

THE SPATIAL HETEROGENEITY AND ANOMALOUS DIFFUSIVITY IN SILICA LIQUID

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ABSTRACT

The dynamic properties of liquid silica (SiO_2) are studied by molecular dynamics simulation. We trace the evolution of coordination units SiO_x ($x = 4, 5, 6$) in network structure of liquid SiO_2 over the simulation time and in the 0-25 GPa pressure range. The result simulation reveals that atomic diffusion is realized through the transition $\text{Si}_x^{[n]} \rightarrow \text{Si}_x^{[n+1]}$ ($\text{Si}^{[n]}$) and the instability of units SiO_5 is the cause of the anomalous diffusivity. As pressure increases, the diffusion coefficient increases and reaches maximum around 12 GPa. Moreover, the transitions are not uniformly distributed through the network structure, but strongly localize in the space. The distribution of coordination units SiO_x in network structure is not uniform but trends to form clusters of SiO_4 , SiO_5 and SiO_6 and this is the origin of localization of transitions resulted in the spatially heterogeneous dynamics in liquid SiO_2 .

I- INTRODUCTION

Liquid silica (SiO_2) is the typical glass-forming liquid. Due to its importance, silica has been studied extensively for many decades. However, many fundamental aspects of its atomic level structural dynamics and diffusion mechanism remain in debate [1-6]. Specially, anomalous behavior (a range of pressure exists for which the diffusivity increases and viscosity decreases upon compression) and spatially heterogeneous dynamics are also observed in kinetic phenomena [1]. Numerous approaches have been employed and several theories have been invoked to interpret the dynamical properties (diffusion mechanism, spatially heterogeneous dynamics). The Adam-Gibbs theory [2] is able to establish a connection between dynamics and thermodynamics, and to rationalize the Vogel-Fulcher law but the validity of the assumptions is still in debate. Another theory that views the glass transition as a process of density fluctuations is Mode Coupling Theory (MCT) [3-4]. The MCT well describes many aspects of supercooled liquids. However the prediction of T_{MCT} at which the dynamical arrest occurs and the system becomes glass, which is higher than the experimental T_g . Stillinger and others [5-6] proposed the concept of an inherent structure base on the Goldstein's idea (free energy landscape). The inherent structure formalism is able to interpret many observations of liquids and glasses, but it has not yet elucidated the physical mechanism that is responsible for slowing down of supercooled liquids.

In this work, we present the simulation results of liquid silica in the 0-25 GPa pressure range. We calculate and analyze the structural, dynamical properties and diffusion

mechanism. Specially, a new approach has been applied to calculate the diffusion coefficient. The diffusion coefficient of Si in liquid SiO_2 is calculated by two methods and is compared to each other to clarify diffusion mechanism. Besides, phenomena of spatially heterogeneous dynamics, anomalous diffusivity and their origin in the relation with structure are also discussed here.

II - COMPUTATIONAL PROCEDURE

The MD simulation of liquid SiO_2 is carried out in a 1998-atom system with periodic boundary conditions using Beest-Kramer-Santen (BKS) potentials. The detail about these potentials can be found elsewhere [9]. The BKS potential has unphysical features that the interaction energy of Si and O diverges to $-\infty$ as their separation goes to zero. Hence we have added a short range term in order to prevent this, but which does not alter the form of BKS potential at large separation. We use the Verlet algorithm to integrate the equation of motion with MD step of 4.77 fs. Initial configuration is obtained by randomly placing all atoms in a simulation box. This sample is equilibrated at temperature of 6000 K and then cooled down to the temperature of 3000 K. A consequent long relaxation has been done in the ensemble NPT (constant temperature and pressure) to obtain a sample at ambient pressure which is denoted to model M1. The model M1 has been compressed to different pressures and then relaxed for a long time to reach the equilibrium. By this way, five models (M2, M3, M4, M5 and M6) compressed to 5, 10, 15, 20 and 25 GPa are constructed. To study the dynamical properties the obtained models are relaxed in ensemble NVE. In order to improve the statistics the measured quantities such as the coordination number, bond angle distribution and partial radial distribution function (PRDF) are computed by averaging over 1000 configurations separated by 10 MD steps.

