The study of diffusion in network-forming liquids under pressure and temperature

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ABSTRACT

In this paper, the molecular dynamics simulation is applied to investigate the diffusion in silica liquids under different temperature and pressure. We show that the diffusion is controlled by the rate of effective $SiO_x \rightarrow SiO_{x \pm 1}$ and $OSi_y \rightarrow OSi_{y \pm 1}$ reaction. With increasing the pressure, the rate of reaction increases and the Si–O bond is weaker. Moreover, the reactions are not uniformly distributed in the space, but instead they happen frequently or rarely in separate regions. We also reveal two motion types: free and correlation motion. The correlation motion concerns the moving of a group of atoms which is similar to that of the diffusion of a super-molecule in the liquid. A detailed analysis of the movement of atoms from specified set shows the clustering of them which indicates structure and dynamics heterogeneity. Further, we find that the correlation motion is very important for the diffusion in network-forming liquid. The observed phenomena such as diffusion anomaly, dynamics heterogeneity and dynamical slowdown are originated from the correlation motion of atom.

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1. Introduction

Despite intensive research on the network-forming liquid [1–14] there remain many fundamental questions concerning this liquid. Namely, when the liquid is compressed to smaller volume, the diffusion may proceed faster. This anomaly has been observed by both experiment and simulation [1–4]. For silica the diffusion anomaly is thought to be caused by weakening of Si–O bond and densification of the melt upon compression. Further, close to the glass-transition point, the liquid suffers a dramatic slowing down of its dynamics within narrow temperature range [5–8]. This is at variance from statistic properties that show the mild change. The non-trivial dynamics are suggested to be the cause leading to such temperature dependence of relaxation. This is indeed the case since the liquid shows the dynamics heterogeneity (DH) [8–14]. According to a study of a dense colloidal suspension by a confocal microscope [15–17], the particle motion is spatially correlated near the glass-transition point. Moreover, the mobile particles do not all move in similar directions, but they seem to be internally rearranged. The molecular dynamics (MD) simulation is widely used to clarify the mechanism in such phenomena because it provides full access to the trajectory of each atom. For instance, the analysis of the trajectory of atoms in ref. [18] shows three moving modes in

the vitreous glass. MD simulation on Lennard–Jones system found the evidence of DH on basis of multi-point correlation function [17,19,20]. Many studies [21–28] explored DH by the visualizing technique. It is shown that the mobility of particle seems to be a result of dynamics facilitation. In general, the DH is expected to be related to the structural heterogeneity. However, the mechanism in DH and diffusion anomaly as well as the relationship between them is still not properly understood yet. This needs more systematic studies.

In previous work [29,30] we have shown that the diffusion in silica liquid is realized through $SiO_x \rightarrow SiO_{x \pm 1}$ and $OSi_y \rightarrow OSi_{y \pm 1}$ reactions. Moreover, the spatial distribution of reactions is also important for the diffusion in the silica liquid. In present study we focus on the relationship between the reactions and phenomena such as diffusion anomaly, DH and dynamical slowdown. Furthermore, we examine the clustering of atoms from specified set in order to clarify the nature of DH and structural heterogeneity in the network-forming liquid.

2. Computational procedure

The models comprising 666 silicon and 1332 oxygen atoms have been generated by means of MD simulation. We used the van Beest–Kramer–van Santen (BKS) potential [31]. The time step is equal to 0.478 fs. Initial configuration is generated by randomly placing all particles in a simulation box. Firstly, the configuration is

a)

b)

c)

d)

