Dynamics and mechanism diffusion in silica liquid: Insight from simulation

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Abstract. In this paper, we numerically study the diffusion mechanism at atomic level in silica liquid via molecular dynamics simulation. The model consisting of 1998 particles and using the BKS potential has been constructed at the temperature from 2600 to 4500 K. Furthermore, we track the evolution of network units with x=4, 5 and 6 over different time. The simulation shows that the diffusivity depends strongly not only on the rate of the exchanging the coordinated oxygens, but also on the correlation effect. This effect is caused by the specific distribution of the exchanging coordinated oxygens (ECO) through the space which leads to spatially heterogeneous dynamics in the liquid. Analyzing the temperature dependence of the correlation coefficient *F* we found that the slowdown in dynamics near glass transition point is ascribed from percolation of the domains where high frequent exchanging coordinated oxygens occurs.

1. Introduction

   Dynamics in network-forming liquids have been intensively studied by both experiment and computer simulation, but our understanding about many their aspects are so far no complete [1-4]. In particular, the spatially dynamic heterogeneity (DH) and anomalous slowdown near glass transition is still debated during many decades [5-6]. In the dynamical heterogeneous system, all particles can be divided into mobile and immobile subsets. These subsets move collectively in space over time [7-8]. Experimentally, DH has been well established for certain liquids such as the Dzugutov liquid [9], polymer melts [10-11]. For silica due to high melting temperature DH is difficult to be detected by experiment, so it is only studied by simulation. Furthermore, when temperature is decreased toward the glass transition, the structure of these liquids appear to change subtly but dynamical properties e.g. the structural relaxation time, the diffusion constant, and the viscosity increase by orders of magnitudes [12-14]. Numerous studies [6-7, 12-15] have attempted to clarify the mentioned problem. Microscopic model of super-cooled liquids involves two important points: i) the particle mobility is a

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result of dynamic facility, i.e. mobile particles assist their neighbors to become mobile; ii) particle mobility is sparse and dynamics are spatially heterogeneous at times intermediate between ballistic and diffusive motion [14]. The mode coupling theory [15] well describes many aspects of dynamic behavior at high temperature, but it predicts the power-law divergence of relaxation time at critical temperature $T_{MCT} > T_g$ (glass transition temperature).

In this study, MD simulation is conducted to examine the dynamics in silica liquid. Our purpose is to clarify the structural dynamics occurred in this material which cause the diffusion anomaly and DH. Furthermore, anomalous slowdown in network-forming liquids was also discussed. This paper is organized as follows: First, in section 1 we give an overview of the problem of search in. The section 2 presents simulation technique. In section 3, the diffusion mechanism and two factors which contribute to the dynamical slowdown are discussed. The last section, we summarize the results and give conclusions.

2. Computational procedure

MD simulation is carried out on silica models consisting of 1998 atoms (666 silicon and 1332 oxygen atoms). The simulation has been performed in a cubic cell where the periodic boundary conditions were applied. We use the BKS potentials and generate an initial configuration by randomly placing all atoms in a simulation box. The equation of motion is integrated using the Verlet algorithm with a time step of 0.46 fs. Then the obtained sample is heated up to 5000 K in order to remove possible memory effects. After that the sample is cooled down to desired temperature. Finally, a consequent long relaxation has been done in ensemble NPT (constant temperature and pressure) by 10^5 MD steps to obtain the equilibrium sample. To study dynamical properties the obtained samples are relaxed in ensemble NVE (constant volume and energy) over 4.10^5 steps. More detail about the method for preparing silica liquid model can be found elsewhere [16]. By this way, five models at ambient pressure and at temperatures of 2600, 3000, 3500, 4000 and 4500 K have been constructed.
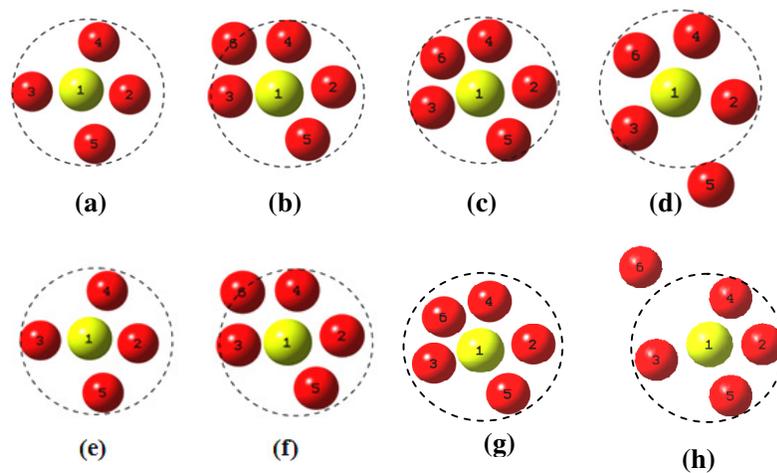
Fig.1. The transition $Si^4 \rightarrow Si^5 \rightarrow Si^4$ and the exchanging of coordinated atom in unit SiO_4;

