Structural and dynamical properties of supercritical H$_2$O-SiO$_2$ fluids studied by ab initio molecular dynamics

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Abstract

In this study we report the structure of supercritical H$_2$O-SiO$_2$ fluid composed of 50 mol% H$_2$O and 50 mol% SiO$_2$ at 3000 K and 2400 K, investigated by means of ab initio molecular dynamics of models comprising 192 and 96 atoms. The density is set constant to 1.88 g/cm$^3$, which yields a pressure of 4.3 GPa at 3000 K and 3.6 GPa at 2400 K. Throughout the trajectories, water molecules are formed and dissociated via the network modifying reaction 2 SiOH = SiOSi + H$_2$O. The calculation of the reaction constant $K = [OH^-]^2/[H_2O][O^2-]$ is carried out on the basis of the experimentally relevant Q$^*$ species notation and agrees well with an extrapolation of experimental data to 3000 K. After quench from 3000 K to 2400 K, the degree of polymerization of the silicate network in the 192-atom models increases noticeably within several tens of picoseconds, accompanied by release of molecular H$_2$O. An unexpected opposite trend is observed in smaller 96-atom models, due to a finite size effect, as several uncorrelated models of 192 and 96 atoms indicate. The temperature-dependent slowing down of the H$_2$O-silica interaction dynamics is described on the basis of the bond

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1. Introduction

Geological processes such as mineral melting and magmatism are governed by the interplay of silicate matter with volatiles such as H$_2$O.[1, 2] The system H$_2$O-SiO$_2$ is a simplified chemical model to study hydrous silicate melt.[3, 4, 5] At conditions of the Earth’s lower crust and upper mantle, the large region of immiscibility in this system closes with increasing pressure and temperature, eventually leading to a single-phase supercritical fluid above 1 GPa and about 1330 K, as indicated by the solubility lines in Fig. 1.[6, 7, 8, 4, 5] The terms silica-rich fluid and H$_2$O-rich melt then become a question of semantics. Since large amounts of H$_2$O are released from the subducted oceanic plate in subduction zones,[1, 9] it is possible that supercritical hydrous melts form in or above the subducted slab.[10, 11] Knowledge about the structure of supercritical H$_2$O-SiO$_2$ fluids will help understanding their physical properties, such as density and viscosity, which are important constraints for the dynamics of petrological and geochemical processes in the subduction systems.[12, 10, 13] Computational models can give valuable insight into the structure and behavior of this material that is very challenging to investigate by in situ experiments.[14, 10]

The structure of silica-rich fluids and silicate melts below 5 GPa is generally considered to be governed by interconnected [SiO$_4$]$^{4-}$ tetrahedra. Their state of polymerization can be characterized in terms of Q$^n$ species, with $n$ indicating the number of oxygen atoms shared with other tetrahedra. This common Q$^n$ species notation is the experimentally intuitive approach to the structural description of a tetrahedral network, since the vibrational and other properties are dominantly governed by the degree of polymerization in a network. A Q$^4$ species is a [SiO$_4$]$^{4-}$ tetrahedron with four Si-O-Si bridging oxygen atoms and therefore highest degree of polymerization, as in pure silica. A Q$^3$ species is a tetrahedron with one hydroxy group and three Si-O-Si bridging oxygen atoms, and a Q$^0$ species is a tetrahedron not attached to any other tetrahedron.[15] H$_2$O in silicate melts exists predominantly in the form of SiOH hydroxy groups and of
molecular H$_2$O that fills voids in the silicate network or forms small clusters.[16, 17] These species mutually exchange in the network breaking reaction

\[ \text{SiOSi} + H_2O \rightarrow 2\text{SiOH} \]  \hspace{1cm} (1)

Figure 1: Black and grey curves indicate the solubility of SiO$_2$ in H$_2$O as a function of temperature and pressure, according to the model of Hunt and Manning.[5] The compositions, temperatures and pressures of the 192-atom models in the present study (indicated by black dots) fall in the composition region of complete miscibility of H$_2$O and SiO$_2$.

