Molecular Dynamic Simulation of Large Model of Silica Liquid

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Abstract: We perform a molecular dynamics simulation to study the microstructure and dynamical properties in large silica model at liquid state. The models consisting of 19998 atoms were constructed under a wide range of pressure (0-20 GPa) and at 3500K temperature. Structural characteristics were clarified through the pair radial distribution function (PRDF), the distribution of SiO_x coordination units and network structure. The result shows that these liquids consist of identical units SiO_4, SiO_5 and SiO_6 and have common partial O—Si—O angle distribution. Furthermore, the major change in the diffusion mechanism under pressure is also considered and discussed.

Keywords: Molecular dynamics, structure, coordination units, diffusion, network structure.

1. Introduction

Silica and silicate minerals (mixture of SiO_2 and other metal oxides) play an important role in geosciences and technology. So, the complete knowledge of the structure and dynamical properties in silica and silicate under conditions of high pressure and temperature is quite necessary. The results of research studies will optimize the process of manufacturing new materials for intended use and controlling geological activities [1-4]. As we have known, the silicate glass- and melt-structures consists of SiO_4 tetrahedra linking to each other form continuous random tetrahedral-network in three-dimensional space [5-7]. In pure silica glass and melt, each SiO_4 tetrahedron connects to four other adjacent SiO_4 tetrahedra via bridging-oxygen (BO). The addition of other oxides (such as Na_2O, CaO, MgO or PbO…) into pure silica (SiO_2) disrupts the basic silica network by breaking part of the Si-O bonds, generating non-bridging oxygen (NBO). The percentage of NBOs in the system increases with the alkali content [8-9]. The detailed degree of mixing between Si-O network and metal ions as well as the distribution of BO and NBO species yields insights into the atomic scale structure that govern

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the mechanical-physical-chemical properties of silicate glass system. The degree of polymerization depends on the ratio between the number of bridging oxygen (BO) and SiO_4 tetrahedral units (the abundance of different $Q^{(n)}$ species, where Q represents the SiO_4 tetrahedron; n is the number of BO). The response of viscosity to pressure is found to be strikingly distinct between polymerized and simple liquid [10-11]. The degree of polymerization is also closely related to the diffusion of atoms in silicate. The neutron, X-ray diffraction (XRD) techniques, magic-angle spinning (MAS) nuclear magnetic resonance (NMR) [12-13] and simulation methods [14-15] have observed these phenomena. Liquid silica is a typical network forming system. Its structure consists of basic structural units SiO_x (x=4, 5, 6) and the SiO_4 units is dominant at low pressure. When the liquid is compressed to smaller volume, the units SiO_5 and SiO_6 become prevalent. Due to its network-forming ability, the liquid silica exhibits a number of peculiar properties, which have been observed in both simulation and experiment. Namely, the compressibility of liquid silica in the interval of pressure up to 10 GPa is substantially higher than that of quartz [16]. Moreover, anomalous behavior diffusion and spatially heterogeneous dynamics are also observed [17-18].

In our previous works, the micro-structure and dynamical properties in silica liquid also have been investigated via through the pair radial distribution function (PRDF), the distribution of SiO_x coordination units, the bond angle distribution and structure network. However, the research model has only 2000 atoms. To check the accuracy of previous research results and evaluate the effect of model size, we have conducted a SiO_2 model consisting of 19998 atoms by mean of molecular dynamic simulation. This is a large model and quite difficult to build it. We will investigate the structural characteristic and coefficient diffusion in silica liquid under different pressure, compare with the experimental results and simulations. Moreover, the major change in the diffusion mechanism under pressure is also considered and discussed.

2. Calculation

We have prepared the model which consists of 6666 Si and 13332 O by means of MD simulation. In this paper, we simulate silica liquid with the BKS potential. The integration is performed using a velocity-Verlet algorithm with time step of 1.0 fs. The integration is performed using a velocity-Verlet algorithm with time step of 1.0 fs. Initial configuration of MD silica liquid model is constructed by randomly in simulation box and heating up to 6000K to remove possible memory effects. Next, a long relaxation has been done in NPT ensemble (moles (N), pressure (P) and temperature (T) are constant) to produce a model at 3500K and upon ambient pressure. We obtain a sample at ambient pressure which is denoted to model M1. The model M1 has been compressed to different pressure (5, 10, 15, 20 GPa). In order to improve statistics, all quantities of considered structural data were calculated by averaging over the 5.000 configurations during the last simulation (10^5 MD steps). To observe the dynamical processes, two above models are relaxed in NVE ensemble (the system is isolated from changes in moles (N), volume (V) and energy (E)) for a long time (10^6 MD steps).

