Molecular Dynamics Study of Pressure Enhancement of Ion Mobilities in Liquid Silica

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Melts of many silicates are known to have an anomalous transport property in that the diffusivity of oxygen atoms drastically increases with pressure. Here we propose a mechanism for the anomalous diffusion process in liquid silica and silicates on the basis of molecular dynamics (MD) results for pressure-induced structural transformations in crystalline silica. The model is successfully tested with a MD simulation for liquid silica with an interatomic potential based on a first-principles calculation. A close relation between the diffusivity of oxygen atoms in molten state and the relative stability of polymorphs of silica is clarified.

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Transport properties of silicate melts have been intensively studied because of geological interest, since they are closely related with the igneous processes in the Earth. A conspicuous and anomalous feature is that the viscosity in the liquid phase of many silicates such as jadeite ($NaAlSi_2O_6$) drastically decreases with increasing pressure [1,2] just as in the case of water and aqueous solutions. Microscopically this implies that the principal elements in the silicate melts, i.e., oxygen and silicon (and aluminum) atoms, diffuse more easily at higher pressures, as confirmed experimentally [3].

The anomalous diffusion property in silicates is characteristic when they have highly polymerized framework structures comprising corner-shared SiO_4 (or AlO_4) tetrahedra. In fact, when the framework is destroyed by a sufficient amount of alkali or alkaline earth metals, as in the melt of diopside ($CaMgSi_2O_6$), the system no longer shows such an anomaly and the viscosity increases with pressure [4].

Molecular dynamics (MD) studies on the anomalous diffusion property were carried out by Angell *et al.* [5,6]. They successfully showed that, in the melt of jadeite composition in which the SiO_4 (AlO_4) tetrahedra are well polymerized, the self-diffusion coefficients of oxygen, silicon, and aluminum atoms have maxima at a pressure of 20–30 GPa, whereas the diffusion coefficient in the less polymerized melt of diopside decreases with pressure. On the mechanism of the anomalous diffusion process, they pointed out the importance of fivefold coordinated silicon atoms, a fraction of which also has a maximum at the pressure corresponding to the maximum diffusivity.

Although their MD results show qualitative agreement with the experimental results, and though their insight into the diffusion might be essentially relevant, the mechanism of the anomalous diffusion process is still not clear because of ambiguities inherent in their simulation. The largest ambiguity concerns the interatomic potential. Angell *et al.* empirically determined the potential on the basis of interatomic distances at low pressures. Inclusion of elements that destroy the framework further complicates the discussion.

In this context, here we reinvestigate the mechanism of the anomalous diffusion process in silicate melt by an MD simulation of silica (SiO_2) with a well-characterized interatomic potential based on a first-principles cluster calculation. Viscosity of the framework GeO_2 has also been shown to have anomalous pressure dependence experimentally [7], and so it is considered that the silica melt should also show an analogous anomaly. Silica, an end member of silicate compounds, has a complete framework structure, so that the material is ideal for theoretical analysis.

The pairwise interatomic potential used in this study was first derived from first-principles electronic structure calculations for small clusters. Although there have been several empirical approaches to obtaining pairwise interatomic potentials for silicate, nonempirical determination of the potential is obviously desirable, and we have in fact succeeded in simulating the structures and bulk moduli of all the known polymorphs of silica at room temperature [8]. The potential was then successfully used in the simulation of the thermally induced phase transition of quartz [9] and pressure-induced amorphization with a slight refinement of the parameters [10]. The validity of the potential has also been examined by a number of groups [11].

Here we summarize our MD results on the pressure-induced amorphization at room temperature, which is quite suggestive for investigating microscopic mechanisms of the atomic diffusion process. In the simulation, hydrostatic pressure was applied to four polymorphs of silica at room temperature. Low quartz and coesite undergo structural transformations with discontinuous volume reduction at pressures of 25–30 GPa and 35–40 GPa, respectively.

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The critical pressures are in good agreement with those for pressure-induced amorphization obtained experimentally [12]. Low cristobalite shows two-staged structural transformation [13], while stishovite is stable up to the highest pressure we examined. Though the detail of the final structures depends on the polymorphs and also on the MD runs, high-pressure phases always contain silicon atoms octahedrally coordinated by oxygen atoms. Similar results are reported with an interatomic potential with slightly different parameters which are also based on the first-principles cluster calculation [14].

