SPATIAL CORRELATIONS OF MOST MOBILE AND IMMOBILE PARTICLES IN SUPERCOOLED SiO_2

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ABSTRACT

Spatial correlations of most mobile or immobile particles in supercooled SiO_2 model at the temperatures of 2100 K have been investigated using molecular dynamics (MD) method. We evaluate the non-Gaussian parameter for the self-part of the van Hove correlation function, cluster-size distributions and spatial connectivity of most mobile or immobile particles in the model. We have found that mean cluster size grows with decreasing temperature. The mean number of neighbors of fast or slow particles compared with the mean ones has been calculated.

1. INTRODUCTION

The existence of dynamical heterogeneities (DH), it is possible to select subsets of particles that rotate or translate farther or shorter distances than the average distance traveled by a particle on the time of order of the structural relaxation time of the liquid, is now well established in experiments and simulations [1-7]. However, computer simulations can provide more detailed informations related to the DH on the atomistic level, among them are spatial correlations of most mobile or immobile particles. Walter Kob et al. evaluated the non-Gaussian parameter for the self part of the van Hove correlation function in Lennard-Jones liquids and used it to identify mobile particles in the system [5-7]. They found that immobile particles form a core of relatively compact clusters, while mobile particles move cooperatively and form quasi-one-dimensional stringlike clusters [6]. DH in charged colloidal suspensions have been obtained and presented [8]. Mobile and immobile particles in Al_2O_3 also formed a cluster but no relation between local structure and dynamics of particles has been found [9]. The spatially heterogeneous structural relaxation dynamics and the possible relation between dynamics of particles and local structural defects in BKS silica model were found [10,11]. However, DH and the spatial correlations between the most immobile particles and relation between local structure and particle mobility in silica at low temperatures have not been investigated. And such problems will be presented in details in current work.

2. CALCULATION

We use the Verlet algorithm with the MD time step of 1.6fs. The system was cooling from the melt by the cooling rate of 4.2945×10^{13} K/s at constant volume corresponding the real density of vitreous silica of 2.2 g/cm^3. The so-obtained configurations at finite temperatures were subsequently relaxed and then were analyzed in order to investigate static and dynamic properties. In order to calculate coordination number distributions and bond-angle distributions in the supercooled SiO_2, we adopt the fixed values $R_{Si\text{-}Si}$ = 3.6 Å, $R_{Si\text{-}O}$= 2.1 Å and $R_{O\text{-}O}$= 3.2 Å. We performed MD simulations of supercooled silica in a 3000-particle system with periodic boundary conditions. The interionic potentials used in current work are of the form:

$$U_{ij}(r)=\frac{q_iq_j}{r}+D_0\{\exp[\gamma(1-\frac{r}{R_0})]-2\exp[\frac{1}{2}\gamma(1-\frac{r}{R_0})]\}$$

where q_i and q_j represent the charges of ions i and j, for Si ion $q_{Si}=+1.30\,e$ and for O ion $q_O=-0.65\,e$ (e is the elementary charge unit);

r denotes the interionic distance between ions i and j; the parameters of the Morse potentials are given below [12,13]:

Interaction	D_0 (eV)	γ	R_0 (Å)
Si-Si	0.0077	15.3744	3.7598
Si-O	1.9960	8.6342	1.6280
O-O	0.0233	10.4112	3.7910

3. RESULTS AND DISCUSSIONS

TABLE 1. Structural characteristics of liquid and amorphous SiO_2.
r_{ij} – Positions of the first peaks in PRDFs; g_{ij} - The heights of the first peaks in PRDFs; Z_{ij} - The average coordination number (1 and 2 denoted for Si and O, respectively).

T (K)	r_{ij} (Å)			g_{ij}			Z_{ij}			
	1-1	1-2	2-2	1-1	1-2	2-2	1-1	1-2	2-1	2-2
Our data at 2100 K	3.07	1.54	2.57	3.99	12.52	3.52	3.89	3.93	1.97	6.17
Data at 1950 K [14]	3.11	1.56	2.51	4.89	14.16	3.22	4.11	4.00	2.00	6.79
Data at 1923 K [15]	3.17	1.64	2.65	3.80	10.90	2.90	5.13	4.39		7.28
Exp. at 300K [16,17]	3.12	1.62	2.65					4.00	2.00	

Before calculating DH in supercooled silica, let us to see the structure of our model at 2100K, which agrees well with experimental and simulation data (Table 1). For the ideal tetrahedral network structure, the O-Si-O angle is 109.47°, and for our liquid SiO_2 model at the temperature of 2100 K, such angle is equal to 107° indicated slightly distorted tetrahedral network structure. The calculated mean Si-O-Si angle is 143° and close to those observed experimentally of 147° [16,17] or 142° [18].

The DH in the system can be detected via the non-Gaussian parameter: $\alpha_2(t) = \frac{3 < r^4(t) >}{5 < r^2(t) >^2} - 1$. Here $< r^2(t) >$ is the mean-squared atomic displacement, if the system is dynamically homogeneous $\alpha_2(t) = 0$ and it has a maximum at lower temperatures due to the existence of DH. The non-Gaussian parameter $\alpha_2(t)$ of Si, O particles for our supercooled silica system at the temperature 2100 K is shown in Fig. 1, and we can see that it has a maximum indicated the existence of DH in the system. However, the amplitude of the DH of Si and O particles is different like those observed previously in [11]. However, the curves in Fig. 1 have many peaks unlike the single-peak curves in [11]. Possibly, it is related to the specific nature of DH at low temperatures or due to different densities and interionic potentials used here and in [11]. Such problems are left for further study.

