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Insight into dynamics and microstructure of aluminum-silicate melts from molecular dynamics simulation

P.K. Hung [a,b], L.T. Vinh [a,*], To Ba Van [a,b], N.V. Hong [c], N.V. Yen [c]

[a] Simulation in Materials Science Research Group & Faculty of Electrical and Electronics Engineering, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
[b] Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
[c] Hanoi University of Science and Technology, Viet Nam

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ABSTRACT

We have conducted a systematic analysis on dynamics and structure of aluminum-silicate melt at various pressures and at 3500 K. Firstly, the analysis with respect to network structure units reveals that the melt contains separate Si-O and Al-O subnets which evidences the micro-segregation of the liquid. We propose a model of solid-like particle to interpret the diffusivity for three types of atom. Secondly, from the analysis on the sets, immobile, mobile and random atoms we reveal the dynamics heterogeneity (DH) in the melt. Moreover the simulation also shows a clear correlation between DH and structural heterogeneity. Finally, the analysis with respect to O-simplex and T-simplex provides a new view on the structure of the melt. It was shown that there are not only T-clusters with one atom that form a simple network structure, but instead the melt contains a number of T-cluster with numerous atoms. The structure heterogeneity of silicate melt concerns two aspects: T-clusters and O-simplexes which contain extremely large number of atom.

1. Introduction

Silicate is a compound of silica and other oxides such as MgO, Al_2O_3, Na_2O, …, which are used in many technology applications [1–3]. It is very challenging to understand the correlation between dynamics and microstructure of those liquids from a physical perspective. Recently, it is shown that silicate liquid exhibits many peculiar properties. Namely, the viscosity of the silica-rich liquids decreases with increasing pressure [4–6]. Meanwhile the silica-poor liquids exhibit the positive pressure dependence. Moreover, the diffusivities of O and Si show a maximum along the isothermal compression. According to X-ray studies [7–8] the Si-O distance remains constant up to pressure of several GPa, whereas the Si-Si distance decreases. The compression of the liquid therefore is accompanied with the increase in high-coordinated Si and reduction in Si-O-Si angle. The degree of polymerization, a ratio of non-bridging oxygen per tetrahedron NBO/T characterizes the interplay between dynamics and structure of silicate melts [9–15]. The induced-pressure polymerization has been revealed by the nuclear magnetic resonance (NMR) and Raman-scattering spectroscopy. Wang et al. [16] showed that the response of viscosities to pressure is strikingly distinct between polymerized ($NBO/T < 1$) and de-polymerized ($NBO/T > 2$) melts. Other studies [17–19] show that with increasing pressure the structure of silicate liquid can no longer be represented by simple corner-sharing tetrahedral network. In addition, the dynamics were affected by both the degree of polymerization and number of oxygen triclusters.

Microstructure of alumino-silicates has been investigated using various experimental techniques [20–22]. As shown from ref. [23], the number of five- and six-fold coordinated Al in the Al_2O_3 - SiO_2 system increase with increasing Al_2O_3 content. Moreover, the chemical ordering of Al is very different from that of Si. More details about the silica liquids can be obtained using the simulations [24–32]. According to molecular dynamics (MD) simulation, the presence of AlO_5, SiO_5 and oxygen triclusters facilitates the dynamics of atoms. Moreover, the packing of AlO_4 strongly differs from that of SiO_4 as a result of oxygen triclusters and edge-sharing AlO_4 tetrahedrons. Other studies found that the structural ordering of $Al_2O_3.2SiO_2$ system is of the length scale about order 1 nm. This intermediate range order (IRO) can be described by micro-phase separation where Al-rich network structure percolates through Si-O network structure. Similar IRO has been observed for other silicate melts such as calcium silicate, sodium silicate and alkali aluminum silicate [33]. Moreover the sodium silicate contains channels which serve as preferential diffusion pathways in the immobile Si-O matrix. Other simulations [34,35] showed that the compression favors the homogeneity of the structure of silicate system.

