, Miendong University of Technology, Dong Nai Province, Vietnam.

\textbf{Abstract.} We have studied the structural and dynamical characteristics of xAl\textsubscript{2}O\textsubscript{3}(1-x)SiO\textsubscript{2} system by means of molecular dynamics simulation at 3000 K using the Born-Mayer potentials. The structural properties have been analysed through the radial distribution function and structural factor. The simulation shows that our results are in good agreement with previous experimental and simulated data. The dynamical heterogeneity (DH) is investigated via the analysis of mobile, immobile, and random atoms. Our simulation indicates that the liquids exists dynamical heterogeneity.

\textbf{Keywords:} Structure, molecular, dynamics, heterogeneity, alumina-silicate.

\textsuperscript{*}Correspondence: dungmv@tdmu.edu.vn; Tel.: +84-0984855192

1. Introduction

The alumino-silicate glasses and melts are of utmost importance in materials and earth sciences for understanding physical properties of these materials in both liquid and glass state [1-4]. Therefore, the structure and dynamics of ones have been studied by various experiments such as X-ray scattering, IR and Raman, and nuclear magnetic resonance spectroscopy [5-8] as well as simulated methods [9-12]. In 1932, Zachariasen showed that the structure of SiO\textsubscript{2} consisting of corner-shared SiO\textsubscript{4} units connect each other to form continuous random network [4]. The network SiO\textsubscript{2} is significantly changed when is added by Al\textsubscript{2}O\textsubscript{3} content. The main issues of the experimental results focus to clarify local environment around Al atoms as alumina content changes. Okuno and co-worker [5] indicated that at low Al\textsubscript{2}O\textsubscript{3} concentrations, the coordination number of Al atoms having a value equal to four are main. However, the five-fold and six-fold coordination increase with increasing Al\textsubscript{2}O\textsubscript{3} content. Besides, the experimental investigation of Poe and co-worker [6] also shows that the coordination number of Al and Si atoms are dependent on both the concentration and quench rate. The simulated results by computer provides the more detailed information about local structure of Al and Si atoms in the liquid xAl\textsubscript{2}O\textsubscript{3}. (1-x)SiO\textsubscript{2}
system. The simulated result of Pfleiderer and co-worker [9] indicates that the structure Al$_2$O$_3$–SiO$_2$ melts at 13 and 47 mol% Al$_2$O$_3$ consists of disordered structural units in that TO$_4$ units (T is Al or Si) are main. The same results are found by Winkler and coworker when they investigate the liquid and amorphous Al$_2$O$_3$–SiO$_2$ system [10].

Dynamical heterogeneity (DH) plays a main role in the glass transition. The formation of clusters with mobile and immobile particles in super-cooled liquids is investigated by the four-point density correlation function [13] simultaneously the relation between the dynamical heterogeneity and the decoupling of relaxation and diffusion is also indicated. Besides, the formation of the dynamical heterogeneity in super-cooled liquids as well as the increase of the dynamic length scale is revealed by the random first-order transition theory [14-18]. The evidence for the dependence-temperature of length scale of correlations of molecular mobility is observed through computer simulations [19-25]. The dynamic heterogeneity is also found in metallic glasses, the evolution of it is clearer than as the temperature reduces and the width of the relaxation rate distribution increases with decreasing temperature [26]. In addition, the regions having the extremely low density or high is also indicated in the silicate melt [27-29] thus, domains consisting of the fast moving atom or slow moving atom is formed. The result also demonstrated that the diffusion is due to the breaking and forming of T-O bonds. Although the dynamics has been studied for a long time. However, the dynamical heterogeneity of the liquid Al$_2$O$_3$–SiO$_2$ system is not fully understood. In this paper, we investigate the structure and DH by molecular dynamic simulation (MD) for xAl$_2$O$_3$ (1-x)SiO$_2$ system, where x is the alumina content and varies from 0.05 to 0.7.

2. Computational method

MD simulation is done for xAl$_2$O$_3$ (1-x)SiO$_2$ system where x = 0.05–0.7 is Al$_2$O$_3$ content. The xAl$_2$O$_3$ (1-x)SiO$_2$ system consists of about 5000 atoms constructed by randomly placing atoms in a cubic simulation box. The degree of accuracy of the simulated result is dependent on the potential function. In this study, we employ the Born-Mayer potential is very successfully performed to calculate the structural and dynamic properties in silicate systems of authors in Refs. [10, 27, 30]. The function of potential is described as Eq. (1).

$$ U_y = \frac{q_i q_j}{r_{ij}} + A_y \exp(-B_y r_{ij}) $$

where $q_i$ and $q_j$ are the effective charges of $i$ and $j$ atoms, $r_{ij}$ is the distance between $i$ and $j$ atoms, and $A_y$ and $B_y$ are constants which can be found in Refs. [10, 27, 30]. In order to solve the motion equation, we adopt the Verlet algorithm with a time step of 1.0 fs. The periodic boundary condition is applied for all directions. Firstly, the model is heated to 6000 K. After that, this model is relaxed for 50 ps to eliminate the initial configuration memory. In the next stage, the model is cooled down to 3000 K with a cooling rate of 10$^{-5}$ K/s and relaxed for a long time at this temperature and zero GPa until reaching the equilibrated model in the NPT ensemble. More detail about model construction can be found in Ref. [31].