3. Results and discussion

3.1. Radial distribution function

Firstly, we examine the structural characteristics of constructed models. The Fig.1 presents the PRDF of Si–Si, Si–O and O-O at different compressions. It can be seen that the first peak all atomic pairs decreases in amplitude and becomes broader under compression. The position of the first peak of

Si–Si, and O–O pairs decreases meanwhile Si–O pairs, the position of the first peak of Si- O increases. Moreover, the shift of the first peak of $g_{Si-O}(r)$ is the least and this indicates that the short-range order of silica liquid is not sensitive to the compression at pressures ranging from 0 to 20 GPa. The detail result is showed in Table 1. The characteristic of the PRDF is in good agreement with the reported data in refs. [19,20]
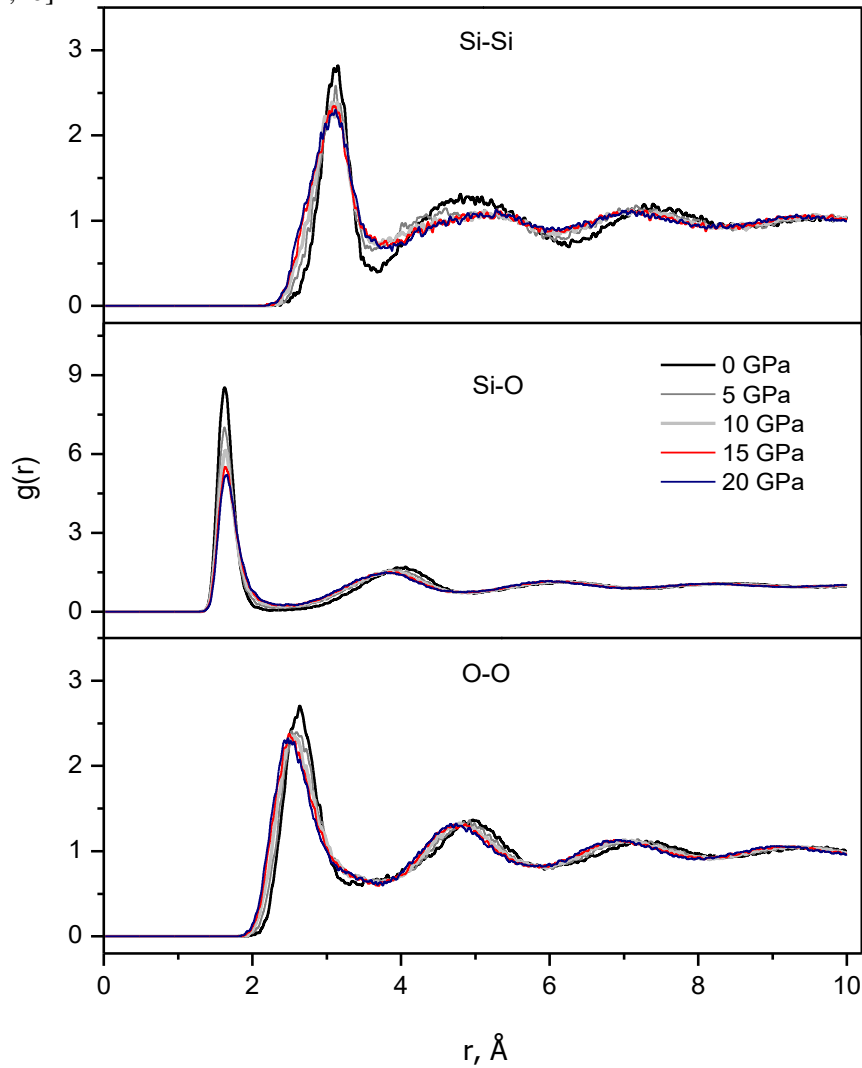

Fig 1. Radial distribution functions of Si−Si, Si−O, and O−O pairs at different pressures.

3.2. Coordination units

The structure of SiO_2 liquid consists of structural units SiO_x (x = 4, 5, 6) and OSi_y (y = 2,3). Figure 2 (a) distribution of coordination units SiO_4 in the model. In which, only coordination units SiO_4 are drawn, while the others are removed. Similarly, Figure 2 (b)–(c) shows the distributions of coordination units SiO_5, SiO_6. The detail dependence of the fraction of coordination units SiO_x and OSi_y on pressure was presented in Table 2.