In this study we conduct a systematic analysis on aluminum-silicate melts. Firstly, we address the structural heterogeneity using the conventional method based on network structure units and then propose a model of solid-like particle to interpret the diffusion of three types of

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[*] Corresponding author.
E-mail address: lethevinh@tdt.edu.vn (L.T. Vinh).

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atom. Secondly, we perform the analysis on the sets, immobile, mobile and random atoms to clarify the DH and structure heterogeneity. Finally, the analysis on O-simplex and T-cluster is performed to give a new view on the local microstructure of the melt.

2. Computational method

MD simulations were carried out for 5 samples consisting of 1000 Si, 3500 O and 1000 Al at 3500 K and over a pressure range from 0.1 MPa to 20 GPa. We employed the Born–Mayer potential of which the parameters are taken from ref. [36]. The periodic boundary conditions were imposed on all faces of simulation box and the Coulomb interactions were taken into account by mean of Ewald method. All atoms moved by applying the Verlet algorithm at the time step of 0.478 fs. Before the start of simulation an equilibrated sample was obtained by randomly placing all atoms in the simulation box and relaxed at 5000 K. Then the sample was cooled down to 3500 K and relaxed for 2–3 ns. The coordinate positions of atoms at the end of the relaxation run were used for following runs with 95.6 ps (i.e. 200,000 steps). In this period the dynamics and structure data were collected to do further analysis. We first prepared a sample at ambient pressure. The constructed model provided the similar structure as one reported in ref. [37] which gives a good agreement with experiment in the structure of the melt. The high-pressure samples were obtained by subsequent compressing and relaxing the equilibrated sample at lower pressure. More detail about preparing the $2SiO_2 \cdot Al_2O_3$ model can be found in refs [36,37]. For the convenience of discussion we denote the sample at 0.1 MPa, 5, 10, 15 and 20 GPa as AS_0, AS_5, AS_{10}, AS_{15} and AS_{20}, respectively.

3. Results

3.1. Analysis with respect to network structure units

The structure of aluminum-silicate liquid can be represented by a network consisting of structure units (TO_x and OT_y, where T is the Si or Al). The cutoff distance for Si-O and Al-O is chosen as a first minimum of the pair radial distribution function. It is equal respectively to 2.4 and 2.55 Å. In Fig. 1 we plot the number of structure unit as a function of the coordination number. One can see that with increasing pressure the number of OT_2 monotonously decreases indicating that the bridging O (BO) are gradually replaced by oxygen-triclusters. Moreover, the structure of high-pressure liquid is described by the high-coordinated units instead the tetrahedral network.

The TO_x (or OT_y) consists of a central atom (C-atom) and x (or y) neighboring atoms where the C-atom forms T—O bonds with its neighboring atoms. TO_x and OT_y possess x and y bonds, respectively. The distance between neighboring atom and C-atom is less than the cutoff distance. During a finite time interval the C-atom can break a T—O bond and then form new bond with another atom. So the list of the neighboring atom as well as the number of neighboring atom for a particular unit changes with time.

The T-O bonds determined for the starting configuration are denoted as the Init-bond. Obviously TO_x and OT_y in the starting configuration is having x and y Init-bonds, respectively. We denote these units in the configuration at the time t by $TO_{(xt)}$ and $OT_{(yt)}$. Here xt and yt is the number of Init-bond. We have $xt \le x$ and $yt \le y$ because some Init-bonds are broken during the time t. The C-atom and xt neighbors of $TO_{(xt)}$ move together like a solid particle (SLP) diffuses for the time t. The size of this SLP is equal to $xt + 1$. By analogy, $OT_{(yt)}$ SLP consists of $yt + 1$ atoms. Thus the diffusion is realized by displacement of different SLPs during the time t. The mobility of atoms differs from each other in that they displace via SPL with different size. In particular, as we show below, the atom moving via large SPL has slower mobility than one moving via small SLP.