Interestingly, these structural transformations occur without atomic diffusion in the sense that no isolated atoms or disordered states appear at the transition. The mechanism of these diffusionless transformations is illustrated in Fig. 1.

A framework of corner-shared SiO_4 tetrahedra in the low-cristobalite structure is represented in Fig. 1(a). When the pressure is increased the framework transforms displacively into the structure shown in Fig. 1(b). This structure can be regarded as comprising a sixfold Si-O coordination on the basis of the Si-O distance. Thus the Si-O coordination number increases smoothly without either breaking any Si-O bonds or introducing global atomic diffusion [15]. This mechanism for compression is essentially the same as that suggested by Stolper and Ahrens for amorphous silica [16].

From the mechanism above, it is naturally expected that the transformation from fourfold to sixfold coordination is reversible. In fact, most high-pressure phases obtained here are unquenchable upon decreasing pressure even at room temperature and become an amorphous phase, in which all silicon atoms are tetrahedrally coordinated. Moreover, the fact that the decompression gives rise to an amorphous rather than a crystalline phase means that the way of unfolding sixfold coordination into fourfold coordination is locally not unique. For example, the highly coordinated structure in Fig. 1(b) does not always resume the structure in Fig. 1(a) but also transforms into a new framework structure in Fig. 1(c).

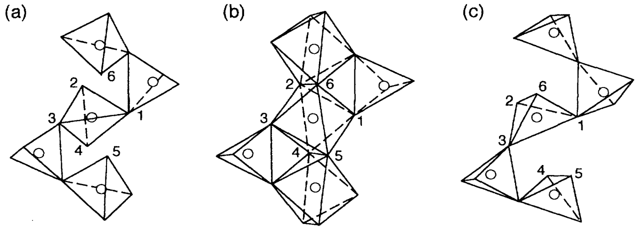

FIG. 1. Pressure-induced structural transformation obtained by MD simulations at room temperature. (a) A framework of corner-shared SiO_4 tetrahedra in a low-pressure phase (low cristobalite), where silicon atoms are shown with circles. Oxygen atoms related with the structural transformation are numbered. (b) The framework structure deformed under pressure. (c) The framework structure after released pressure.

Based upon the MD results given above, we propose a microscopic model for atomic diffusion in silica. We have stressed that the obtained structural transformations are diffusionless. However, this is in a specified meaning of the word, in which a diffusive transition is defined as the one accompanied by the appearance of isolated atoms. The diffusionless transformation modes contribute to the mechanism of diffusion in the following sense. When the low-pressure structure in Fig. 1(a) is compressed into the high-pressure structure in Fig. 1(b) and then decompressed to the structure in Fig. 1(c), the framework of the corner-shared SiO_4 is topologically rearranged, although no isolated atoms appear during the process. The coordination of silicon atoms changes from fourfold to sixfold and then to fourfold again with different oxygen atoms. If we envisage a process in a disordered phase in which the compressions and decompressions are repeated, this could result in a diffusion of atoms. Since local pressure or stress is thought to fluctuate in a melt, we can expect such a diffusion in a liquid phase. Sixfold coordination is then realized as a local and transient state for diffusion. Note that the diffusion considered here does not accompany isolated atoms but is regarded as continuous changes of Si-O coordination numbers, which will require much less energy than that needed for stripping an oxygen atom from a fourfold coordinated silicon atom.

Now the anomalous diffusion property can be simply explained as follows. The crucial factor for atomic diffusion in the present model is the activation energy needed for forming sixfold coordination from fourfold coordination locally. Then the activation energy is considered to be highly correlated with the enthalpy difference between fourfold and sixfold coordinated phases. As is well known, low-pressure phases of silica allow only fourfold coordination and have relatively small bulk moduli, while the high-pressure phase is characterized by sixfold coordination and large bulk modulus. So the enthalpy of the fourfold coordinated phase and that of the sixfold coordinated phase have different pressure dependence and coincide with each other at a certain critical pressure P_C. Thus the activation energy decreases up to P_C and the diffusion coefficient will have a maximum there. Above P_C, the activation energy for diffusion will be the energy required to make a fourfold coordination in a sixfold coordinated system, which is an increasing function of pressure, so that the diffusion coefficient now decreases with pressure. Although in real situations the average coordination number should be somewhere between four and six, the present picture still holds.

