Simulation of Diffusion Mechanism and Heterogeneous Dynamics in Network-forming Liquid

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Abtract: We have studied the diffusion mechanism in network-forming liquids via molecular dynamics simulation. Two models of silica liquid at temperatures of 2600 and 3500 K have been constructed. The motion of atoms is analyzed through reactions $SiO_x{\rightarrow}SiO_{x\pm1}$, $OSi_y{\rightarrow}OSi_{y\pm1}$ and coordination cells. It was shown that the reactions happen not randomly in the space, but they occur more frequently with some coordination cells and bonds Si-O. This effect enhances upon lowering the temperature. The number of reactions happening in the coordination cells is strongly correlated with the mobility of CC atom. We found that there are large rigid clusters which compose of immobile atoms and exist for long time. Further, the dynamics heterogeneity (DH) is determined via sets of: (1) most mobile or immobile atoms; (2) atoms belonging to large rigid clusters. We show that the percolation rigid cluster responds to the dynamical slowing down present near glass-transition.

Keywords: Simulation, silica, liquid, dynamic heterogeneity, rigid cluster.

1. Introduction

The glass-forming liquids, when cooled down below melting point fast enough, will form a glass at the temperature T_g called the glass-transition temperature. Close to 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 [1-3]. The reason for the dynamical slowing down is still not properly understood and represents a major challenge in the condensed matter. Moreover, the liquid near glass transition exhibits the dynamics heterogeneity (DH) [4-6]. The examination of particle motion in a dense colloidal suspension [7-8] reveals that close to the glass-transition, particle motion is strongly spatially correlated. Recent simulations studied the

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correlation functions for Lennard-Jones systems and finding the evidence for the DH [9-10]. In other works [11-13] one visualized the set of most mobile and immobile particles and showed that they form large clusters which migrate in the space over times. A group of particles follows one another along string-like paths. The particle mobility seems to be a result of the dynamics facilitation [14].

In previous work [15] we study reactions $SiO_x \rightarrow SiO_{x\pm1}$ and $OSi_y \rightarrow OSi_{y\pm1}$ which happen in the liquid and govern the diffusion. 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 reactions affect the DH and the dynamical slowing down. Moreover, the clustering of mobile or immobile particles may be the result of specific distribution of reactions in the space. However, this is not clarified yet and motivates us to perform a detail numerical study in this direction.

2. Computational procedure

MD simulation is carried out for the liquid model composing 666 silicon and 1332 oxygen atoms. We used the van Beest–Kramer–van Santen (BKS) potential [16]. The MD step is equal to 0.47 fs. Initial configuration is generated by randomly placing all particles in the simulation box. Then this configuration is heated to 5000 K and cooled down to the specified temperature. After that, the sample has been relaxed in N-E-V ensemble (the constant volume and energy) until the system reached the equilibrium. The pressure is kept to zero. We have prepared two liquid models at 2600 and 3500 K. More details about the procedure of preparing BKS model can be found elsewhere [17].

The diffusion mechanism is analyzed through the coordination cell and reaction. The coordination cell consists of a central atom (CC atom) and neighbors. The CC atom (Si or O) is linked with neighbors via bonds Si-O. The cutoff distance used to determine the coordination cell is 2.28 Å. We have labeled the coordination cell by the label of CC atom. As a reaction happens in the coordination cell, a bond breaks or new bond is created. Most reactions are $SiO_x \rightarrow SiO_{x\pm1}$ and $OSi_y \rightarrow OSi_{y\pm1}$. During the simulation we have determined the mean square displacement of CC atom and the number of reactions happening in the coordination cell. In order to clarify DH we determine the cluster of atoms. A cluster is defined as a set of atoms that forms at least a bond with another atom in the set. Here, a bond is created by two atoms Si and O, the distance between which is less than the cutoff distance. The schematic illustration of coordination cell and cluster is shown in Fig. 1