III- RESULTS AND DISCUSSION

III.1. Structural properties

Firstly, to assure the reliability of constructed models, we have investigated the structural characteristics of constructed models such as PRDFs, coordination number distribution. Figure 1 shows that, the first peak of the PRDF $g_{\text{Si-O}}(r)$ decreases in amplitude but its position is almost unchanged. This shows that the Si-O bond length is almost not depended on compression and it also demonstrates that short-range order of liquid SiO_2 is not sensitive to compression. For the PRDF $g_{\text{Si-Si}}(r)$, the first peak is decreases in amplitude and becomes broader with compression but its position does not depend on compression. The other peaks depend strongly on compression (both in the position and amplitude). For the PRDF $g_{\text{O-O}}(r)$, the amplitude of the first peak decreases strongly as pressure increases from 0 to 15 GPa. At pressure beyond 15 GPa, the first peak of PRDF $g_{\text{O-O}}(r)$ is almost unchanged in amplitude. The position of peaks for $g_{\text{O-O}}(r)$ systematically shifts to a smaller distance as the compression increases. The peaks of PRDFs $g_{\text{Si-Si}}(r)$ and $g_{\text{O-O}}(r)$ relate to the intermediate-range order. The change of these peaks under compression shows that intermediate-range order is very sensitive to the compression. The characteristic of PRDFs is in good agreement with previous calculations [7, 10]. Figure 2 shows the pressure dependence of fraction of coordination units SiO_x and OSi_y . It can see that, in the 0-25 GPa pressure range, the fraction of units OSi_4 is very small (less than 5 %). At ambient pressure the coordination units SiO_4 are dominant

(over 96%) in comparison with the coordination units SiO_5 and SiO_6 (total about 4%), indicating a tetrahedral network structure. As pressure increases, the liquid transforms from a tetrahedral to octahedral network structure (at 25 GPa, most of coordination units are SiO_6). This result is in good agreement with calculated results in the works [7, 8, 10]. From figure 2, we can see that under compression, the fraction of SiO_5 and SiO_6 increases then fraction of OSi_3 and OSi_4 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 or OSi_4 .

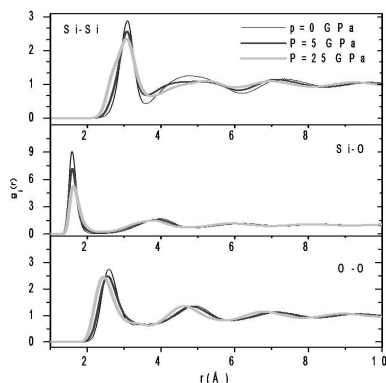


Fig.1. Radial distribution functions of Si-Si, Si-O and O-O pairs at different pressures.

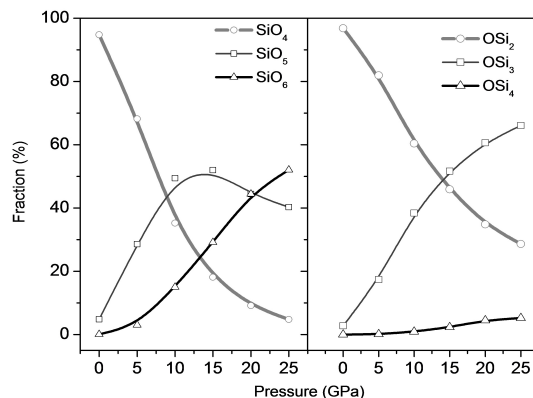


Fig.2. Distribution of coordination units SiO_x (left) and OSi_y (right) as a function of pressure.