Silica liquid at ambient pressure consists of units SiO_x which form a spatial network structure. Obviously, the diffusivity of silicon in such system is impossible if no exchanging the coordinated oxygen in SiO_x occurs. Fig. 1 illustrates as an example the exchanging coordinated oxygen in network unit SiO_4. As shown in Fig.1 (a-d) there are three stages: At first stage (SiO_4) consists of one Si atom numbered to 1, four oxygen atoms labelled to 2, 3, 4, 5; second one (SiO_5) has oxygen atoms 2, 3, 4, 5, 6; and final stage (SiO_4) contains 2, 3, 4, 6. As a result, the oxygen 5 in former SiO_4 is exchanged by oxygen 6. Here we also see two transitions: SiO_4 into SiO_5 and SiO_5 into SiO_4. In Fig.1 (e-h) we also display two other transitions: $SiO_4{\rightarrow}SiO_5$ and $SiO_5{\rightarrow}SiO_4$. Unlike first case the former SiO_4 remains unchanged, i.e. the coordinated oxygens are 2, 3, 4 and 5. This implies that only part of $SiO_x{\rightarrow} SiO_{x\pm1}$ leads to exchanging the coordinated oxygen (ECO) and hence we can classify all $SiO_x{\rightarrow} SiO_{x\pm1}$ into two types: first type is shown in Fig.1 (a-d) and second one in Fig.1 (e-h). Let M_{exch}, M_{trans} be the number of ECO and number of $SiO_x{\rightarrow} SiO_{x\pm1}$, respectively; hence $M_{exch}<M_{trans}$.

The diffusion coefficient of particles in MD simulation usually is determined via Einstein equation

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

Where $<R(t)^2>$ is mean square displacement (MDS) over time t. If we define

$$d_{trans} = \lim_{m_{trans} \to \infty} \frac{<R(t)^2>}{M_{trans}} \qquad (2)$$

The equation (1) can be reduced to

$$D = \lim_{m_{trans} \to \infty} \frac{<R(t)^2>}{6M_{trans}} \lim_{t \to \infty} \frac{M_{trans}}{t} = \frac{d_{trans}V_{trans}}{6T_{MD}} \qquad (3)$$

We estimate the dynamics slowdown in the considered temperature range given as

$$N_{sld}(T) = \frac{D(T)}{D(4500)} = \frac{V_{trans}(T)}{V_{trans}(4500)} \frac{d_{trans}(T)}{d_{trans}(4500)} = V_{transR}(T)F(T) \qquad (4)$$

Where $t=N.T_{MD}$; N is number of MD steps; T_{MD} is MD step and equals to 4.78 fs; M_{trans} is total number of $SiO_x{\rightarrow}SiO_{x\pm1}$; $V_{trans}= M_{trans}/N$ is rate of $SiO_x{\rightarrow}SiO_{x\pm1}$; $F(T)$ is correlation coefficient. To clarify the diffusion mechanism at atomic level, we have calculated the diffusion coefficient by both method, equation (1) and (3).

3. Results and discussion

Table 1. The coordination distribution for liquid SiO_4 at different temperatures; C_4, C_5 are the fraction (%) of four- and five-told coordination, respectively; C_{other} is fraction of another type coordination (3 or 6).

T(K)	2600	3000	3500	4000	4500
C_4	**93.90**	**92.28**	**86.37**	**76.10**	**70.80**
C_5	5.87	7.43	12.70	21.12	24.91
C_{other}	0.23	0.29	0.93	2.78	4.29

The constructed models have the structural characteristics closed to simulation result in ref.[17] which are consistent with experimental data for silica liquid. The structure of all samples is similar

each other in terms of positions of PRDF peaks, density and that the units SiO_4 are dominant. As temperature increases the fraction of tetrahedral units C_4 monotonously decreases, meanwhile fractions C_5 (SiO_5) and C_{other} (SiO_3 and SiO_6) increases in considered temperature interval (see Table 1).

