

The study of dynamics heterogeneity and slow down of silica by molecular dynamics simulation

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Abstract. We have numerically studied the diffusion in silica liquids via the $\text{SiO}_x \rightarrow \text{SiO}_{x\pm 1}$, $\text{OSi}_y \rightarrow \text{OSi}_{y\pm 1}$ reactions and coordination cells (CC). Five models with temperatures from 1000 to 3500 K have been constructed by molecular dynamics simulation. We reveal that the reactions happen not randomly in the space. In addition, the reactions correlated strongly with the mobility of CC atom. Further we examine the clustering of atoms having unbroken bonds and restored bonds. The time evolution of these clusters under temperature is also considered. The simulation shows that both slow down and dynamic heterogeneity (DH) is related not only to the percolation of restored-rigid clusters near glass transition but also to their long lifetime.

1. Introduction

The dynamical slowing down in super-cooled liquids when the temperature approaches to their glass transition point T_g is one of challenging problems of physics in condensed matter. There are many theoretical approaches developed to provide useful theoretical guides to understand and analyze various aspects of dynamical heterogeneity and slowing down, such as mode-coupling theory [1], the Adam-Gibbs hypothesis [2], the random first-order transition theory [3], dynamic facilitation [4]. . . The mode coupling theory predicts a power-law divergence of relaxation times at a critical temperature $T_{MCT} > T_g$ [5]. The Adam-Gibbs study suggests the glass transition phenomenon as resulting from an increase of cooperation of molecular dynamics upon cooling [5]. The simulations have shown that liquid silica behavior differs from strong liquid under wide temperature range. At high temperature, the diffusion violates the Arrhenius law and is well described by a power law $D \sim (T - T_{MCT})^\gamma$; here γ is close to 2.1 (compared to 1.4 for water); $T_{MCT} \approx 3330\text{K}$ [6]. This means that at high temperature, liquid silica behaves like a fragile liquid. The heterogeneous dynamics is well established by experiment [7, 8] and simulation [9, 10, 11]. However, experimental studies of strong glasses are rare due to the high T_g , and the structural relaxation is not result of simple bond-breaking process at random positions [5]. In previous work [12], we show that the diffusion constant depends not only on the rate of reactions, but also on the spatial distribution of reactions. It is interesting to determine how the spatial correlation of reactions affects the DH and the dynamical slowing down. Moreover, the clusters are predicted as result of specific distribution of reactions in the space.



2. Computational procedure

Molecular dynamics (MD) simulation is carried out for the silica model composing 666 silicon and 1332 oxygen particles. We used the van BeestKramervan Santen (BKS) potential which is commonly applied to reproduce structural and dynamical properties of silica liquid and glass [13, 14, 15]. The MD step is equal to 0.47 fs. Initial configuration is generated by randomly placing all particles in the simulation box. This configuration is heated to 5000 K and then cooled down to the desired temperature. After that the obtained sample is relaxed in N-E-V ensemble (constant volume and energy) for long times. The pressure is kept to zero. The time consumed to construct a well-equilibrated model is about 10^7 MD steps. We have prepared five models at temperatures of 1000, 1400, 1800, 2600 and 3500 K. More details about the procedure of preparing the BKS MD model can be found elsewhere [12]. The dynamics are analyzed through the CC which is determined as a set of central atom and its neighbors. We calculated the coordination cell of Si or O by integrating the Si-O or O-Si radial distribution function up to first minimum (cut off distance), respectively. Here, the bond is created by two atoms Si and O, whose distance is less than the cut off distance. A cluster is defined as a group of particles that resides in the first-neighbor cell of each other [9, 10]. So, atoms form at least a bond with another atom in the cluster. During this time simulation, if a bond remains unchanged from initial point, this bond is called unbroken bond. Atoms linked via unbroken bonds forming the cluster called rigid cluster. The bond may break then restore after some times, however, which is called restore bond. The cluster of atoms linked via these bonds is called restored rigid cluster. A reaction corresponds to a bond broken or a new bond being created inside a coordination cell, such as $\text{SiO}_x \rightarrow \text{SiO}_{x'}$ and $\text{OSi}_y \rightarrow \text{OSi}_{y'}$.