Therefore, oxygen atoms occur in three species in the system H$_2$O-SiO$_2$: Molecular water (MWO), Bridging oxygen (BO) in the silica network, and non-bridging oxygen (NBO) in the form of hydroxy groups at its terminal branches. Structure, viscosity, self-diffusion coefficients and other properties of silica-rich supercritical fluid or of sub-critical hydrous silicate melt are governed by the extent to which reaction 1 proceeds to either side. This reaction is particularly temperature-dependent and less affected by pressure. Considerable experimental effort has been dedicated to determine the temperature-dependent speciation of H$_2$O in hydrous silicate glasses and melts,[18, 19, 15] Fig. 2 shows an experimentally established temperature-dependence of the reaction constant \( \ln K = [\text{OH}^-]^2/[H_2O][O^2-] \) for hydrous rhyolitic glasses,[20] with an extrapolation to the higher temperatures accessible to molecular dynamics (MD) modeling. This reaction constant is concentration-independent at low water contents, where dissociation of H$_2$O to SiOH groups (NBO) is the predominant dissolution.
At higher \( H_2O \) concentrations, the dissolution mechanism is assumed to shift from the chemical dissolution via dissociation to physical dissolution via the accommodation of increasingly clustered \( H_2O \) molecules in the partially broken silica network.

Indications for a shift in the dissolution mechanism have been found in several studies. Newton and Manning\[4\] predicted for 1350 K and 1 GPa a plateau of \( H_2O \) activity at about 50 mol% \( H_2O \). The content of molecular water, as opposed to hydroxy groups, is expected to steeply increase in this compositional region. In related systems, such as hydrous albitic melts, a similar change in the \( H_2O \) dissolution mechanism has been assumed for about 30 mol% \( H_2O \).[19, 21] Since the temperature and pressure conditions make experimental investigation very challenging, computational data may be insightful. Fig. 2 compares the extrapolated experimental reaction constant\[20\] to the calculated \( K \) values for several computational studies. For the calculation of \( K \), the activity coefficients of all species are assumed unity, and the concentration values are calculated assuming that the presence of oxygen species other than SiOH, \( H_2O \) and SiOSi are negligible.

In their ab initio MD study on \( SiO_2 \) with 11.8 mol% \( H_2O \), Pöhlmann \textit{et al.} observed molecular water as low as 0.06 mol% at 3000 K and 0 bar.[22] Karki and Stixrude\[23\] found by ab initio MD that in a silica melt with 23 mol% \( H_2O \) at 1.5 GPa and 3000 K, only 8.3% of the nominal \( H_2O \) forms molecular water. Anderson \textit{et al.}\[24\] found in a Reverse Monte-Carlo study using the classical Garofalini-potential,[25] that in a supercritical fluid of 40 mol% \( H_2O \) in \( SiO_2 \) at 3000 K and 1 GPa, only 1% of the nominal water was molecular \( H_2O \).

As described above, \( \ln K \) is expected to be concentration-dependent at high \( H_2O \) concentrations, and it is then expected to deviate downward from the shown linear relation of the type \( \ln K = a/T + b \). However, the agreement of the computational data and the extrapolated experimental data in Fig. 2 is surprisingly good. In the inset in Fig. 2, \( \ln K \) is plotted for selected data points as a function of nominal \( H_2O \) content. The \( \ln K \) up to 40 mol% nominal \( H_2O \) content indicates only a weak downward trend. This raises the question whether the downward trend (arrow in inset of Fig. 2) increases when the \( H_2O \) concentration is increased to the level of 50 mol%, where Newton and
Manning[4] found a plateau of H$_2$O activity.

The modeling results by Pöhlmann et al. show a peculiarity: The resulting ln K increases from 3500 K to 3000 K, which contrasts to what is expected from thermodynamics. One reason may be the low density of their models, which leads to a pressure of 0 bar.[22] Another reason could be a non-equilibrated model within their trajectory length of 22.5 ps. However, it is also possible that the small number of 102 atoms used in their models, causes a finite size effect that obstructs the structural adaptation after lowering the temperature.

In the present study, we aim to investigate the structure of supercritical H$_2$O-SiO$_2$ fluid with 50% H$_2$O, and to explore whether the assumed change in dissolution mechanism at this high H$_2$O content can be evidenced in the model. At the same time, we intend to establish, under which temperature conditions ab initio MD can contribute to verifying thermodynamical predictions as those regarding the shift in solution mechanism in supercritical H$_2$O-SiO$_2$ fluids.[4] Once these conditions are clarified, the predictive power of high-temperature ln K relations derived from ab initio MD models would increase. This will eventually allow a hand-shake with experiments on the important relaxation processes in hydrous silicate melts,[26] for which ab initio modeling accuracy is so important.