Table 1. Structural characteristics of SiO$_2$ 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 [19,20]
r_{Si-Si}, [Å]	3.16	3.12	3.14	3.12	3.12	3.12
r_{Si-O}, [Å]	1.62	1.62	1.62	1.64	1.62	1.62
r_{O-O}, [Å]	2.64	2.52	2.56	2.5	2.48	2.65
g_{Si-Si}	2.86	2.67	2.45	2.37	2.35	-
g_{Si-O}	8.62	7.14	6.19	5.54	5.26	-
g_{O-O}	2.72	2.44	2.37	2.39	2.37	-

(a)
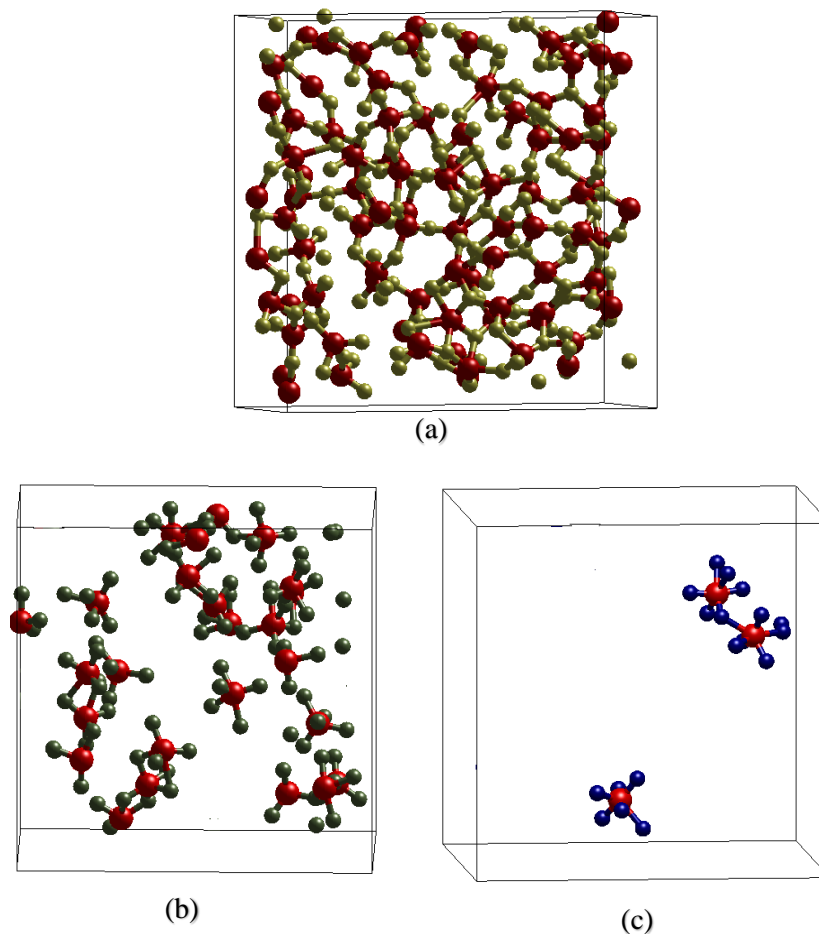

(b)   (c)

Fig 2. Snapshots of coordination unit distributions SiOx in model at ambient
pressure: (a) distribution of coordination units SiO$_4$, (b) distribution of
coordination units SiO$_5$, (c) distribution of coordination units SiO$_6$.

It has been seen that the number of SiO$_4$ and OSi$_2$ unit is domain at ambient. When increasing pressure, the fraction of SiO$_5$ and SiO$_6$ increases meanwhile fraction of OSi$_3$ and OSi$_2$ also increases. This demonstrates that a transition from SiO$_4$ to SiO$_5$ or SiO$_6$ should be accompanied by a transition

from OSi_2 to OSi_3. It means that increasing pressure, there is a transformation from four-fold coordination (SiO_4) to five- and six-fold coordination (SiO_5 and SiO_6).