The model for the anomalous diffusion process may be confirmed by demonstrating a correlation between the diffusivity and the enthalpy difference. The interatomic potential we have developed has two virtues for this purpose. First, the potential can reproduce the structures and bulk moduli of both fourfold and sixfold coordinated polymorphs of silica. Second, we can tune the relative stability of fourfold and sixfold coordinated polymorphs by a slight modification of a potential parameter without losing the first virtue.

The interatomic potential has the following functional form:

$$U_{ij}(r)=\frac{Q_iQ_j}{r}+f_0(b_i+b_j)\exp\left[\frac{a_i+a_j-r}{b_i+b_j}\right]-\frac{C_{ij}}{r^6}, \tag{1}$$

where r is the distance between the ith and the jth atoms and $f_0 = 1$ kcal Å^{-1} mol^{-1}. The potential parameters used in the simulation of the pressure-induced amorphization [10] are $Q_{\mathrm{Si}} = +2.4$ and $Q_{\mathrm{O}} = -1.2$ in elementary charge, $a_{\mathrm{Si}} = 0.86$, $a_{\mathrm{O}} = 2.05$, $b_{\mathrm{Si}} = 0.176$, and $b_{\mathrm{O}} = 0.033$, in Å, $C_{\mathrm{SiSi}} = 0$, $C_{\mathrm{SiO}} = 1633$, and $C_{\mathrm{OO}} = 4956$ in kcal Å^6 mol^{-1}. As the relative stability of fourfold and sixfold coordinated systems is sensitive to the atomic radius ratio $a_{\mathrm{Si}}/a_{\mathrm{O}}$, we purposely vary this ratio to tune the relative stability to investigate its correlation with the diffusion coefficient.

We consider three sets of potential parameters, where $a_{\mathrm{Si}} = 0.86$ Å (type I), $a_{\mathrm{Si}} = 0.87$ Å (type II), and $a_{\mathrm{Si}} = 0.88$ Å (type III), and the values of other parameters are fixed as above. As reference systems of the fourfold and sixfold coordinated phases, we have chosen coesite and stishovite, respectively, since they are the most stable representatives that we tested so far with the present interatomic potentials [17]. Densities and bulk moduli of coesite and stishovite are reproduced by the three sets of potentials with at most 15% error at room temperature, since they are rather insensitive to a_{Si}. However, the relative stability of coesite and stishovite is substantially different for the three. The critical pressure P_C is estimated by MD simulations at room temperature to be 9.9 (type I), 4.7 (type II), and 0.7 (type III) GPa, respectively. Experimentally, P_C is estimated to be about 6–8 GPa [18].

Starting from crystalline (low-cristobalite) configuration for the ambient pressure we melt the system at 4000 K for 100 psec in the MD run. The pressure is then increased by 4 GPa up to 32 GPa. The pressure was controlled by keeping the cubic symmetry of the basic cell and the temperature was controlled by a simple scaling of momenta in this simulation. After at least 40 psec (20 000 MD steps) equilibration at each pressure, the diffusivity or diffusion coefficient D is determined from the data accumulated over 120 psec using Einstein's relation. We found, even at 4000 K, a long-term simulation of more than several tens of psec is necessary for deriving a reliable D free from fluctuation. The above process is repeated for each of the three parameter sets.

The number of particles contained in the basic cell for the periodic boundary condition is 567 (192 $\mathrm{SiO_2}$). We have also looked into a larger system with 768 particles with type I potential to check the size effect and found no appreciable difference within all the pressure range. The only difference is that the fluctuation in D against time is relatively small for the larger system. A smaller system with 324 particles gives qualitatively similar results, while D is slightly underestimated except around P_C [19].

The key result for the pressure dependence of D for oxygen at 4000 K for the three types of parameter sets is shown in Fig. 2. The results for silicon are qualitatively very similar to those for oxygen. A common characteristic for the three parameter sets is that the diffusion coefficients show maxima in D-P relation as reported for silicate by Angell *et al.* [5,6]. This is exactly the anomalous diffusion property. Moreover, a new finding here is that there exists a conspicuous correlation between the pressures which give the highest diffusivity and the P_C's estimated before.

