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Microstructural and Dynamical Heterogeneity Characteristics in Al_2O_3- $2SiO_2$ Liquid

Nguyen Thi Thanh Ha[1,*], Kankham Keopanya[2], Le Van Vinh[1]

[1]*Department of Computational Physics, Hanoi University of Science and Technology, Vietnam*
[2]*Department of Physics, Thai Nguyen University of Education, Thai Nguyen, Vietnam*

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Abstract: In this paper the structural and dynamical characteristics in alumina- silicate Al_2O_3–$2SiO_2$ (AS2) liquid are investigated by molecular simulation method. Structural properties are clarified through the pair radial distribution function, distribution of TO_n (T= Si, Al) coordination units and distribution of partial bond angle in TO_n. Furthermore the change in diffusion mechanism between low and high pressure is revealed by transition of the structural units $TO_x \rightarrow TO_{x\pm1}$. At the low-pressure, liquid AS2 exhibits the dynamics heterogeneity (DH). The origin of dynamic heterogeneity is identified and liquid AS2 consists of separate mobile and immobile regions.

Keywords: Molecular dynamic, structure, dynamics heterogeneity, diffusion, network structure.

1. Introduction

Silicate, glass-forming mixtures of SiO_2 with an oxide such as Al_2O_3, Na_2O, or K_2O are an important class of materials used in many technological applications [1-4]. Therefore the microstructure and dynamical properties of liquid silicates have been studied by many experiments, theory and simulation. The results show that the structure of silicates consists of basic structural units TO_x (x = 4,5,6) and the coordination units TO_4 are dominant at ambient pressure. With increasing pressure, there is a gradual transformation from tetrahedral to octahedral network structure, bridging oxygen bonds are being broken [5-8]. The T–O–T bond angle reduces and the average coordination number of Al increases. At high pressure, the coordinated units such as TO_5 and TO_6 play a significantly role [9-10]. Furthermore the existence of dynamics heterogeneity (DH) has been revealed in liquid silicates. It means that there are distinguish regions where the mobility of particles is fast or slow in systems. To clarify the original DH, the numerical techniques such as multi-correlation

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[*] Corresponding author. Tel.: 84-983012387.
Email: ha.nguyenthithanh1@hust.edu.vn

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function, visualization and cluster analysis are widely used [11-16]. However, the physical mechanism behind this phenomenon has not been successfully identified in these studies.

Aluminum-silicate is a simple pseudo-binary silicate and well recognised reference material in high pressure applications. Hence knowledge of its structure and dynamical properties is important and fundamental. In this paper, we use molecular dynamics simulation to investigate network structure, DH and mechanism diffusion in Al_2O_3–$2SiO_2$ (AS2). This paper is organized as follows: First, we give an overview of the search in section 1. The section 2 presents simulation technique. In section 3, the microstructure characteristics and dynamical properties (diffusion, DH) are discussed. The last section, we summarize the results and give conclusions.

2. Computational procedure

The AS2 models consist of 1000 Si, 1000 Al, 3500 O atoms at temperatures of 3500 K and in 0-20 GPa pressure range investigated via molecular simulation method. We have used the Born–Mayer potential function. It has form:

$$u_{ij}(r) = z_i z_j \frac{e^2}{r} + B_{ij} \exp\left(-\frac{r}{R_{ij}}\right)$$

Detail about potential parameters can be found in Ref [6]. Initial configuration of the sample is created by randomly placing all atoms in a simulation box and heating up to 6000K. Then the sample is cooled down to the temperature of 3500K. To obtain a sample at ambient pressure, the sample has been done long relaxation in the NPT ensemble (constant temperature and pressure). To study dynamical properties the obtained samples are relaxed in NVE ensemble (constant volume and energy). The models at different pressures were constructed by compressing model 3500K and 0 GPa and then relaxed for a long time to reach the equilibrium state.

The Fig.1 presents linkage, LK-clusters and transition of the structural units $TO_x \rightarrow TO_{x\pm1}$. Two atoms form a linkage if the distance between them is less than a defined radius r_{lk}. Here r_{lk} is equal to 4.5 and 5.63 Å for oxygen and Si or Al, respectively. A LK-cluster is defined as a set of atoms where each atom connects to another one through a path consisting of linkages.