Table 2. The percentage fraction of the coordination units in silica liquid at different pressure

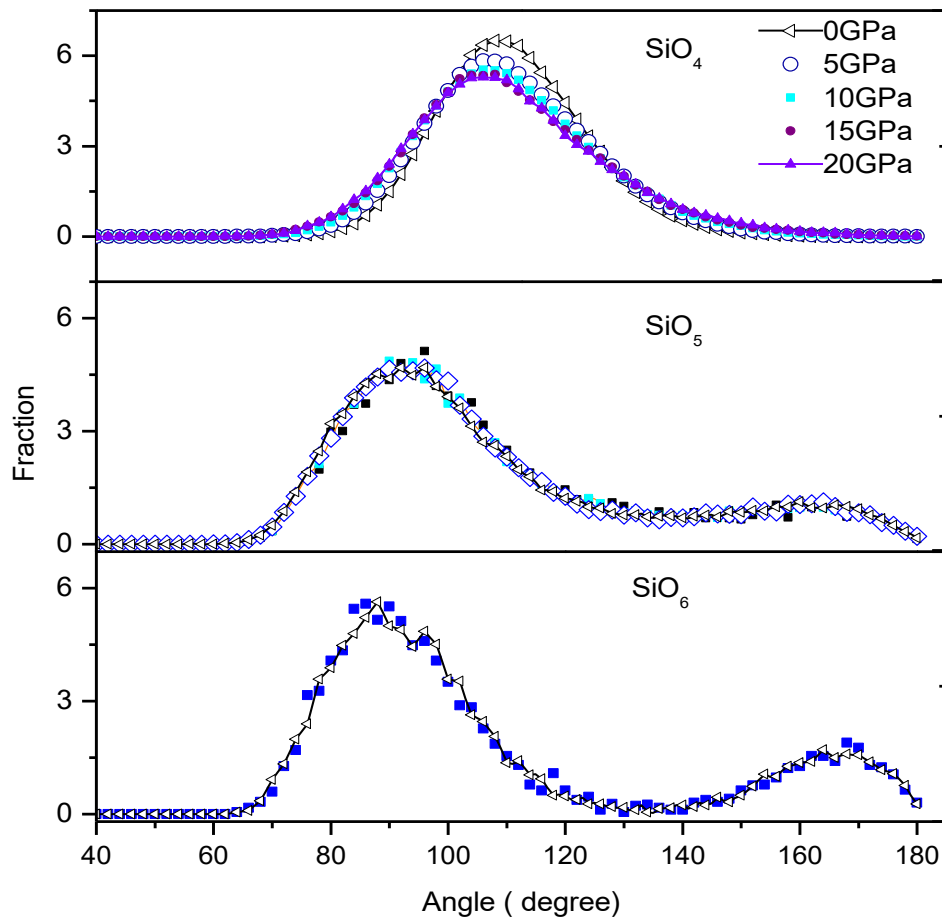| Model	0GPa	5 GPa	10 GPa	15 GPa	20 GPa
SiO_4	93.94	77.26	59.89	44.89	35.69
SiO_5	3.90	19.34	34.65	45.66	50.13
SiO_6	0.03	0.79	3.51	8.14	12.77
OSi_2	95.72	86.26	75.53	66.01	59.95
OSi_3	4.28	13.74	24.47	33.99	40.05

Fig. 3. Partial bond angle distributions for structural units SiO_x (x = 4, 5, 6) at different pressures.