The activation volume ΔV defined by $D(P) \propto \exp(-P\Delta V/k_BT)$ is about (–3)–(–5) cm^3/mol around 0 GPa. This is very close to the difference of the molar volume per oxygen in coesite and stishovite, and comparable with -6.3 ± 1.2 cm^3/mol for jadeite obtained experimentally [1].

Diffusivity of an atom can be written approximately as

$$D \sim a^2\nu\exp\left(-\frac{\Delta E}{k_BT}\right), \tag{2}$$

where a is a typical length scale for the elementary process of diffusion, ν is a trial frequency, and ΔE is an activation energy for diffusion. a is proportional to $V(P)^{1/3}$ where $V(P)$ is the molar volume at pressure P known from the simulation of melt. Along the present mechanism, we postulate that ΔE is proportional to $|H_{\mathrm{coe}}(P) - H_{\mathrm{st}}(P)|$, except for a constant independent of pressure, where $H_{\mathrm{coe(st)}}(P)$ is the enthalpy of coesite

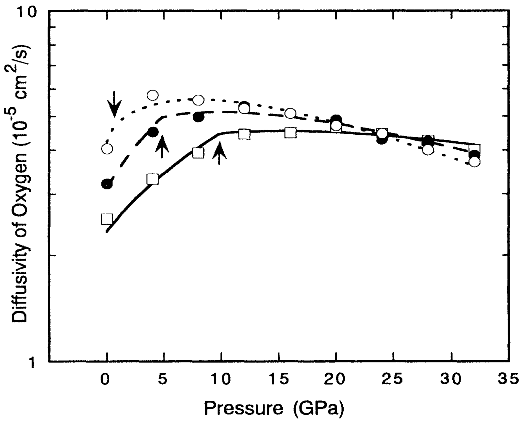

FIG. 2. Pressure dependence of the diffusivity of oxygen atoms at 4000 K. Three kinds of symbols and lines correspond to three types of potential parameters: type I (□, solid line), type II (●, dashed line), and type III (○, dotted line), where the size of the symbols approximates the error bars. The lines are the results of the least-square fitting with Eq. (3). P_C's for each potential are denoted with arrows.

(stishovite) obtained from simulations at room temperature with some extrapolation. Finally we assume that ν is proportional to $K(P)^{1/2}$, where $K(P)$ is the bulk modulus of the melt at each pressure derived from the simulations of melt. It should be noted that, if we do not include the pressure dependence of $a^2\nu$, D is symmetrical below and above P_C. Thus we obtain

$$\begin{aligned} \ln D = {} & \tfrac{2}{3}\ln V(P) + \tfrac{1}{2}\ln K(P) \\ & - \frac{c_1}{k_B T}\,|H_{\mathrm{coe}}(P) - H_{\mathrm{st}}(P)| + c_2 \,. \end{aligned} \qquad (3)$$

We found that two fitting parameters (c_1, c_2) for each type of potential are sufficient to reproduce the tendency of the pressure dependence of D as shown by lines in Fig. 2. Note that the pressures corresponding to the maximum diffusivity are systematically larger than P_C's owing to the second term in the right-hand side of Eq. (3). The cusps in the fitting lines come from the third term in Eq. (3), which will be smoothed if we take account of the thermal fluctuation. For more precise discussion, thermal expansion of the system should also be considered in the estimation of $|H_{\mathrm{coe}}(P) - H_{\mathrm{st}}(P)|$. Nevertheless the agreement of the fitting lines with the MD results is sufficient to show that the potential parameter dependence of the D-P relation is primarily governed by the difference in P_C. This serves as clear evidence that the mechanism for the atomic diffusion in silica melt presented in the above is indeed in action.

In summary, we have provided a realistic mechanism on the diffusion process in the melts of silica and framework silicates: The atomic diffusion arises from the transient increase of the coordination number of silicon atoms, which results in rearrangement of the framework structure. The anomalous diffusion property is explained in a natural way in this picture. The mechanism has been tested successfully with the MD simulation.

Finally it should be stressed that the interatomic potential used here is based on a first-principles electronic structure calculation and is reliable enough to reproduce the pressure dependence of the enthalpy of the polymorphs of silica. Such a realistic interatomic potential combined with moderate control of the potential parameter has first enabled us to clarify the close relation between the diffusivity of oxygen atoms in molten state and the relative stability of the polymorphs of silica.

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