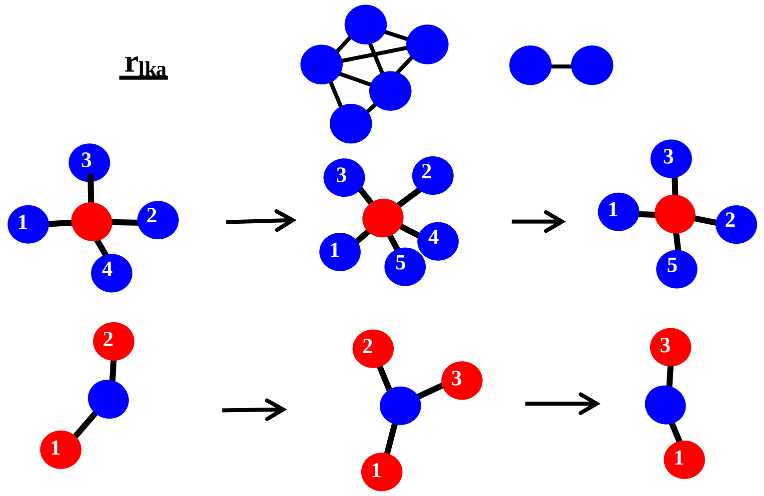

Fig 1. The schematic illustration of linkage and two LK-clusters formed from a set with 7 atoms; The replacement of T-O bond in TO_4 and OT_2. Here the red and blue circle represents cation T (Si or Al) and O atom, respectively.

3. Results and discussion

3.1. Structure properties of AS2

The micro-structure of liquid AS2 system is raveled by the pair radial distribution function (PRDF) of all atomic pairs. Fig 2 shows the PRDF of Si–Si, Al– Al, O–O and Si-O, Si-Al, Al-O pairs at 3500K and 0 GPa. PRDF of liquid AS2 systems at temperatures of 3500 K and in 0-20 GPa pressure range is shown Table 1.

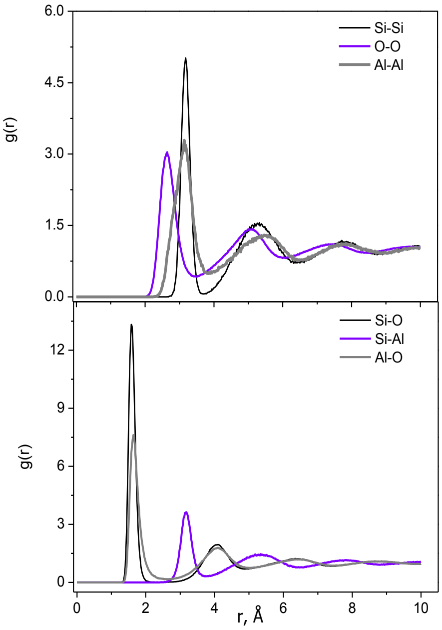

Fig 2. Partial radial distribution functions of liquid aluminum-silicate (AS2) at ambient pressure.

Table 1. Structural characteristics of AS2 liquid, r_{lk} is positions of first peak of PRDF, g_{lk} is high of first peak of PRDF

Model	0GPa	5 GPa	10 GPa	15 GPa	20 GPa	Ref [17]
$r_{Si\text{-}Si}$, [Å]	3.18	3.16	3.14	3.14	3.14	
$r_{Si\text{-}O}$, [Å]	1.58	1.58	1.6	1.6	1.62	1.61
$r_{O\text{-}O}$, [Å]	2.64	2.62	2.58	2.56	2.52	2.79
$r_{Si\text{-}Al}$, [Å]	3.18	3.14	3.12	3.12	3.1	-
$r_{Al\text{-}O}$, [Å]	1.64	1.66	1.68	1.7	1.72	1.74
$r_{Al\text{-}Al}$, [Å]	3.14	3.08	3.08	3.06	3.04	-
$g_{Si\text{-}Si}$	5.02	3.89	3.41	3.21	3.15	-
$g_{Si\text{-}O}$	13.33	9.42	7.38	6.22	5.76	-
$g_{O\text{-}O}$	3.04	2.48	2.3	2.26	2.3	-
$g_{Si\text{-}Al}$	3.63	3.06	2.89	2.96	3.02	-
$g_{Al\text{-}O}$	7.61	5.32	4.43	4.01	3.82	-
$g_{Al\text{-}Al}$	3.29	3.14	2.91	2.76	2.72	-