3. Result and discussion

Fig.1 shows the number of reactions as a function of MD steps. All points fall well on straight lines. The slopes of these lines are used to determine the rate of reactions (ξ). The diffusion constant is calculated via Einstein equation using the mean square displacement of atoms (the values are showed in table 1). When temperature is lower than 1800K, the rate of reactions and diffusion constant are increase with the same proportion. However, ξ increases much slower than diffusion constant as temperature is higher than 1800K. It means that γ is just one of factors affecting the diffusion process. It suggests that the temperature changes, how reactions happen in the considered samples is not by the same way. The diffusion is a result of the reactions at CC, but it is one of the keys to effect to the diffusion.

Table 1. The diffusion constant and the rate of reactions

Temperature, K	The rate of reactions (ξ)	D_{Si} , cm ² /s	D_{O} , cm ² /s
1000	0.1599	2.5E-08	2.6E-08
1400	0.3307	4.0E-08	4.4E-08
1800	0.3992	4.4E-08	5.0E-08
2600	0.8540	2.1E-07	2.6E-07
3500	2.0209	3.4E-06	4.7E-06

Here m_{cc} is the number of coordination cells happening reactions; m_{unbr} is the number of unbroken bonds; m_b is the number of bonds inside sample including unbroken bonds and restored bonds. The reaction processes can analyze through m_{cc} , m_{unbr} , m_b . We can see that the reactions spread on more coordination cells when increasing the number of steps. In the case of 3500K,

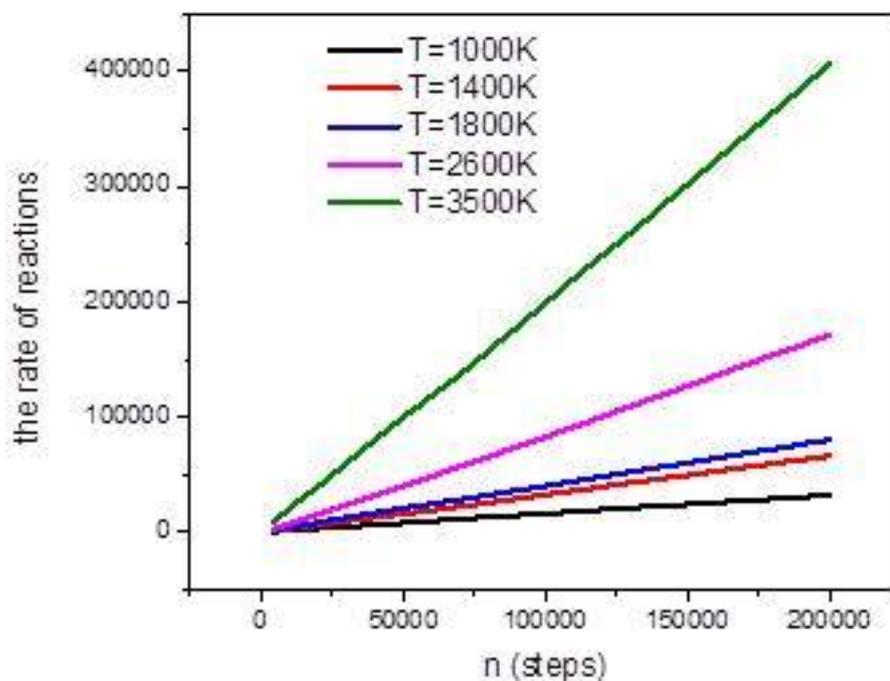


Figure 1. The number of reactions as function of steps.

the reactions expand to the entire sample approximately 60000 steps. At the same number of the steps, the temperature is higher, the number of reactions is bigger. But, it is not clearly the indication of spatio-temporal distributions. In fig.3, reactions can be showed via the process of breaking and restoring bonds. These processes occur simultaneously at any temperature. However, we can look at the different picture at high and low temperature. The reactions happen more frequently with some coordination cells or bonds, m_{cc} becomes smaller and m_{unbr} bigger than for the case when the distribution of reactions among coordination cells or bonds is ununiformed. Therefore, the spatial distribution of reactions becomes more heterogeneously upon lowering the temperature.