To study the clustering, we consider sets of mobile and immobile atoms for about 86.04 ps. These atoms have the mean square displacement per atom $\langle r_t^2 \rangle$ (MSD) larger and smaller than the one of remaining atoms in the same span time $t$, respectively. MSD is a distance that atoms move from a starting configuration to the configuration at time $t$. Sets of mobile and immobile atoms denoted by SMA and SIMMA, respectively, are taken from the system. The number of atoms of these sets are 10 % total atoms in the model. Besides, we also consider set of atoms extracted randomly from total atoms in the model and signed by SRA.

A linkage is formed between two atoms if the distance between them is less than a defined distance $r_{lk}$. In this study, the value of distance $r_{lk}$ is chosen equal to 4.5 Å for both oxygen and cation atoms in the system. In the chosen sets of atoms, they can link each other through a path commuting of linkages to form a LK-cluster. To clarify the dynamical heterogeneity (DH) in the system, we compute number of LK-clusters $N_{LKC}$ and number average of linkages per atom $<N_{LK}>$ of mobile and immobile atoms.
The clustering of atoms in the sets is found in the model if $N_{LKC}$ and $<N_{LK}>$ for SMA and SIMMA are larger and smaller the one for SRA, respectively.

3. Results and discussions

3.1 Structure of liquid $x\text{Al}_2\text{O}_3. (1-x)\text{SiO}_2$ system

To evaluate reliability of constructed model, we compare our simulation with other simulation and experiment results. In order to describe local structure properties of liquids, the partial pair correlation functions is the fair suited quantity. Figure 1 displays the radial distribution function of the $x\text{Al}_2\text{O}_3. (1-x)\text{SiO}_2$ system at $x=0.5$. The position of first peak of pair Si-O locates at 1.60 Å. It means that the nature of the Si–O bond is strong covalent bond. This result is mostly in line with experimental results in Refs. [32, 33] and simulation of Winkler and coworker [10]. However, this value is bigger than the results of 1.50 – 1.51 Å of Hoang and coworker [34]. We can see that the function $g_{\text{SiO}}(r)$ exists a blank between 2 to 3 Å. This is reflected by the fact that the range between a silicon atom and a nearest oxygen atom have to be another silicon or aluminium atom. Figure 1 also shows that the graph of function $g_{\text{AlO}}(r)$ looks like the graph of function $g_{\text{SiO}}(r)$. However, the height of peak of function $g_{\text{AlO}}(r)$ is lower and broader the one of function $g_{\text{SiO}}(r)$. It can see that the position of the first peak has a value of 1.67 Å. This shows that the Al-O bond is weaker than the Si-O bond. This result is well consistent with simulation [34]. However, our simulation is slightly smaller than the results in Refs. [10, 32, 33]. The first peak position of function $g_{\text{OO}}(r)$ locates at 2.63 Å. This value is bigger than the result in Ref. [34]. The functions $g_{\text{SS}}(r)$, $g_{\text{SA}}(r)$ and $g_{\text{AA}}(r)$ have the first peak positions at 3.15, 3.13 and 3.11 Å, respectively, which is in good agreement with results [10, 34].

![Figure 1](image.png)

**Figure 1.** The partial pair radial distribution functions of $x\text{Al}_2\text{O}_3. (1-x)\text{SiO}_2$ at $x=0.5$.

In Figure 2, the total partial pair radial distribution function of this study is compared with the experiment of Wilding et al. It can see that the positions of peaks of function $g(r)$ and the shape are in relative agreement with experiment. However, the height of peaks is overestimated in comparison with the experimental data of Wilding et al. This can be due to in our calculation, the dipole and quadrupole interactions are ignored in the Born-Mayer potential.
Figure 2. Total partial pair radial distribution functions of this study and experiment of Wilding et al [33].

In order to further clarification the structure of $x\text{Al}_2\text{O}_3, (1-x)\text{SiO}_2$, we also compare the structural factor with experiment of Wilding et al [33]. Figure 3 shows that the graphs of the function of the structural factor at $x=0.2$ have the very similar shape and positions. This means that our calculation is well consistent with experimental data.