The tracking the coordination for Si shows that during the simulation run each atom Si undergoes a series of stages where it locates in the unit SiO_x, i.e. no any coordinated oxygen moves outside this unit and its coordination is unchanged. The lifetime of those stages may be different and varies strongly from one to another place. The lifetime of those stages may be different and varies strongly from one to another place. The averaged lifetime for different SiO_x is presented in Fig.2 and one can see that the averaged lifetime of tetrahedral units monotonously decreases with the temperature.
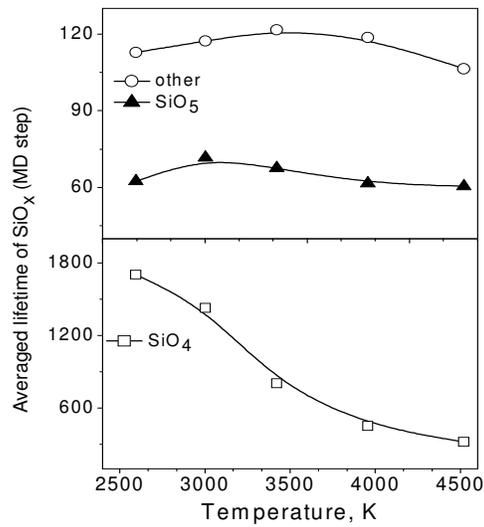
Fig.2. The temperature dependence of averaged lifetime of coordination units SiO_x

T(K)	D x 10^5cm^2/s	V_{trans}	V_{exch} x 10^3	D_{trans}, Å^2/ one $SiO_x \rightarrow SiO_{x\pm1}$
2600	0.0172	1.1117	0.0715	0.0715
3000	0.0376	1.2689	0.1195	0.1195
3500	0.4806	2.2500	0.2639	0.2639
4000	1.3456	3.7542	0.3512	0.3512
4500	3.7163	5.1634	0.4397	0.4397

Table 2. Dynamic characteristics for silica liquids; V_{trans}, V_{exch} - the rate of transitions and exchanging coordinated oxygen in unit SiO_x per a MD step and per silicon atom.

The quantity M_{trans} which measures the number of mentioned stages is plotted in Fig.3. Well straight lines are seen and their slope is used to determine the rate of transitions V_{trans}. The dependence of M_{exch} as a function of N is also well described by straight line and the rate of ECO V_{exch} is listed in Table 2. The result shows that both quantities V_{trans} and V_{exch} depend on temperature, distribution of

SiO_x and fraction C_5. Besides, V_{exch} depend on distribution of transitions $SiO_x \to SiO_{x\pm1}$. Furthermore, $V_{transR}(T)$ is very close to $C_{5R}(T) = C_5(T)/C_5(4500)$, hence the equation (4) can be rewritten as

$$N_{sld}(T) = V_{transR}(T)F(T) = C_{5R}(T)F(T) \qquad (5)$$

This result appears to confirm the model reported in ref. [18, 19] that the diffusion is performed via five-coordinated silicon.
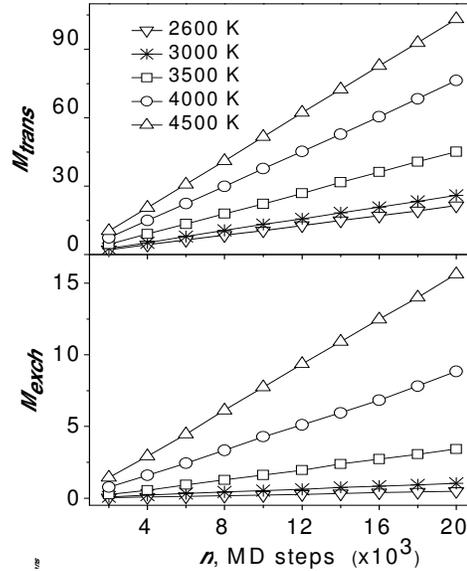
Fig.3. The dependence of M_{trans} and M_{exch} as a function of MD steps n

Consider the mobility of Si which moves together with x coordinated O; $x = 0, 1, 2, 3, 4$. The mean square displacements of Si with different x over 2.10^4 MD steps are listed in Table 3. As expected, $<R(t)^2>$ decreases with increasing x. This indicates the diffusivity of Si strongly depends on rate V_{exch}, because of the fraction of Si^x is directly related to the number of ECO. Therefore the change in $F(T)$ directly relates to V_{exch}.

Table 3. The mean square displacement for silicon atoms with different number x					
x	2600 K	3000 K	3500 K	4000 K	4500 K
0	-	-	-	17.47	24.48
1	-	-	11.01	10.67	17.71
2	-	1.81	5.13	6.38	14.21
3	1.31	1.61	3.02	4.31	-
4	0.37	0.48	1.62	3.8	-

We now measure the distribution of transitions $SiO_x \to SiO_{x\pm1}$ for low- and high-temperature samples in order to identify the diffusion mechanism. For this purpose we have prepared model M1 at temperature 2600 K and two models M2, M3 at temperature 4000 K. For comparison we perform the relaxation on M2 and M3 over the time that M_{trans} and M_{exch} of model M1 is closed to those quantities for M2 and M3, respectively. The main characteristics of constructed models are presented in Table 4.