a)   **b)**   **c)**
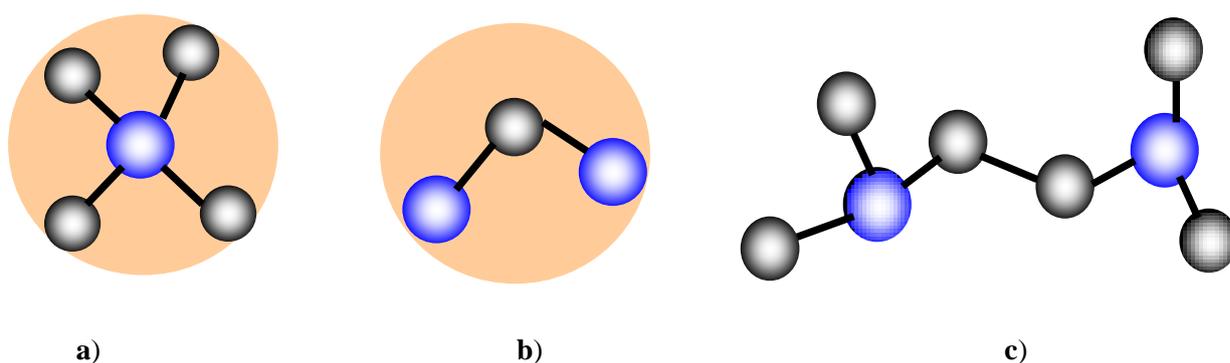
Fig1. The schematic illustration of (a) and (b) the coordination cell SiO_x, OSi_y, (c) the cluster. Here the black, blue sphere represents silicon and oxygen, respectively. The black line indicates a bond between two atoms.

We consider set A_1 of N atoms which are chosen randomly from the system. The mobility of atoms of A_1 in average is close to $m_{average}$ (averaging the mobility of all atoms in the system).

We also consider the motion of N atoms for time t_{DH}; N is smaller than 15% of all atoms in the system. These atoms are chosen so that their mobility in average strongly deviates from the value $m_{average}$. It means that the set of N atoms includes the mobile or immobile atoms. We denote the set of these N atoms to A_k. Two quantities of interest are the number of atoms in the largest cluster M_{ACL} and the number of clusters M_{CL} which are found from A_1 and A_k. We calculate M_{ACL}, M_{CL} of A_1 and A_k at 11 moments within time t_{DH}. Then we compare M_{ACL}, M_{CL} of A_k with ones of A_1. In the case when M_{CL} of A_1 is bigger and M_{ACL} of A_1 is smaller than ones of A_k, the system shows DH. The difference in M_{ACL}, M_{CL} indicates the degree of DH.

If a bond remains unchanged for time t_{DH}, this bond is called unbroken bond. The cluster of atoms linked via unbroken bonds is called the rigid cluster. The bond may break and then restore after some times. For instance, an oxygen atom leaves the coordination cell SiO_4 breaking a bond. Then this oxygen comes back. As a result, the broken bond Si-O is restored. If the bond breaks at $t < t_{DH}$, and then restores at $t = t_{DH}$, we call it the restored bond. The DH, as we see below, can be seen by monitoring the motion of atoms of rigid clusters.

3. Results and discussion

The constructed models have the structural characteristics closed to previous works result in ref.[17,18]. The result is consistent with the experiment in the positions and heights for peaks of PRDFs. In Table 1 we show the dynamics and structure characteristics. 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 The diffusion constant is calculated from the mean square displacement of atom via Einstein equation. We determine the rate of reaction (ξ) from the time dependence of number of reaction.
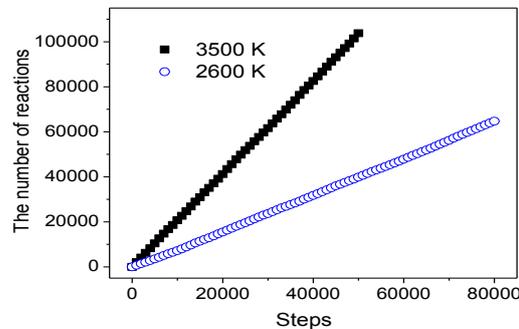
Fig.2. The number of reactions as a function of n steps.

Fig.2 shows the number of reactions for two samples. All points fall well on straight lines. The slopes of these lines are used to determine the rate of reactions. One can see that both diffusion constant and rate of reaction strongly decreases with decreasing the temperature. However, ξ decreases much slower than diffusion constant. This indicates the correlation between reaction and diffusivity but the reactions happen in these samples not by the same way. This effect can be seen from Fig.3. Here m_{cc} is the number of coordination cells in which the reactions happen; m_{unbrb}, m_{resb} is the number of unbroken bonds and restored bonds, respectively. If the reactions happen more frequently with some coordination cells or bonds, m_{cc} becomes smaller and m_{unbrb} bigger than for the case of homogeneous distribution of reactions. As shown in Fig.3, when the same number of reactions

happens in both samples, m_{cc} is smaller for low-temperature sample and m_{unbrb} in contrast is significantly bigger. Therefore, the reactions are stronger spatially correlated upon lowering the temperature.