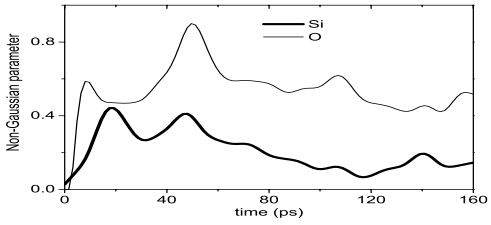

FIG. 1. The non-Gaussian parameter $\alpha_2(t)$ of particles in silica model at 2100 K.

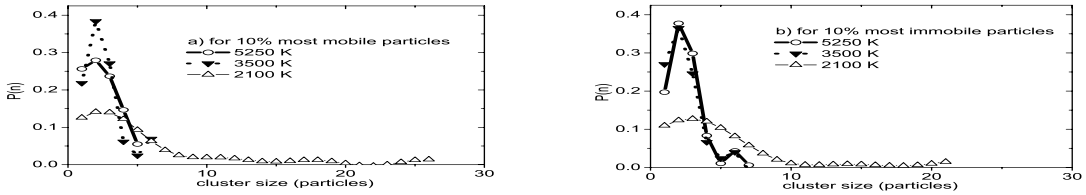

FIG. 2. Cluster size distributions of most mobile or immobile particles in SiO_2 models.

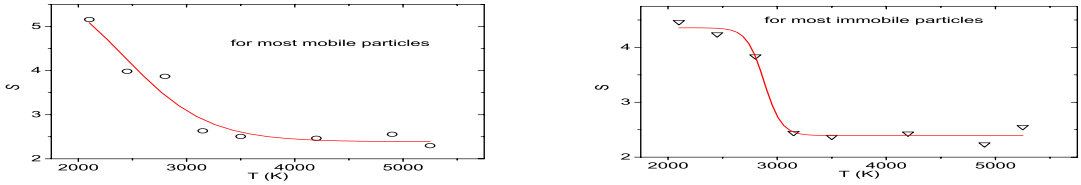

FIG. 3. Mean cluster size $S(T)$ for 10% most mobile and immobile particles.

Particles of extremely low or fast mobility have a tendency to form a cluster and temperature dependence of the mean cluster size, S, of most mobile or immobile particles in Lennard-Jones system showed a power law, $S \sim (T - T_p)^{\gamma}$ unlike those observed for the SiO_2 BKS liquid models [11]. And indeed the most mobile and immobile particles in our system also formed clusters, whose mean size grows with decreasing temperature (Figs. 2 & 3). However, it shows an exponential decay for the most mobile particles, $S = S_0 + A\exp(-T/t_1)$ with $S_0 = 2.307$, $A = 55.037$ and $t_1 = 712$. In contrast, the mean cluster size of most immobile particles strongly increases at around 3000 K and relatively constant with T at lower temperatures. This may be because immobile particles are relatively well packed and can not grow beyond some limiting size [6].

We have accounted the average total number of neighbors of mobile Si and O particles (e.g. $Z_{m\mathrm{Si,Si+O}}$, $Z_{m\mathrm{O,Si+O}}$, see Fig. 4) or of immobile Si and O ones (e.g. $Z_{im\mathrm{Si,Si+O}}$, $Z_{im\mathrm{O,Si+O}}$, see Fig. 4). For comparison, we also calculate the average total number of neighbors of all Si and O particles in the system (e.g. $Z_{\mathrm{Si,Si+O}}$, $Z_{\mathrm{O,Si+O}}$). As shown in Fig. 4, systematic differences in the temperature dependence of average number of neighbors of 10% most mobile or immobile Si, O particles in comparison with the number of neighbors of an average Si and O particles have not been found . This means that there is no relation between local coordination and particle mobility in our SiO_2 system unlike those observed in Lennard-Jones system [7].

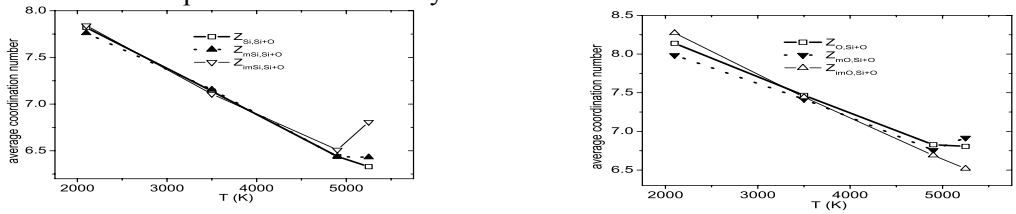

FIG. 4. Average total number of neighbors of most mobile or immobile particles in comparison with the average total number of neighbors of any particles in the system.

4. CONCLUSION

For the first time the existence of dynamical heterogeneities in supercooled SiO_2 at low temperature of 2100 K was established. The time dependence of non-Gaussian parameter of components in our silica system at low temperature of 2100 K was unlike those observed in BKS silica system at higher temperatures by the occurrence of many peaks. We found that particles of extremely low or fast mobility form clusters and the mean cluster size increases upon cooling. The temperature

dependence of mean cluster size of most mobile particles shows an exponential decay unlike those obtained for Lennard-Jones systems. In contrast, upon cooling the mean cluster size of immobile particles increases strongly at around 3000 K and reaches a steady value at lower temperatures.

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