III.2. Diffusion mechanism

To clarify the dynamical properties and diffusion mechanism at atomic level, we examine the evolution of network units SiO_x ($x = 4, 5$ and 6) over different time. Figure 3 shows the pressure dependence of lifetime of coordination units SiO_x . It can be seen that, as increasing pressure the average lifetime of units SiO_4 decreases strongly. The average lifetime of coordination units SiO_5 increases from about 120 MD steps (at ambient pressure) to 150 MD steps (at 10 GPa), then decrease down to 100 MD step (at 25 GPa). The lifetime of coordination units SiO_6 monotonously increases from about 70 MD steps (at ambient pressure) to 160 MD steps (at 25 GPa). As increasing pressure, the liquid SiO_2 transforms gradually from tetrahedral network structure to octahedral network structure [8]. Because of having network structure, the diffusivity of Si and O atoms in liquid SiO_2 is impossible unless there is exchange of coordinated oxygen atoms amongst units SiO_x . Figure 4 demonstrates the diffusion mechanism by exchanging of coordinated oxygen atoms. The process of the nearest-neighbor exchange (in sequence: $a \rightarrow b \rightarrow c \rightarrow d$) leads to diffusion, the other process (in sequence: $a \rightarrow b \rightarrow e \rightarrow f$) does not lead to diffusion. From figure 4, it can be seen that the process consists of 4 transition stages, two with $\text{SiO}_4 \rightarrow \text{SiO}_5$ (Fig. 4a \rightarrow Fig. 4c and Fig. 4d \rightarrow Fig. 4e, here Fig. 4b is the transition between Fig. 4a and Fig. 4c) and two with $\text{SiO}_5 \rightarrow \text{SiO}_4$ (Fig. 4c \rightarrow Fig. 4d and Fig. 4e \rightarrow Fig. 4f). Note that the stage in figure 4a is similar to one in figure 6f where both contain one Si

atom and four O atoms 2, 3, 4 and 5. The stage in figure 4c and figure 4e is similar to each other. Hence, only 3 stages (Fig. 4a, Fig. 4c, and Fig. 4d) are different. We call these stages “non-repeated stage” (N_{N-stg}) and N_{stg} be the number of all stages. N_{tr} and N_{nr-tr} are the number of transition and non-repeated transition, respectively. Figure 5 shows the time dependence of the number of transitions and non-repeated transitions at different pressures. We can determine the rate of transition and non-repeated transition.

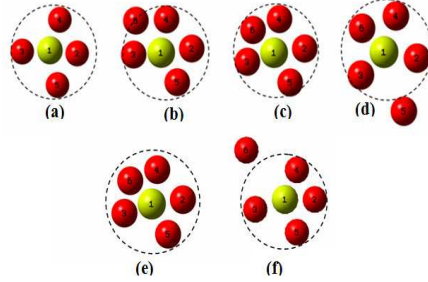


Fig.4. Demonstration of diffusion mechanism in liquid SiO₂.

Table 1 shows the values of the rate of transition and non-repeated transition (v_{tr} and v_{nr-tr}) at different pressures. It can see that the rate of transition monotonously increases as pressure increases. In contrast, as increasing pressure, the rate of non-repeated transition increases and get maximum value at 20 GPa afterward it decreases.

Table 1. The dynamical characteristics of liquid SiO ₂ under compression: v_{tr} and v_{nr-tr} is the rate of transition and non-repeated transition number; D_{tr} is calculated by equation (2).						
P (GPa)	0	5	10	15	20	25
v_{tr}	0.91	3.05	4.51	5.21	5.55	5.59
v_{nr-tr}	0.15	0.65	1.13	1.31	1.37	1.15
D_{tr} (Å ² / one transition)	0.0118	0.0254	0.0312	0.0235	0.0177	0.008

Conventionally, diffusion coefficient of atoms is determined via Einstein equation:

$$D = \lim_{t \rightarrow \infty} \frac{\langle r(t)^2 \rangle}{6t}, \quad (1)$$

where $\langle r(t)^2 \rangle$ is mean square displacement (MSD) over time t . If we define:

$$D_{tr} = \lim_{m_{tr} \rightarrow \infty} \frac{\langle r(t)^2 \rangle}{m_{tr}} \quad (2)$$