Table 1. The diffusion constant, rate of reactions ξ, 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).

Temperature, K	D_{Si}, cm^2/s	D_O, cm^2/s	ξ	C_4	C_5	C_{other}
2600	1.70×10^{-7}	2.32×10^{-7}	4.07×10^{-4}	93.90	5.87	0.23
3500	2.79×10^{-6}	3.95×10^{-6}	1.03×10^{-3}	86.37	12.70	0.93

Table 2. The main characteristics of coordination cells of UNBRB groups at 3500 K and $t_{DH} = 5\times10^4$ steps; Here N_{group} is the number of coordination cells; $<d^2>$ is the mean square displacement of CC atom; $<m_{reaction}>$ is the averaged number of reactions happening in the coordination cell.

Group	SiO$_x$			OSi$_y$		
	N_{group}	$<d^2>$, Å^2	$<m_{reaction}>$	N_{group}	$<d^2>$, Å^2	$<m_{reaction}>$
0	389	5.68	96.25	994	7.69	45.87
1	187	3.80	60.07	298	4.04	20.46
2	80	3.22	37.69	40	2.22	5.40
3	9	4.55	16.78	-	-	-
4	1	0.08	12.00	-	-	-

We have calculated the number of unbroken bonds (UNBRB) in each coordination cell for time t_{DH}. The coordination cells can be divided into UNBRB groups. The kth group includes coordination cells that have k unbroken bonds. The main characteristics of UNBRB groups for the case $t_{DH} = 5\times10^4$ steps (23.9 ps) are presented in Table 2. The atoms in the system move in average on the distance of 1.52σ; here σ is the position of first peak of PRDF for pair Si-O; $\sigma = 1.62$ Å. As shown in Table 2, there are a large number of CC atoms belonging to k^{th} groups with $k > 0$. During time t_{DH} these CC atoms and its neighbors move like a "large molecule" which consists of CC atom and k neighboring atoms. The liquid likely contains different types of "molecule" such as Si, SiO$_x$, O and OSi$_y$ where x=1, 2, 3, 4; y=1, 2. The parameter k plays the role of the size of "molecules". It is interesting to note that CC atoms in the group with smaller parameter k move in average over larger distance (larger $<d^2>$). Moreover, the larger $<m_{reaction}>$, the smaller parameter k is. It means that the number of reactions happening in the coordination cell is strongly correlated with the mobility of the CC atom. The "small molecule" is more mobile than "large molecule". The existence of different size "molecules" within long time t_{DH} is related to the DH in the liquid.
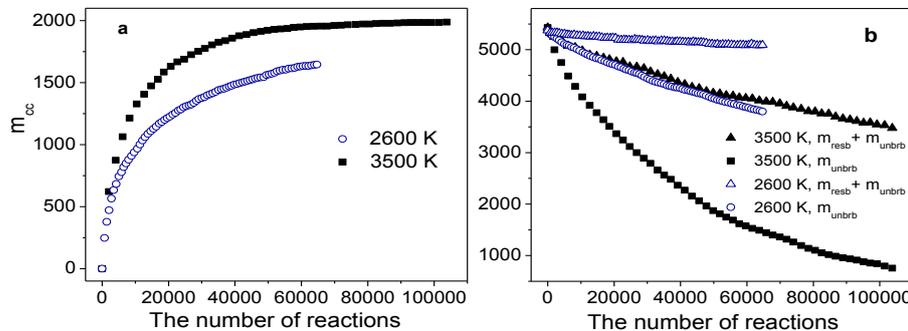
Fig. 3. The dependence of m_{cc} (a) and the dependence of m_{unbrb} and $m_{unbrb}+m_{resb}$ (b) as a function of number of reactions.
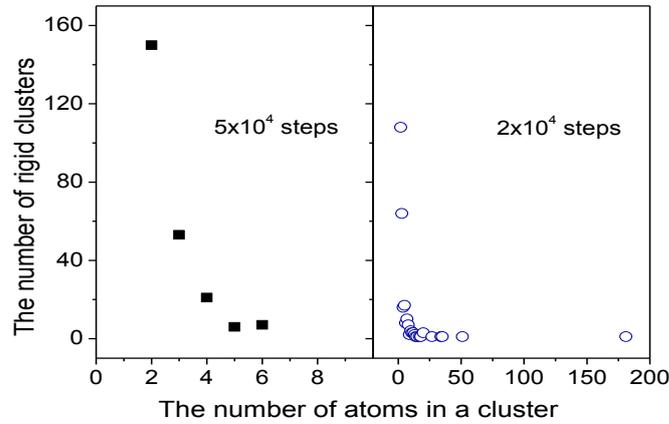
Fig.4. The size distribution of rigid clusters for the cases of $t_{DH} = 2 \times 10^4$ and 5×10^4 steps.
The temperature is 3500 K.
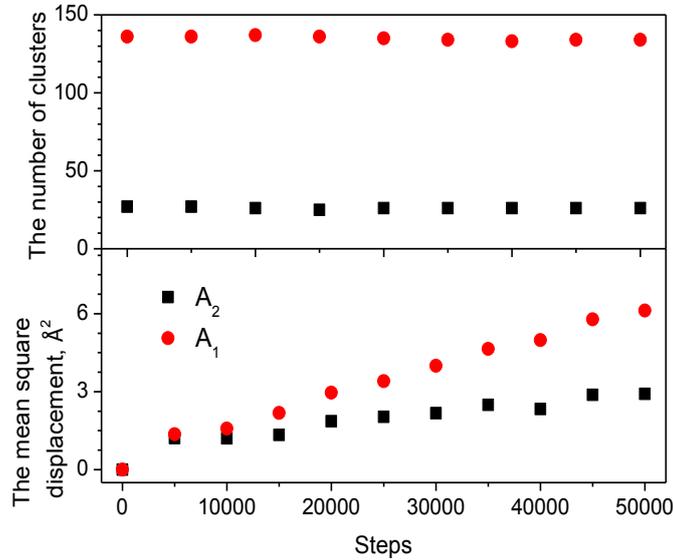
Fig.5. The number of clusters M_{CL} and mean square displacement per atoms at 11 moments.
The temperature is 3500 K.