In Fig. 2 we present the number of total Init-bonds available in the system at different time t. One can see that it decreases monotonously with time. Moreover the decrease in total Init-bonds for AlO_x proceeds faster than one for SiO_x, which means that the Si—O bond is stronger than Al—O bond. With increasing pressure, such decrease for both AlO_x and SiO_x is faster. This means that the T—O bond in high-pressure liquid is weaker. Thus the diffusivity of Al could differ from Si due to that the Al—O bond is weaker than the Si—O bond.

Fig. 3 shows the fraction of $TO_{(xt)}$ and $OT_{(yt)}$ together with the mean square displacement of C-atom $<r_t^2>$. As expected, the fraction of SLP with large size (large SLP) is replaced by SLP with smaller size (small SLP) as the time increases. The $<r_t^2>$ for large SLP are always smaller

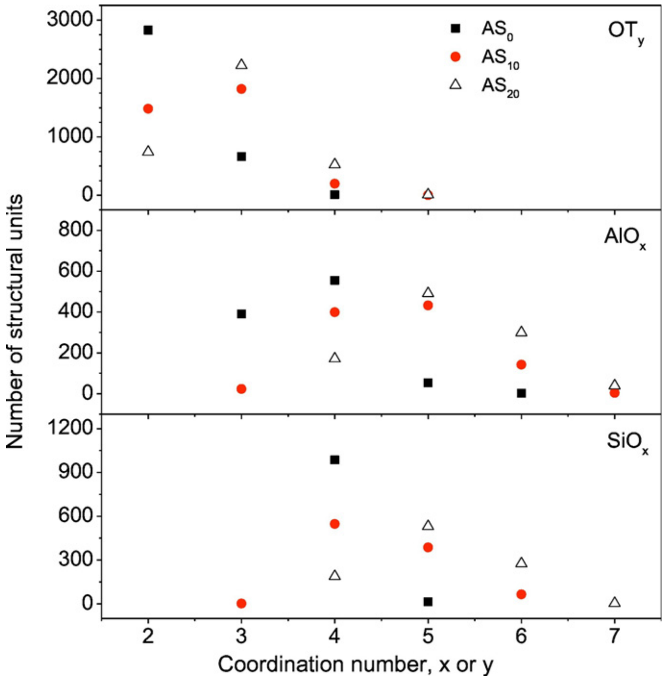

Fig. 1. The dependence of number of structural units as a function of coordination number.

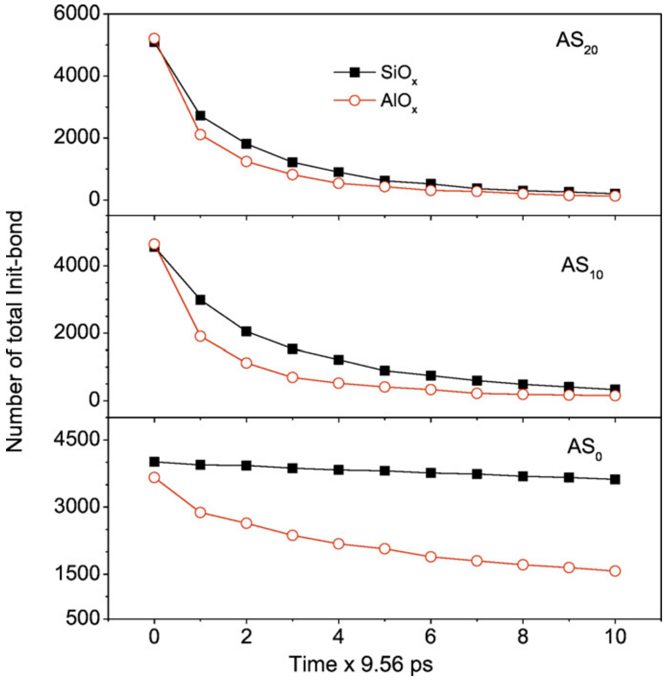

Fig. 2. The time dependence of number of total Init-bond for AlO_x and SiO_x.