Atoms are linked with neighbors via unbroken, restored or new bonds. We have considered the clusters which are formed through unbroken bonds (rigid-cluster) and their role for dynamic heterogeneity and slowing down. The image of rigid cluster composing 33 atoms is presented in fig.4. The mean square displacement (MSD) per atom is approximately 1.4315 \AA^2 , is smaller than MSD per atom in the entire sample (about 1.8803 \AA^2). Their shape changes slightly. The number of atoms of the biggest cluster and the number of rigid cluster at three moments are showed in table 2. These results tell us that these rigid clusters tend to decay when increasing time simulation. However, in table 3, as temperature is continually cooled down, the largest rigid cluster is expanded. It proves that rigid cluster exists in the liquid for long time and percolates over the sample at low temperature. Because of the rigidity of the atoms of rigid cluster, the dynamics decreases dramatically. So, the existence of percolation rigid cluster can be a result of slowing down at near glass transition.

Next, we describe results of our study on the restored-rigid cluster, which include atoms linked through unbroken bonds and restored bonds. We consider a group of Si and O having

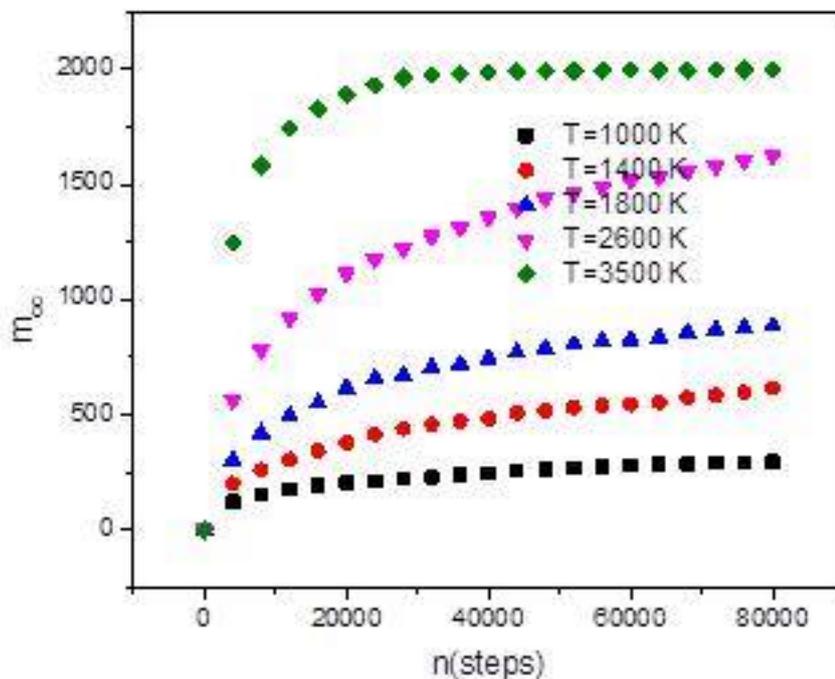


Figure 2. The dependence of m_{cc} (a) as a function of number of steps.

4 or 2 bonds like initial time, respectively. For case of 2600 K and 2×10^5 steps, we found a set containing 1513 atoms, with MSD is about 1.2394 \AA^2 . The number of atoms in largest cluster detected at 11 moments (from 0 steps to 2×10^5 steps) changed from 1507 atoms to 1513 atoms. It means that during 2×10^5 steps, there are larger cluster of immobile atoms which percolates over entire sample.

Table 2. The main characteristics of atoms of rigid clusters for the sample at 2600 K and three interval times

Steps	sdam	mtam	$\langle d^2 \rangle, \text{ \AA}^2$	$\langle dd^2 \rangle, \text{ \AA}^2$
40000	18	1852	0.6998	0.8685
80000	46	1672	0.749	0.9168
200000	158	268	1.0698	1.8803

sdam: the number of rigid clusters; mtam: the number of atoms of the largest rigid cluster; $\langle d^2 \rangle$: the MSD per atom in the largest rigid cluster; $\langle dd^2 \rangle$: the MSD per atom in entire sample.