The equation (1) can be reduced to

$$D = \lim_{m_{tr} \rightarrow \infty} \frac{\langle r(t)^2 \rangle}{6m_{tr}} \lim_{t \rightarrow \infty} \frac{m_{tr}}{t} = \frac{D_{tr} v_{tr}}{6 \cdot \Delta t} \quad (3)$$

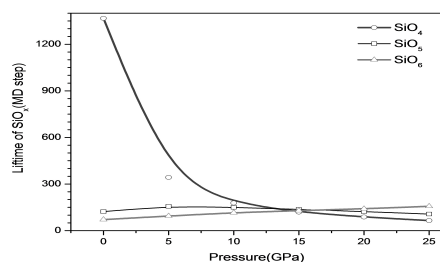


Fig.3. The pressure dependence of lifetime of coordination units (MD step)

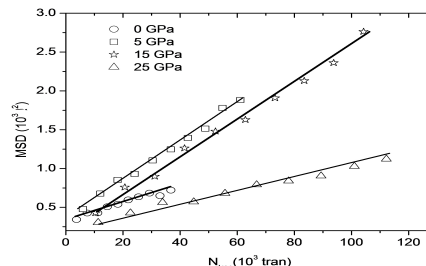


Fig.6. The dependence of mean square displacement on the number of transitions

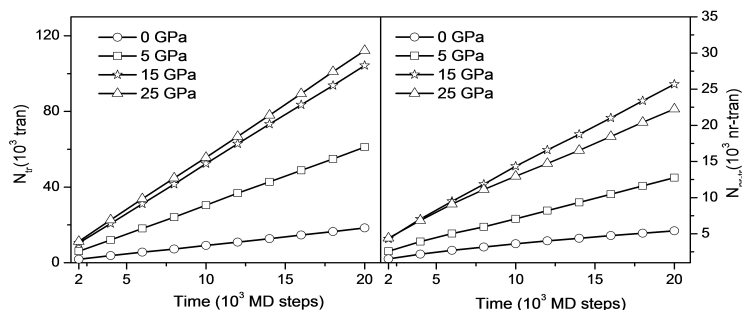


Fig.5. The dependence of the number transition (N_{tr}) and the number of non-repeated transition (N_{nr-tr}) as a function of time

Figure 6 shows the dependence of MSD on the number of transitions at different pressures. It is clearly that, the MSD is also linear with the number of transition. The MSD is linear with both time and the number of transitions. This demonstrates that the diffusion mechanism is realized by the exchange of nearest-neighbor atoms amongst coordination units. From the Figure 6 we can calculate the diffusion coefficient D_{tr} by equation (2). The value of D_{tr} at different pressures is presented in table 7. Figure 7 shows the pressure dependence of diffusion coefficient D calculated by two methods. It can see that the diffusion coefficient calculated by new approach (equation (3)) is in good agreement with the one that is calculated by conventional method (Einstein equation).

Figure 7 also reveals the anomalous behavior of diffusion in liquid silica. As pressure increases, the diffusion coefficient increases and reaches maximum at around 12 GPa. The anomalous behavior of diffusion in liquid silica can interpret as follows: 1) In the 0-10 GPa pressure range, the network structure of liquid SiO_2 mainly consists of the coordination units SiO_4 and SiO_5 (see figure 2). As pressure increases from 0 to 10 GPa, the lifetime of SiO_4 decreases strongly but the lifetime of SiO_5 increases very little (see figure 5). Consequently, the diffusion increases as pressure increases. 2) In the 10-15 GPa pressure range, the network structure consist of units SiO_4 , SiO_5 and SiO_6 (mainly units SiO_5). As

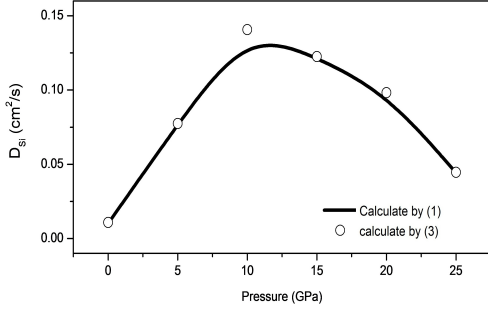


Fig. 7. The pressure dependence of diffusion coefficient is calculated by two methods.