One can see that the first peak all atomic pairs decreases in amplitude and becomes broader under compression. Moreover the position of the first peak of Si–Si, Si–Al, Al– Al, and O–O pairs decreases but for Al–O and Si–O pairs, the position of the first peak increases. This reveals reason to understand an increase in the Si–O, Al–O, O-Si, and O–Al average coordination number and there is T–O–T bond angle reduction when increase of density of the liquid. These are shown Fig 3, Fig 4 and Fig 5.

In Fig 3, we can see distribution of TO_n (T= Si, Al) coordination units in liquid AS2 system as a function of pressure. At ambient, the number of SiO_4, AlO_3 and AlO_4 unit is domain. As temperature increases the fraction of SiO_4, AlO_3 and AlO_4 decreases meanwhile the fraction of TO_5, TO_6 (T= Si, Al) units increases in considered pressure interval. It means that increasing pressure, there is a transformation from four-fold coordination (TO_4) to five- and six-fold coordination (TO_5 and TO_6).

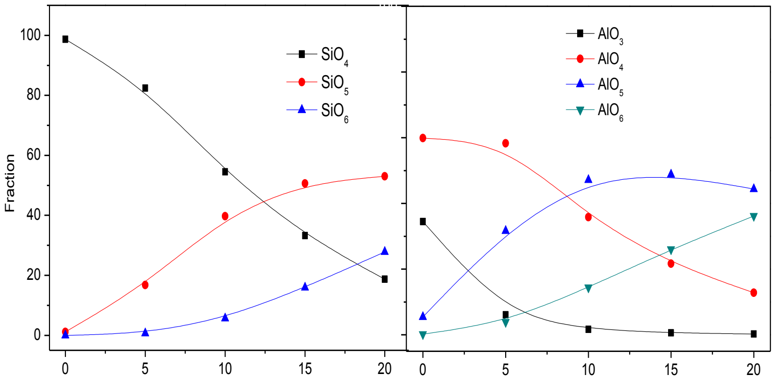

Fig 3. The distribution of TO_n (T= Si, Al) coordination units in liquid aluminum-silicate (AS2) system as a function of pressure.

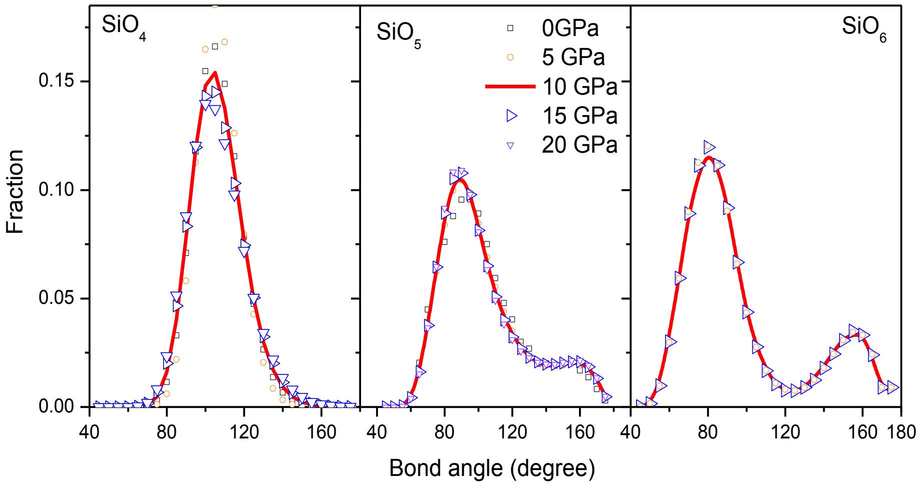

Fig. 4. The distribution of partial bond angle in SiO_n units as a function of pressure.