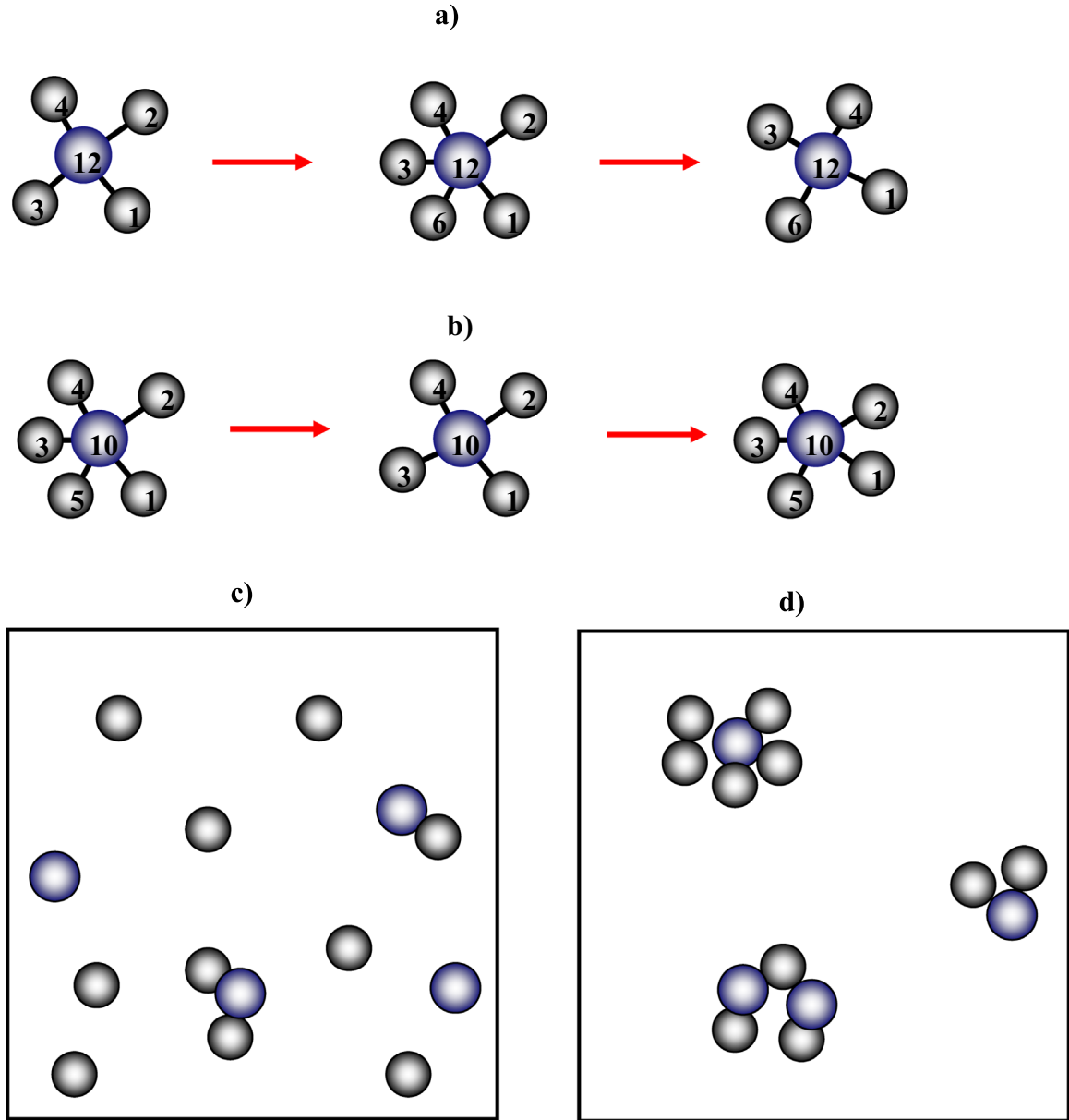**Fig. 1.** The rearrangement of atom in the coordination cell when two reactions happen: a) $SiO_4 \rightarrow SiO_5$, $SiO_5 \rightarrow SiO_4$ reactions happen and $Si^{12}–O^2$ bond is replaced by $Si^{12}–O^6$; b) $SiO_5 \rightarrow SiO_4$, $SiO_4 \rightarrow SiO_5$ reactions happen and $Si^{10}–O^5$ bond is broken, and then restored. The spatial distribution of atoms from A_1 (c) and A_i (d) when the clustering occurs; $mc_{Ai} < mc_{A1}$; $ma_{Ai} > ma_{A1}$. Here the black and blue sphere represents the oxygen and silicon, respectively; the black line indicates the Si–O bond. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

heated to 5000 K and then cooled down to 3000 K. Next, the sample has been compressed to higher density and relaxed in N–T–V ensemble (the constant volume and temperature). To collect dynamical data the obtained model is relaxed in N–E–V ensemble (the constant volume and energy) until reach the equilibrium. The temperature and pressure is calculated by averaging over 1000 last configurations separated by 10 steps. The volume and temperature are maintained many times to reach the desired temperature and pressure. More details about the preparing BKS model can be found elsewhere [32]. We have prepared a number of samples at temperature from 2600 to 3500 K under different pressure. To study the influence of size effect a few samples consisting of 3000 atoms have been also constructed.

The coordination cell consists of a central atom (C-atom) and neighbors. The cutoff distance used is equal to 2.38 Å. The bond is formed by a pair of O and Si between which the distance is less than the cutoff distance. As a reaction happens, the current bond

breaks or new bond is created. Most reactions are $SiO_x \rightarrow SiO_{x \pm 1}$ and $OSi_y \rightarrow OSi_{y \pm 1}$. Other types also occur, for instance $SiO_x \rightarrow SiO_{x+2}$. However, they happen extremely rarely. Fig. 1a and b shows how atoms rearrange when two reactions occur. For the first case, a bond is replaced by new bond. In the second case, a bond is broken and then restored. The reaction in the first case is called an effective reaction. The diffusion constant can be described by

$$D = \langle d_{er}^2 \rangle \xi f \tag{1}$$

Where $\langle d_{er}^2 \rangle$ is the mean square displacement of atom per effective reaction which weakly depends on the pressure; ξ is the rate of reaction; f is the fraction of effective reaction. The rate of effective reaction is the product ξf.

The starting configuration comprises a number of bonds which are denoted to Init-bond. Let M_{b0}, M_{bt} be the number of Init-bonds