In table 4, we considered Si and O atoms having k bonds (including unbroken bonds and restored bonds) at time simulation. We can see that the MDS and the number of reactions decreases when k increase. At final time, we can choose 180 atoms having largest MSD, monitor the cluster creating process and track the evolution of these clusters at 11 moments during 2×10^5 steps. The size of biggest cluster varies from 13 to 19 atoms, with the MSD of biggest

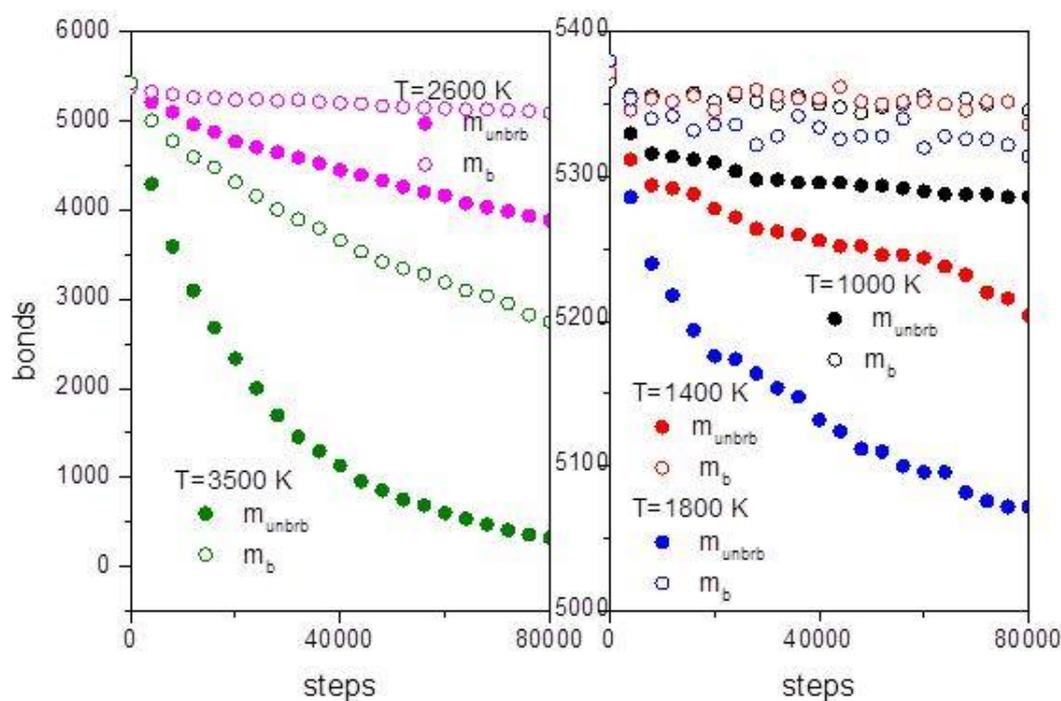


Figure 3. The dependence of m_{unbr} and m_b as a function of number of steps.

Table 3. The main characteristics of atoms of rigid clusters for the sample at three temperatures, $n=2 \times 10^5$ steps

Temperature	sdam	mtam	$\langle d^2 \rangle, \text{\AA}^2$	$\langle dd^2 \rangle, \text{\AA}^2$
2600K	158	268	1.0698	1.8803
1800K	2	1967	0.5370	0.5370
1400K	2	1981	0.4612	0.4804

cluster increase monotonically from 0 to 12.7653\AA^2 . So, in the entire simulation time, the atoms of clusters tend to move together. These clusters of most mobile atoms and rigid clusters are convincing evidence of heterogeneity in silica liquid. At the same time, the trajectories distinguish widely from one atom to another atom in the sample. Some particle can undergo many jumps, even, link together to move; while some particles are nearly immobile over time simulation, they only vibrate around well-defined locations and link to another atoms by lasting bonds called rigid bonds. The most mobile atoms can be answer of the problem what is origin of diffusion beside the reaction of CC, especially, their trajectories. It is suggested that these atoms are bridge between these rigid clusters. When temperature is decrease near glass transition, the bonds exist a longer and longer time. The reactions in private CC is said that being only cause of the diffusion. We stress that the percolation in whole sample of the rigid cluster is associated with slowing down.