Table 4. The main characteristics of models M1, M2, M3;; M_{trans}, M_{exch} are the total number of transitions $SiO_x \rightarrow SiO_{x\pm1}$ and ECO, respectively.

Model	Number of MD steps	Temperature	M_{trans}	M_{exch}	$<x_n^2>$
M1	60000	2600 K	44674	1162	0.57 Å^2
M2	17685	4000 K	44675	5102	6.39 Å^2
M3	4335	4000 K	10747	1163	2.15 Å^2

Here we see that although both models M1 and M2 have very close value of M_{trans} the mobility of Si in model M2 is much faster than one in model M1 evidenced by quantities $<x_n^2>$. The origin of this is clearly related to the number of transitions $SiO_x \rightarrow SiO_{x\pm1}$. The value of M_{exch} for high-temperature sample is about 5 times bigger than low-temperature sample. This implies that the frequency of forward-to-backward transitions $SiO_x \rightarrow SiO_{x\pm1}$ (see Fig.1 (e-h) in M1 is much bigger than in M2. In other word the correlation effect for low-temperature sample is stronger than for high-temperature sample.
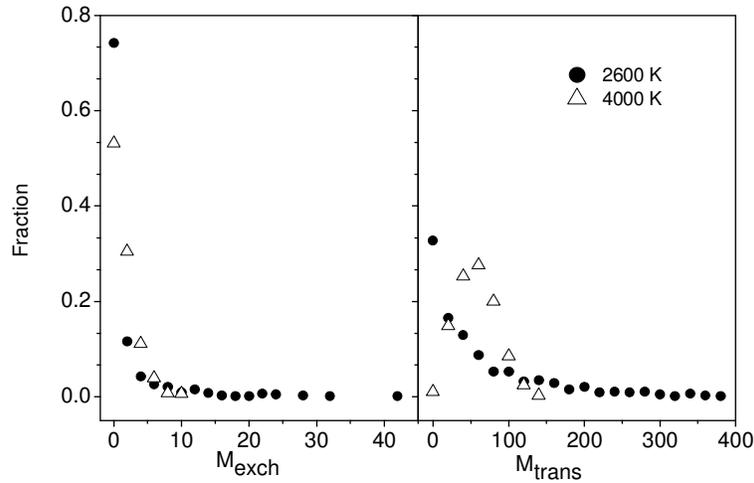
Fig.4. The distribution of transition and exchange for silica liquid at 2600 and 4000 K

Comparison between sample M1 and M3 shows that $<x_n^2>$ of M1 significantly differs from one of M3 despite both samples having the same M_{exch}. Fig.4 shows the distributions of transitions $SiO_x \rightarrow SiO_{x\pm1}$ and ECO for high- (M2, M3) and low-temperature (M1) samples. One can see that the transitions M_{trans} as well as M_{exch} is spread in wider interval for low-temperature sample. For M1 the value of M_{trans} varies in the interval 0-360, whereas this interval is 0-40 for M2. The shape of the distribution of transitions $SiO_x \rightarrow SiO_{x\pm1}$ is also quite different for high- and low-temperature samples. Further, the sample M5 attains a pronounced peak and it located at M_{trans} =52. Regarding M_{exch} we see that there are a large number of units SiO_x where not any ECO occurs. The number of such units SiO_x in M1 is significantly larger than in M3. As shown in Table 4 silicon atoms in these units move more slowly than others and they prevent the remaining atoms to diffuse through the system. Combining these facts we can conclude that compared to M2 and M3, the slower diffusivity in M1 is caused by that the dynamics in low-temperature sample is more heterogeneous comparing to high-temperature

sample. Therefore, the anomalous dynamics slowdown near the glass transition temperature can be explained by the high localization of $SiO_x \rightarrow SiO_{x\pm1}$ in liquid structure.

4. Conclusions

The diffusion mechanism in high- and low-temperature silica liquids is studied by mean of molecular dynamic simulation. The simulation reveals that each silicon atom undergoes a series of stages. We found that the diffusivity depends not only on the rate of transitions $SiO_x \rightarrow SiO_{x\pm1}$ with x= 4, 5, 6 but also on the rate of exchanging the coordinated oxygen atoms which monotonously increases with increasing temperature. The frequency of forward-backward transitions in low-temperature sample is more often than in high-temperature sample. As a result, the correlation coefficient *F* considerably decreases with decreasing the temperature.

We also have examined the distributions of transitions $SiO_x \rightarrow SiO_{x\pm1}$ and exchanging the coordinated oxygen atoms for low- and high-temperature samples. The result shows that the transitions $SiO_x \rightarrow SiO_{x\pm1}$ and exchanging the coordinated oxygen atoms are more uniformly distributed in high-temperature sample than in low-temperature sample indicating the heterogeneous dynamics in low-temperature sample. This causes the decrease in diffusivity with decreasing the temperature.

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