To investigate the short-range order, the O−Si−O bond angle and Si−O bond length distribution in the coordination units SiO_x (main coordination units) have been calculated. Figure 3 presents the partial bond angle distributions for structural units SiO_x (x = 4, 5, 6) at different pressures. The results show that the partial O-Si−O bond angle distribution in each kind of coordination unit SiO_x is almost the same for different pressure. This means that the distribution of partial bond angle in SiO_4, SiO_5, and SiO_6 units is not dependent on pressure. 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. This result is similar to experimental and other simulated data reported in [19, 21] and indicates a slightly distorted tetrahedron with a Si atom at the center and four O atoms at the vertices. In the case of angle distribution in SiO_6, there are two peaks: a main peak locates at 90° and small one at 165°. The partial Si−O bond length distribution in coordination units SiO_4, SiO_5, and SiO_6 is shown in Fig. 4. It shows that The Si – O bond length distributions in SiO_4, SiO_5, and SiO_6 units have peaks at 1.62, 1.64, and 1.74 Å, respectively. This structural characteristic has been explained via the Coulomb repulsive force between anion and anion (O^{-2} and O^{-2} ions).The force in SiO_5 and SiO_6 units is much stronger than the one in SiO_4. This leads an increase of Si–O bond length in SiO_5 and SiO_6.
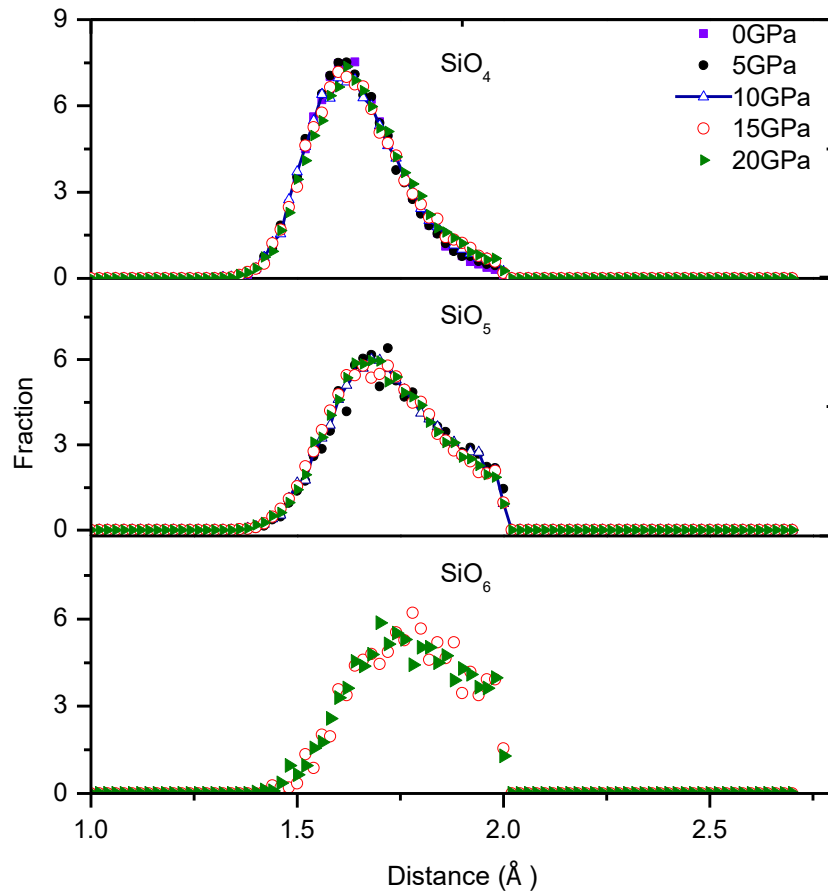

Fig 4. The Si−O bond length distributions for structural units SiO_x (x = 4, 5, 6) at different pressures.

The diffusion process in silica under compression

The diffusion coefficient of particles is determined from the mean square displacement (MSD) of atom via Einstein equation

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

Where $t = N.T_{MD}$; N is number of MD steps; T_{MD} is MD steps and equal 1.0 fs, The Fig 5 describes the time dependence of Silicon (or Oxygen) MSD under different pressure. One can see that the data fall on straight- line plot. We have calculated coefficient diffusion from the slope of these lines.
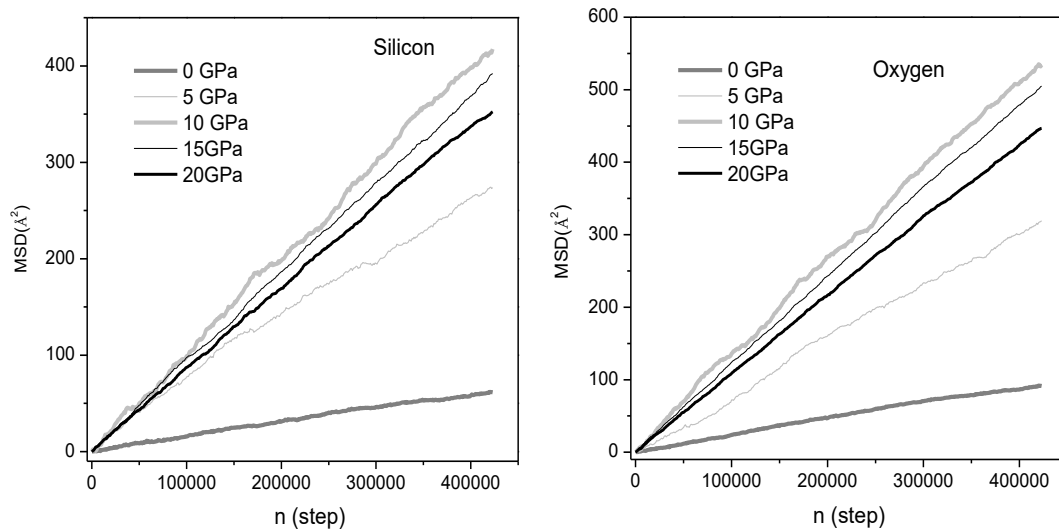