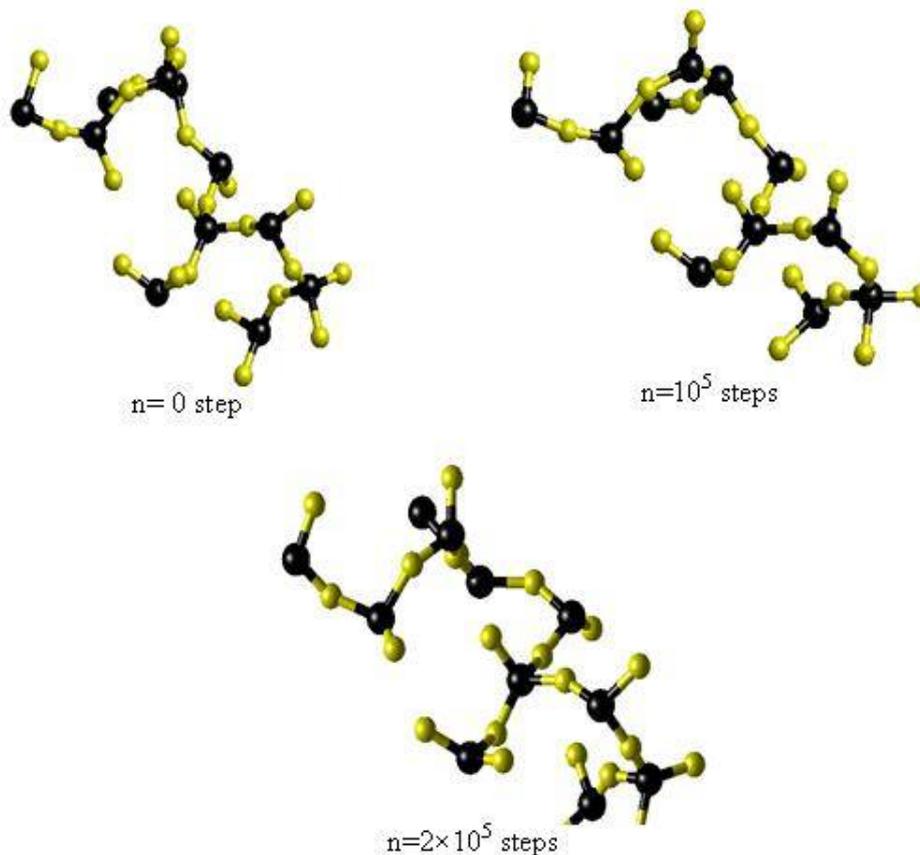


Figure 4. The image of five rigid clusters obtained at three moments within $n = 2 \times 10^5$ steps; the temperature is 2600 K; the black and yellow spheres are the atom Si and O, respectively.

Table 4. The main characteristics of atoms in rigid and restored bond groups for the sample at 2600 K and $n = 2 \times 10^5$ steps;

Group(k)	Si			O		
	N_{group}	$\langle d^2 \rangle, \text{\AA}^2$	$\langle m_{\text{reaction}} \rangle$	N_{group}	$\langle d^2 \rangle, \text{\AA}^2$	$\langle m_{\text{reaction}} \rangle$
0	1	11.5018	448	19	14.6135	250.3158
1	5	9.3522	453	190	4.79	132.2842
2	40	3.7553	303.225	1122	1.351	49.016
3	128	2.4358	212.875	1	0.3392	620
4	492	1.0826	88.2114			

N_{group} is the number of atoms having k bonds (including rigid bonds and restored bonds) at final time, which is the same with initial time.

4. Conclusion

The reactions affect strongly the diffusion, but diffusion is not a result of a simple bond breaking process occurring at random positions. As the temperature decreases, the rate of reactions

decreases slower than the diffusion constant. As the temperature is lower, the rigid cluster spans a longer and longer period of time and a larger restored-rigid cluster percolated over whole system making diffusion can no longer be detected. It is mean that they are origin of dynamics slowing down near glass transition. The DH can be seen from the sets of atoms belonging to rigid clusters or restored rigid clusters or most mobile atoms. We conclude that DH is a result of none-uniform distribution of reactions in the space.

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