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# Molecular dynamics study of liquid silica under high pressure

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ABSTRACT

Structural changes of liquid silica are investigated under high pressure by molecular dynamics simulation. It is well known that high-silica liquids display anomalous pressure-dependent behavior in their diffusivities. The potential model, the so-called 'soft potential', is used, as it is expected to simulate the structural changes of silica at high temperature well. With increasing pressure, above the glass transition temperature, the simulated silica melt shows the so-called diffusivity maximum under a pressure of 20 GPa, as already shown by the previous studies. However, it is also found that this diffusivity maximum disappears above 2800 K. The analysis of Si coordination number suggests that the competition between the increase of five-fold and that of three-fold controls the extent of the anomaly. Secondly, the analysis of 'local oxygen packing number (LOPN)', that had been developed to investigate geometrical features in amorphous structures, is applied. In a complementary manner to the analysis of the Si coordination number, the local structure in the silica melt shows the gradual structural transformation from a low-density to high density packing on compression. Finally, a model explaining the two types of change of diffusivity in silica melt was proposed in combination with the LOPN analysis and the structon analysis that had been developed to investigate the thermal change of local structures.

## 1. Introduction

It has been suggested that liquid silica shows several anomalous features under compression, such as the existence of a density maximum [1,2], a diffusivity maximum [3–6], and a specific heat anomaly [7]. It is speculated that the local density maximum appears at around 1820 K with an increase in temperature at ambient pressure. Several molecular dynamics (MD) simulations demonstrated the existence of the density maximum [8–11]. MD studies [8–11] also provided insight into its microscopic origin according to which the network structure of silica becomes a compact structure at the corresponding temperature. In a further detailed analysis [23,24], the 'structon analysis' suggested that the expanded structural fragments in common with the ideal β-cristobalite started corrupting and disappearing around the density maximum point. It is interesting to note that this anomaly is thought to be linked with the so-called thermo-mechanical anomaly, e.g. stiffening upon heating and softening upon cooling in silica glass. A further MD simulation explained that the increase of structure fragment similar to that observed in β-cristobalite would be the origin of such thermo-mechanical anomaly upon heating [13]. We speculate that if more β-cristobalite-like fragments exist in the glass, then more corruption of such fragments occurs leading to the system showing a stronger density maximum in the melt.

As for the diffusivity maximum, the local maximum appeared at a pressure of between 10–30 GPa with an increase in pressure above the glass transition temperature. After a pioneering MD study [3] using the WAC potential suggested the existence of the diffusivity maximum at 6000 K, its subsequent study [4] correlated this with a prevalence of five-fold coordination of Si atoms. Related to the coordination change, it was proposed that the diffusion of oxygen atoms occurs through a transient structure with higher coordination [5]. In addition, another MD study [6] also indicated the existence of the diffusivity maximum at 2100 K under a pressure of 20 GPa using a different potential model. The study suggested that the generation of many five-fold coordinated Si atoms increases the diffusivity, while, in contrast, the generation of many six-fold coordinated Si atoms decreases the diffusivity upon further compression. On the other hand, there is no experimental data on the existence of the diffusivity maximum for liquid silica, but several experimental data for the other silicate melt systems, e.g. albite ($NaAlSi_3O_8$) and an equimolar albite/sodium tetrasilicate ($Na_2Si_4O_9$) mixture showed such tendency [14].

Related to the diffusion maximum, it is interesting to investigate how the glass composition changes the pressure dependence of the viscosity of the silicate melts around ambient pressure. The viscosity and the diffusivity are expected to have an inverse relation through the Stokes-Einstein equation. It is well known that lower-silica, highly

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depolymerized aluminosilicate melts behave like normal ionic liquids under compression. Their viscosity, however, increases upon compression. In contrast, higher-silicate melts show an anomalous behavior under compression. Their viscosity decreases upon compression. The positive and negative pressure dependence of the viscosity are explained by a decrease and increase in the entropy of mixing of bridging and non-bridging oxygen atoms [15].

As to the specific heat anomaly, the earlier MD study [7] showed that there is a heat capacity maximum around 4000 K, at which temperature the so-called fragile-to-strong transition was also found using the same BKS potential model [16]. Therefore, this study speculated that the heat capacity anomaly is related to poly-amorphic behavior between a low-density and high-density glass. If any poly-amorphic behavior exists under ambient pressure rather than high pressure, particular attention should be given to the point that two glasses with different density only comprise four-fold coordinated Si atoms. A more recent MD study [17] estimated that the poly-amorphic critical point occurs near 4000 K and 5 GPa by using the WAC potential. In addition, the diffusivity increased monotonically over a temperature range of 3000 K to 8000 K up to a pressure of 16 GPa [18]. For a review of progress on silica simulations over forty years focusing on the glass transition, critical points, and liquid-liquid transitions, we refer to [19].

In this study, MD simulations are used to study the structural transformations in liquid silica under high pressure. The so-called 'soft potential' [12] is used, because the potential could reproduce several high-temperature structural transformations of silica at reasonable temperatures when compared with experiment. The diffusivity of liquid silica is calculated at varying temperature and pressure. Next, the distribution of coordination number around Si atoms and the 'local oxygen packing number (LOPN)' [20] are analyzed at each (P, T) point. Finally, we discuss the dominant structural mechanism relevant to the diffusivity maximum occurring under high pressure.