If a number of "molecules" link to each other by unbroken bonds, then it forms large rigid cluster. Fast atoms move through the paths where no large rigid clusters locate; slow atoms locate near or inside large rigid clusters. Because large rigid clusters spontaneously decay with times, hence the size distribution of rigid clusters depends on the time t_{DH}. In Fig.4, we show the size distribution of rigid clusters. The curves for different time t_{DH} significantly differ from each other. In particular, for $t_{DH} = 5 \times 10^4$, the largest cluster found has the size of 6 atoms, meanwhile in the case of $t_{DH} = 2 \times 10^4$ steps, the size of largest cluster is 181 atoms.

For $t_{DH} = 5 \times 10^4$ we consider a set A_2 of atoms which belong to the rigid clusters composed of 4, 5 and 6 atoms. The total number of atoms in A_2 is 156. We also consider the set A_1. It consists of 156 atoms which are randomly chosen from the system. The clusters for A_1 and A_2 are determined at 11

moments. The result is shown in Fig.5. In the case of A_1, the number of clusters found varies from 133 to 137. The largest cluster has the size of 4 atoms. Meanwhile for A_2, the number of clusters varies from 24 to 27 that significantly smaller than of A_1. The largest cluster found has 16 atoms. It follows that large rigid clusters do not move in different places in the system, but tend to locate together in some small volume. On the other hand, the mean square displacement per atom for A_2 is significantly smaller than for A_1 (see Fig.5). It means that the groups of immobile atoms locate in some small volumes for 5×10^4 steps. This indicates the existence of DH. The reason of DH observed therefore is the rigid clusters which are formed due to none-uniform distribution of reactions in the space.