Figure 3. The factor of this study comparison with experiment of Wilding et al [33].
3.2. Analysis on subsets of immobile, mobile and random oxygen atoms

Figure 4 displays the time dependence of MSD for all oxygen atoms, SMA, SIMMA and SRA subsets. In Figure 4 the graph of MSD for the SMA subsets is separate from the remaining ones for all oxygen atoms, SIMMA and SRA subsets. In the same span time from 19.12 ps to 96.5 ps at $x=0.05$ the MSD of SMA oxygen atoms is much larger MSD of SIMMA and SRA oxygen atoms. Namely, MSD of oxygen atoms SMA has a value of 4.2 Å, meanwhile the one of SIMMA is very small. The MSD for all oxygen atoms is very close the one of SRA and has a value of 0.26 Å. We can see that the MSD subset of oxygen atoms SMA, SRA, and all oxygen atoms is strongly dependent on $\text{Al}_2\text{O}_3$ content. The MSD of subset of oxygen atoms SMA, SRA, and all oxygen atoms increases considerably as $\text{Al}_2\text{O}_3$ content grows in that the MSD of SMA travels over a distance of 30 Å, and the one of SRA and all oxygen atoms is 8 Å, meanwhile for oxygen atoms SIMMA is almost unchanged. The strong change of MSD of subset SMA with $\text{Al}_2\text{O}_3$ concentration can see further clear through the calculation the slope. One see that the slope of the graph for SMA at high $\text{Al}_2\text{O}_3$ content is significantly larger than the one for SMA at low $\text{Al}_2\text{O}_3$ content. Their slopes are $0.05\ \text{Å}^2.\text{ps}^{-1}$ and $0.39\ \text{Å}^2.\text{ps}^{-1}$, respectively.

![Figure 4](image-url)

**Figure 4.** The time dependence of MSD for SRA, SIMMA, SMA oxygen subsets and all oxygen atoms at $x = 0.05, 0.70$

To clearly understand the dynamics of oxygen atoms in liquids, we studied $<N_{LK}>$ and $N_{LKCL}$ for mobile, immobile and random oxygen atoms. The results are shown in Figure 5 and 6. Here $<N_{LK}>$ and $N_{LKCL}$ are the average number of linkages per atom and the number of LK-clusters, respectively, for the subsets. In Figure 5, the $<N_{LK}>$ for SMA is much larger than the one for SIMMA and SRA at low $\text{Al}_2\text{O}_3$ content ($x=0.05$). By contrast, according to Figure 6 the $<N_{LKCL}>$ of SIMMA and SRA is bigger than the one of SMA. This means that the subset of SMA and SIMMA oxygen atoms have a tendency to clustering at low $\text{Al}_2\text{O}_3$ content. However, at $x=0.7$ can see that the $<N_{LK}>$ and $N_{LKCL}$ of SRA, SIMMA, and SRA is close each other. So, the clustering is found at low $\text{Al}_2\text{O}_3$ content meanwhile the one is not observed at high $\text{Al}_2\text{O}_3$ content. Therefore, we can conclusion that the liquids exhibits
dynamical heterogeneity for oxygen atoms. A question is set. Do the Al and Si atoms exhibit the dynamical heterogeneity?

Figure 5. The time dependence of $\langle N_{L,K} \rangle$ for oxygen subsets and all oxygen atoms at $x = 0.05, 0.70$

![Figure 5. The time dependence of $\langle N_{L,K} \rangle$ for oxygen subsets and all oxygen atoms at $x = 0.05, 0.70$](image)

Figure 6. The time dependence of $\langle N_{L,KCL} \rangle$ for oxygen subsets and all oxygen atoms at $x = 0.05, 0.70$

To answer this question, we calculate $\langle N_{L,K} \rangle$ and $N_{L,KCL}$ for SMA, SIMMA and SRA for Al and Si atoms. Figure 7 and 8 show $\langle N_{L,K} \rangle$ and $N_{L,KCL}$ for Si and Al subsets when the $Al_2O_3$ content at 0.05 and 0.75. We can see that the aluminum and silicon atoms also exhibit DH. However, this phenomena occurs not clearly at high $Al_2O_3$ concentration.
Figure 7. The time dependence of $\langle N_{LK} \rangle$ for aluminum and silicon subsets at $x = 0.05$ and $0.70$

Figure 8. The time dependence of $N_{LKCL}$ for aluminum and silicon subsets at $x = 0.05$ and $0.70$

4. Conclusion
The structure of liquids is analysed via the radial distribution function and the structural factor. The simulated result indicates that the bond length of the Si-O and Al-O pairs is 1.60 and 1.67 Å, respectively. These values are in good agreement with previous experimental and simulated data. In our simulation, the function of the structural factor has the shape and position of peaks in good agreement
with the experimental result of Wilding et al. The DH of liquids is studied through subset of mobile and immobile atoms. The result shows that the liquids exhibits dynamical heterogeneity and this phenomena is weaker than at high Al$_2$O$_3$ content.

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