Fig 4 presents the distribution of partial bond angle in SiO_n (n=4,5,6) units as a function of pressure. It shows that the pressure independent of distribution of partial bond angle in SiO_n units. Here angle distribution in SiO_4 units has a form of Gauss function and a pronounced peak at 105° and

90° with SiO_5 unit. In the case of SiO_6 units there are two peaks: a main peak locates at 90° and small one at about 160°. The result is in agreement with the values measured in Refs [9]. Fig 5 displays the distribution of O–Al–O bond angle in AlO_x (x=3,4,5,6) units as a function of pressure. With AlO_3 and AlO_4 units, the O–Al–O bond angle distribution undergoes a slight change as the pressure increases in the 0–5 GPa pressure range. The height of peak in AlO_3 changes significantly mainly. For the O–Al–O bond angle distribution in AlO_4 unit, the peak shifts from 110° to the one of 105°. At a pressure range beyond 5 GPa, the O–Al–O bond angle distributions in AlO_3 and AlO_4 units are almost not dependent on pressure. The O–Al–O bond angle distributions in AlO_5 and AlO_6 units are almost unchanged under compression.

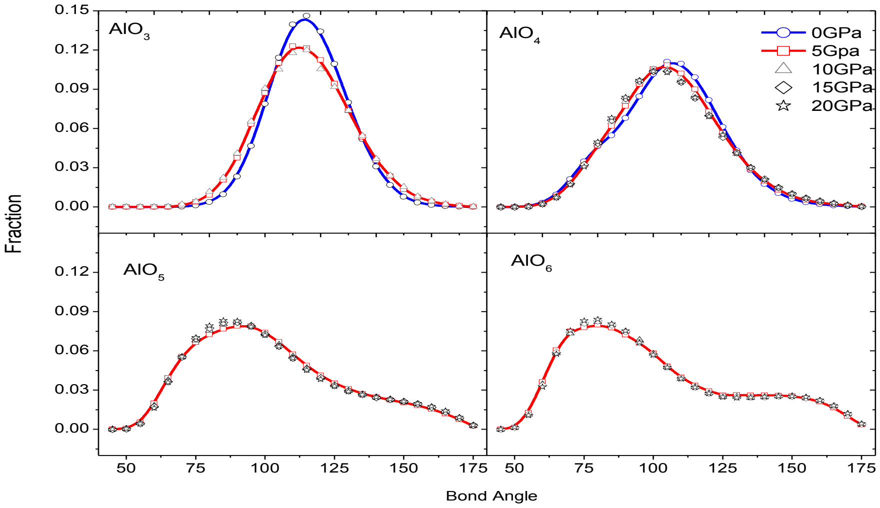

Fig 5. The distribution of partial bond angle in AlO_n units as a function of pressure.

3.2. Diffusion and dynamical heterogeneity

The diffusion coefficient of particles is determined via Einstein equation

$$D = \lim_{t\to\infty} \frac{< R(t)^2 >}{6t} \quad (1)$$

Where $t=N.T_{MD}$; N is number of MD steps; MD steps (T_{MD}) is equal to 0.478 fs,. The pressure dependence of self-diffusion and the anomalous behavior for all atoms (Si, O, and Al) diffusivity is presented in Table 2.

Table 2. The self diffusion coefficient of Si, O and Al atom at diffirent pressure.

Model (GPa)	D_{Si} x 10^{-6}cm^2/s	D_O x 10^{-6}cm^2/s	D_{Al} x 10^{-6}cm^2/s
0	0.12297	0.22389	0.36871
5	0.84521	1.1096	1.2536
10	1.4591	1.953	1.9321
15	1.2443	1.8556	1.5367
20	1.1438	1.6654	1.3641

There is a pronounced maximum at pressure around 10 GPa. In the 0÷10 GPa, the self-diffusion coefficient increases with increasing pressure meanwhile the self-diffusion coefficient decreases with pressure at 10÷20 GPa. Moreover diffusivity of aluminum is noticeably faster than both oxygen and silicon diffusivity ($D_{Al} > D_O > D_{Si}$) in 0–10 GPa pressure range. But diffusivity of oxgen is faster than aluminum and Silic ($D_O > D_{Al} > D_{Si}$) in 0–20 GPa pressure range.