In the case of 2600 K and $t_{DH} = 2 \times 10^5$ steps (95.6 ps) we found rigid clusters composing of 268 and 216 atoms (about 24% all atoms in the system). It follows that as the temperature decreases rigid clusters in the liquid are bigger and exist for longer times. If one continues cool down the liquid, this rigid cluster becomes percolate over whole system. Because the atoms of large rigid clusters are immobile, hence the dynamics in the liquid decreases dramatically. On the other hand, due to small change in the structure the rate of reactions decreases much weaker. So we can suggest that the dynamical slowing down may be related to the percolation rigid cluster present near glass-transition
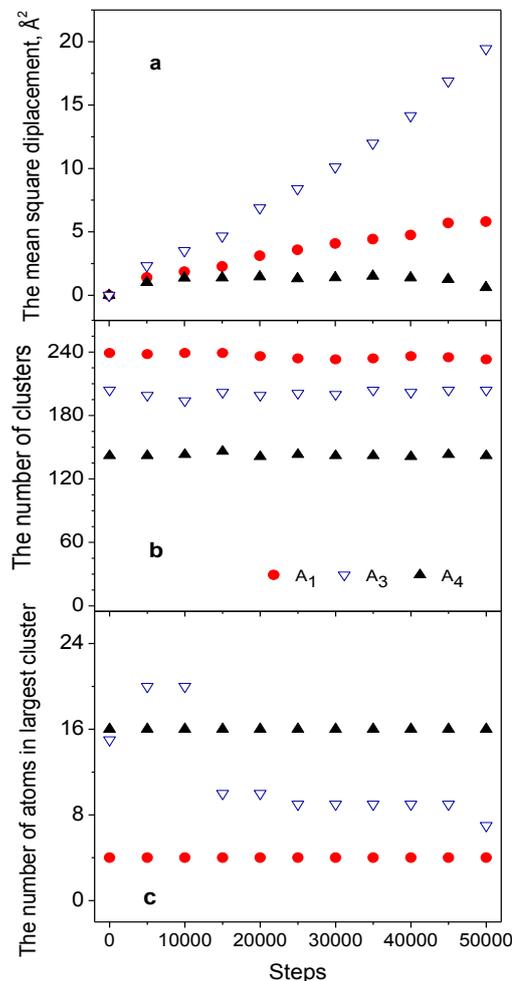
Fig.6. The mean square displacement per atom, the number of clusters M_{CL} and the number of atoms in largest cluster M_{ACL} for A_1, A_3 and A_4.

We consider three sets A_1, A_3, A_4 which have 291 atoms (about 14% all atoms in the system). The A_3, A_4 include the most mobile and immobile atoms, respectively. We have calculated M_{CL}, M_{ACL} and mean square displacement per atom at 11 moments during 5×10^4 steps. The result is presented in Fig.6. As shown in Fig.6a, the mean square displacement per atom for A_3, A_4 significantly differs from ones of A_1. It means that A_3, A_4 represent the set of mobile or immobile atoms. The M_{CL} for A_1 varies from 225 to 240 that significantly larger than ones for A_3 and A_4. The M_{ACL} of A_1 in contrast is significantly smaller. As shown in Fig.6b and 6c, M_{ACL} for A_3 and A_4 varies less 20 atoms. M_{CL} for A_3 and A_4 varies from 8 to 24. It is interesting to clarify how large clusters behave in the space with times. For A_3 the cluster may split or merge during time t_{DH}. Therefore, the motion of atoms of A_3, A_4 evidences the DH in the liquid.

4. Conclusions

The MD simulation shows that the diffusion is realized via reactions $SiO_x \rightarrow SiO_{x\pm1}$ and $OSi_y \rightarrow OSi_{x\pm1}$. As the temperature decreases, the diffusion constant decreases much faster than the rate of reactions. The reason is that the reactions happen not randomly in the system, but they occur more frequently on some atoms and bonds Si-O. Moreover, a large amount of reactions occur to restore the bonds and the diffusion constant depends on the fraction of those reactions. The coordination cells can be divided into UNBRB groups. The CC atoms in the group with smaller parameter k move in average over larger distance. Here k is the number of unbroken or restored bonds in the coordination cell. It was shown that the number of reactions happening in the coordination cell is strongly correlated with the mobility of CC atoms. We found rigid clusters which exist in the liquid for long time t_{DH}. The atoms of large rigid clusters are immobile. Until the times t_{DH} when the number of rigid bonds is large, there are specific microscopic regions in the liquid. The network structure of these regions changes a little and the atoms in the region move slowly. The clusters of slow atoms are observed there. The atom rearranging occurs outside those regions.

The simulation shows that the DH can be seen from the sets of: (1) most mobile or immobile atoms; (2) atoms belong to rigid clusters. The effect is most pronounced from the atoms of rigid clusters. The DH can be seen by atoms of rigid clusters until the sum of rigid and restored bonds is enough small.

Acknowledgements

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