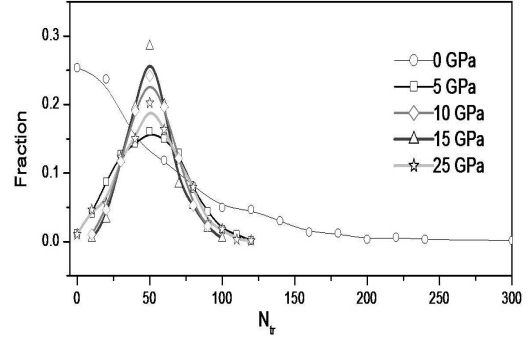


Fig. 8. The distribution of transitions for 20000 MD step.

pressure increases, the average lifetime of units SiO_5 is almost unchanged. Meanwhile the average lifetime of units SiO_4 is decreases and the average lifetime of units SiO_6 increases very little. Consequently, as pressure increases, the diffusion decreases very little. 3) In the 15-25 GPa pressure range, the network structure mainly consists of units SiO_5 and SiO_6 (mainly units SiO_6). As pressure increases, the average lifetime of units SiO_6 increases meanwhile the lifetime of SiO_5 decreases very little and consequently the diffusion decreases. The diffusion mechanism in liquid silica is realized by exchanging the nearest-neighbor atoms amongst coordination units (transition $\text{Si}^{[n]} \leftrightarrow \text{Si}^{[n+1]}$). Figure 8 shows the distribution of transitions for 20000 MD steps at different pressures. It reveals that at ambient pressure (0 GPa), the distribution has the non-Gaussian form. The number of transitions per an atom distributes in a wide range (from 0 to 300 transitions). Conversely, at higher pressures (5, 15 and 25 GPa), the distributions have the Gaussian form with the peak at 50 transitions. These distributions are the evidence of the spatially heterogeneous dynamics. From the distribution, it is clearly that there are coordination units that have the number of transitions very high. Conversely there are units that have the number of transitions very low. In the space, where one contains coordination units with the number of transitions higher than the average value, then the atoms at that location have higher mobility and vice versa. In other word, the mobile atoms are sparse and dynamics are spatially heterogeneous. Mobile atoms assist their neighbors to become more mobile. This is dynamic facilitation and form mobile areas where there are atoms with high mobility. It evidences that the dynamics is spatially heterogeneous.

IV. CONCLUSIONS

The microstructure, structural dynamics and diffusion mechanism in liquid SiO_2 have studied by mean of molecular dynamic simulation. We trace the evolution of coordination units SiO_x ($x = 4, 5, 6$) in network structure of liquid SiO_2 over the simulation time and in the 0-25 GPa pressure range. Simulation results have shown that each atom undergoes a series of stages where the coordination SiO_x that it belongs to is unchanged. The lifetime of coordination units is strongly depend on pressure and varies from one to other units. The MSD is linear to the number of transitions. The atomic diffusion in liquid SiO_2 is realized through the transitions $\text{Si}^{[n]} \leftrightarrow \text{Si}^{[n+1]}$. Diffusion coefficient in liquid

SiO_2 depends strongly on the lifetime of coordination units SiO_x (the rate of transition $\text{Si}_{\leftrightarrow}^{[n]} \text{Si}^{[n+1]}$). The atomic diffusion in liquid SiO_2 exhibits anomalous behavior. As pressure increases, the diffusion coefficient increases and reaches maximum around 12 GPa. The instability of coordination units SiO_5 is the origin of anomalous diffusivity. At ambient pressure, the distribution of transitions over atoms has the non-Gaussian form. Conversely, at higher pressure, the distribution has the Gaussian form. Distributions of atomic displacement have asymmetric-Gaussian form and strongly depend on compression. The distribution of coordination units is not uniform but it trends to form clusters of SiO_4 , SiO_5 and SiO_6 . The atoms belong to cluster of SiO_5 is more mobile than other one. This results in spatially heterogeneous dynamics.

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