As mention above, the structure of AS2 liquid consists of the structural units TO_x (T= Si, Al; x = 3÷ 6), which are connected to each other by common bridging oxygen atoms and form a spatial network structure. So, the anomalous behavior of atom is performed via transition of the structural units $TO_x \rightarrow TO_{x\pm1}$. At low pressure, Al atoms incorporate into Si–O network via non bridging oxygens. The Al–O bond is weaker in comparison to Si–O bond so that Al is more mobile than Si [18]. This leads to the bond easy to break into AlO_3 units and SiO_4 units. The T–O bonds in the units are very stable; therefore the diffusion is mainly via cooperative motion of TO_n units (whole TO_n moves as a particle). The AlO_2 and AlO_3 units have small size, and they are more mobile than SiO_4. Therefore $D_{Al} > D_O > D_{Si}$. The case of high pressure, the fraction of TO_5 units in liquid AS_2 increases; these TO5 units are defected units and not stable. The TO_5 units are easy to break into TO_4 units and free O. There is an increase in the mobility of both T and O atoms and the free O is more mobile than TO_n. So, diffusivity of oxgen is faster than aluminum and Silic ($D_O > D_{Al} > D_{Si}$). This result is clear evidence of the change in diffusion mechanism between low and high-pressure samples.

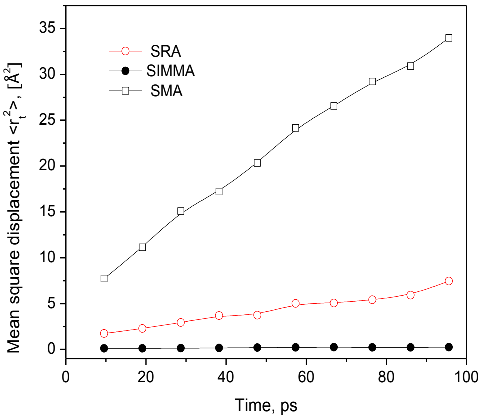

Fig.6. The time dependence of $<r_t^2>$ for the subset of random (SRA), immobile (SIMMA) and mobile (SMA) oxygen atom at ambient pressure.

AS2 liquids exhibit the DH. To clarify the original DH, we calculate time dependence of mean square displacement $<r_t^2>$ for the subset of random (SRA), immobile (SIMMA) and mobile (SMA) oxygen atom at ambient pressure (Fig 6). The mobile oxygen displaces in average over a distance (5.83 Å) is bigger than the immobile oxygen (0.49 Å). We find that N_{LKCL}, $< N_{LK} >$ quantities for immobile and mobile oxygen significantly differ from that for random oxygen (Fig 7, 8). In particular, $<N_{LK}>$ for SRA is smaller than one for SIMMA (or SMA) meanwhile N_{LKCL} *is* larger. Thus, the existence of DH for oxygen atoms has been revealed. Furthermore DH is observed for aluminum and silicon subnet. The $<N_{LK}>$ and N_{LKCL} of aluminum (or silicon) for SRA is smaller and larger than one for SIMMA (SMA), respectively. These results support that in system the mobile and immobile atoms tend to locate in separate regions where the mobility of particles is fast or slow. These regions are called mobile and immobile region and liquid AS2 consists of separate mobile and immobile regions