Fig 5. The step dependence of mean square displacement in silica liquid at different pressure.

The anomalous diffusion is observed via Fig.6. It can be seen that there is a monotonous growth of coefficient diffusion with upon compression and a maximum point near P=10 GPa that consistent with previous simulation [22-23]. The self-diffusion coefficient increases with increasing pressure (0÷ 10 GPa) meanwhile the self-diffusion coefficient decreases with pressure at 10÷20 GPa. We find that the change in diffusion mechanism between low and high-pressure in silica liquid. The change in diffusion mechanism can be explained by that upon compression the SiO_4 unit transforms to SiO_5 and SiO_6 where the Si–O bond is much weaker. This leads an increase in mobility of Si and O atoms. On the other hand the liquid becomes much denser under pressure and diffusion process more difficult. One can see that the bond weakening and the liquid densification affect the diffusion coefficient in opposite directions. At the low-pressure configuration, the influence of the bond weakening of Si, O in the newly formed structure units SiO_5 and SiO_6 is larger than that of liquid densification. Therefore, the coefficient diffusion increases. However, at the high-pressure configuration, rate of transition from SiO_4 to SiO_5 or SiO_6 decreases and effect of liquid densification predominate. The coefficient diffusion decreases and Fig.6 has a maximum point.
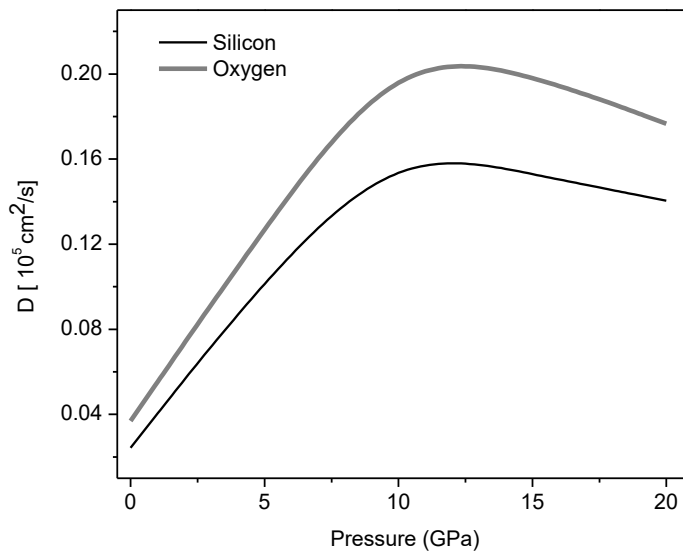
Fig 6. The pressure dependence of diffusion coefficient of silicon and oxygen in silica liquid.

4. Conclusion

In this work, microstructure and dynamic properties of large model of silica liquid at pressures ranging from 0 to 20 GPa were investigated in detail. Results reveal that the structure of SiO_2 liquid consists of structural units SiO_x (x = 4, 5, 6) and OSi_y (y = 2,3). At ambient, the number of SiO_4 and OSi_2 unit is domain. Upon compression, the fraction of SiO_5 and SiO_6 increases meanwhile fraction of OSi_3 and OSi_2 also increases. The distribution of partial bond angle and bond length in SiO_4, SiO_5, and SiO_6 units is not dependent on pressure. The cation–cation, anion–anion Coulomb repulsion is the origin of the increase of the mean Si-O bond length under compression. Furthermore, the diffusion in silica liquid shows anomalous behavior and the origin of anomalous diffusivity is due to the change of SiO_5 and SiO_6 concentration under compression. These results are similar to our previous simulation. These demonstrate that the model silica liquid consisting of 2000 atoms was good enough for us to study structural properties and diffusion. However, the large model will help us further study the original of dynamical heterogeneity that is difficult with the small model (2000 atoms).

Acknowledgement

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