## 2. Computational model

### 2.1. Potential model and molecular dynamic simulation

Three main MD methods are now available. The most accurate is the first-principles method based on quantum mechanics (e.g. [21]). No interatomic potential model is necessary; however, calculations of diffusivity always require huge computation time. The second model employs the polarizable interatomic potential model (e.g. [22]). By taking the polarizability of the oxygen atoms with an additional degree of freedom, the model can reproduce a spectroscopic feature more precisely. However, the model still requires more computation time than the third model, i.e. the rigid ion model, especially when structure is calculated at high temperature because of slow convergence of the polarizable effects. Although this model is the most efficient in terms of computation time, the choice of interatomic potential model is very important. In this study, the rigid ion model was used enabling long time scale simulations.

Many potential models have been developed for $SiO_2$. Each has its merits and demerits. To simulate liquid silica, it should be noted that the real boiling point of silica is around 2505 K, suggesting that the superheated liquid state above the boiling point is in fact being used to simulate liquid silica; and the further the simulation deviates from the real experimental conditions the more difficult become real quantitative discussions. Two potential models, the 'BKS' potential [16] and the 'soft potential' model, which can be easily implemented in any MD code, were critically examined and their features compared from an objective point of view [25]. The main difference between the two models lies in the magnitude of atomic charges. The charge on the oxygen atoms is $-1.2$ for the BKS and $-0.65$ for the 'soft' model. It is noted that the magnitude of the charge is the smallest for the 'soft potential' model compared to the WAC [3], the BKS, TTAM [5] and CHIK [6] models. It is known that the BKS potential overestimates the melting temperature of crystals by more than 1000 K [30]. It estimated that BKS simulations give the melting temperature of cristobalite at 3600 K, although the experimental temperature is 2000 K. In contrast, the 'soft' potential estimates it at 2400 K. In addition, the 'soft potential' model can estimate the glass temperature at 1400 K compared with the experimental value of 1470 K [12]. The model has reproduced reasonably the structural changes in silica especially at high temperature [23,24] due to the smaller values of the atomic charges. Therefore, the 'soft potential' model was employed in this study.

The functional forms and parameters are listed in a previous paper [12]. The number of atoms in the simulation box is 990 (330 Si and 660 O) in order to ensure consistency between this and a series of previous studies [12,23,24]. Any error analysis due to sample dependency was omitted in this study, such an analysis having been performed in the previous study [24].

The initial structures at each temperature (from 2000 K to 4000 K at 200 K intervals) used the stabilized models calculated in our previous study [12].

At each temperature, the structure was compressed stepwise from 0 GPa up to 32 GPa at 4 GPa intervals and stabilized for 10 ns in the NPT ensemble. After stabilization, the data calculated for 100 ns at each pressure were analyzed to calculate the diffusivity, the coordination numbers and to perform the local oxygen packing number (LOPN) analysis. The diffusivity was calculated from a slope of mean square displacement curve of oxygen atoms. The calculated conditions for the coordination numbers and the LOPN were explained in the previous studies [12,20]. Calculations were performed with the CONDOR High End facilities at UCL.

### 2.2. 'Local oxygen packing number (LOPN)' analysis

The LOPN analysis is a geometrical modeling technique developed by the author [20], especially to investigate the local structural changes in the amorphous and liquid states on compression. Conventional modeling regards the whole structure as comprised of polyhedra that are calculated from the coordination number around a cation atom. In the case of silica system, this modeling is convenient to distinguish between polyhedra with four-fold, five-fold, and six-fold Si atoms. On the other hand, it cannot distinguish between the low-density and the high-density tetrahedral structures, because both are comprised of the same four-fold Si atoms. In contrast, the LOPN can distinguish between the low-density structure with the four-fold coordination, the high-density with four-fold, and the ultra-high-density structure with the six-fold as shown in the previous study [20]. The LOPN is calculated for each O atom as a number of its surrounding O atoms within a cut-off distance of 3.03 Å. In the case of silica crystal structures, the LOPN of cristobalite (or quartz), coesite and stishovite have each a sharp peak of 6 and 7, and 12. In contrast, silica glass has a broader distribution of the LOPN. It is expected that the LOPN of 5–6, 7–8, 11–12 each corresponds with the low-density with four-fold coordination, the high-density with four-fold coordination and the ultra-high-density local structure with six-fold coordination in either amorphous or liquid.

### 2.3. 'Structon' analysis

The 'structon' analysis was developed to investigate the thermal structural changes in silica glass and liquids [23]. Each $Si_2O_7$ unit found in simulated structures was categorized into four 'structons' based on two indices that seemed to represent the structural features. As temperature increases, each structon converts from $\alpha$- to $\delta$-structon through $\beta$- and $\gamma$-structon. The first index is a standard deviation of torsion angles between two neighbouring $SiO_4$ units. The index distinguishes between $\alpha$- and $\beta$-structon. The second index is a 'bonding state' depending on temporal changes in Si—O bonds. The index distinguishes between $\beta$- and $\gamma$-structon, and between $\gamma$- and $\delta$-structon. The calculated procedures are explained in Ref. [23]. At the moment, this

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