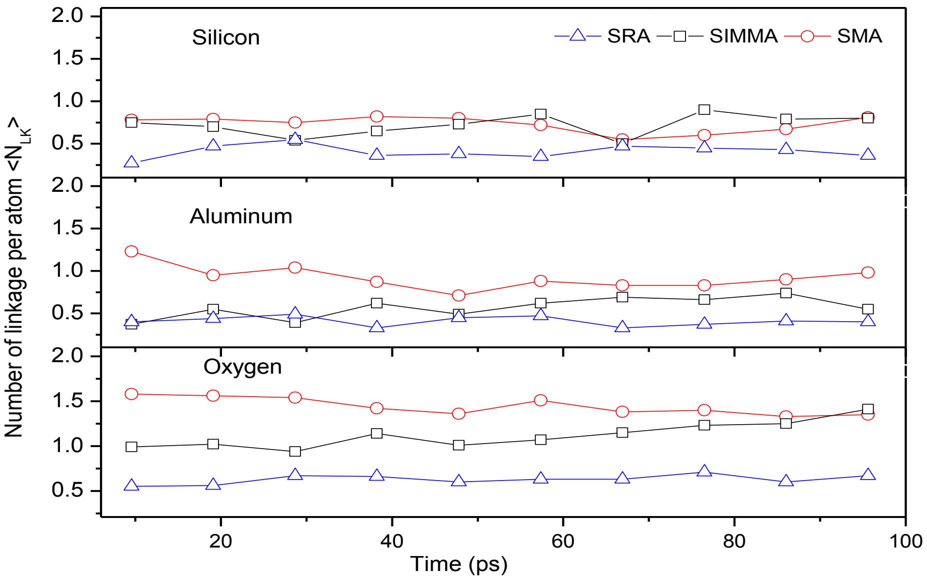

Fig.7 The time dependence of <N_{LK}> for the subset of random (SRA), immobile (SIMMA) and mobile (SMA) at ambient pressure.

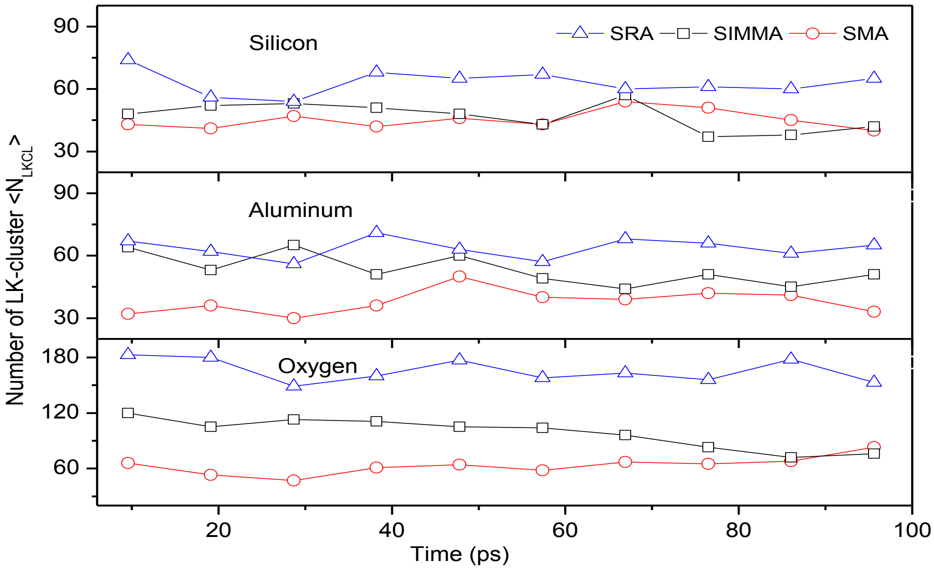

Fig 8. The time dependence of <N_{LKCL}> for the subset of random (SRA), immobile (SIMMA) and mobile (SMA) at ambient pressure.

4. Conclusions

The structure and dynamical properties in high and low pressure AS2 liquids are studied by mean of molecular dynamic simulation. The structure of AS2 liquid consists of the structural units TO_x (T= Si, Al; x = 3÷ 6), which are connected to each other by common bridging oxygen atoms and form a spatial network structure. As increasing pressure, there is a transformation from four-fold coordination (TO_4) to five and six-fold coordination (TO_5 and TO_6). The distribution of partial bond angle in SiO_n

units is independent on pressure meanwhile the distribution of O–Al–O bond angle in AlO_x (x=3,4,5,6) units as a function of pressure. The existence of DH in AS2 liquid at low-pressure configuration is observed. The liquid comprises separate mobile and immobile regions of atoms where the mobility of atom is extremely low or high. Furthermore the change in diffusion mechanism between low- and high-pressure samples is performed via transition of the structural units $TO_x \rightarrow TO_{x\pm1}$.

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