The structure of this study on the single-phase supercritical equimolar H$_2$O-SiO$_2$ fluid is as follows: The modeling approach is described in Section 2. Routines were chosen to generate unbiased and mutually independent starting configurations (Section 2.2). In a first modeling step at 3000 K, we established a simple P-V relationship to find a realistic and suitable density (Section 3.1). Then we set up several models of two different sizes to evaluate the uncertainty due to finite size effects. The structure at 3000 K is described in terms of Q$^c$ species and oxygen species in Subsections 3.2 and 3.4.

The smaller size models were then cooled in two successive steps to 2400 K to explore the slowing-down of bond dynamics, which has to persist if structural equilibrium is to be sampled (Subsection 3.3). We found the Si-O bond dynamics to be high enough, at least to observe structural adaptation after quenching all models to 2400 K. The results at 2400 K point at substantial differences between the two different model
Figure 2: Comparison of the equilibrium constant $K$ of the reaction $\text{H}_2\text{O} + \text{BO} = 2 \text{OH}$ from various sources. Solid black line: Experimental data of rhyolitic melt between 0.1 and 0.3 GPa and 1.27 to 5.15 wt% $\text{H}_2\text{O}$\cite{20}; large empty circle: model results of ab initio MD of 23 mol% $\text{H}_2\text{O}$ in $\text{SiO}_2$ at 3000 K and 0.01 GPa\cite{23}; empty squares: results of Reverse Monte Carlo for 40 mol% $\text{H}_2\text{O}$ at 3000 K and 2.5 GPa\cite{27}; small empty circles: for 40 mol% $\text{H}_2\text{O}$ at 3000 K and 0.25 GPa\cite{27}; triangles: values by Pohlmann et al. for 11.8 mol% $\text{H}_2\text{O}$; Inset: ln $K$ values from inside the ellipse, plotted as a function of $\text{H}_2\text{O}$ concentration. The arrow indicates a possible downward trend of ln $K$, assumed on the basis of experimental observations\cite{19, 21} and results of thermodynamic modeling\cite{4}.

sizes (Subsections 3.4 and 3.5). We conclude this study with a comparison of our results to literature data and a possible explanation for the observed structural differences between the two different model sizes.

2. Methods

2.1. Modeling technique

We used density functional theory\cite{28} in the plane wave pseudopotential approach as implemented in the CPMD code\cite{29} PBE was used as exchange-correlation functional\cite{30}. Disordered network forming systems have been found to be better described by generalized gradient approximation functionals than by those functionals of the local density approximation type.\cite{31, 32, 33, 34, 35} Martins-Troullier type pseudopotentials were used.\cite{36} Spin polarization was not considered.\cite{37} The Kohn-Sham wavefunctions were expanded at the $\Gamma$-point with a cutoff energy of 80 Ry. Dependence of elec-
tronic potential on more extended k-point sampling was found to be negligible. Forces were within about 1% deviation compared to those obtained with larger plane wave cutoffs of 140 Ry. All modeling runs were performed in the canonical (NVT) ensemble in periodic boundary conditions. Temperature was controlled by a Nosé-Hoover thermostat.[38] Pressure was calculated from the trace of the continuously calculated stress tensor, which was corrected by the Pulay pressure for incompleteness of the basis set.[39, 40, 41]

We used Car-Parrinello molecular dynamics[42] with a fictitious electronic mass of 400 a.u. (3.64·10^{-28} kg) and an integration time step of 4 a.u. (0.097 fs).[43, 44, 45] The ratio of fictitious electronic mass to the mass of hydrogen is 0.22. It has been shown that this reduces the effect of the electronic dynamics on the structure H\textsubscript{2}O at 300 K to a negligible level in comparison to Born-Oppenheimer molecular dynamics.[44] This is also valid for dynamical properties. For instance, the effect of Car-Parrinello molecular dynamics on the diffusion coefficient in H\textsubscript{2}O at 300 K has been found to be on the order of factor 2,[44] which is of the same magnitude as is the effect of the choice of the exchange-correlation functional.[46]

Atomic positions and velocities were recorded every 40 a.u (0.97 fs). The fictitious electronic kinetic energy was thermostated. The Car-Parrinello forces agreed to 98% with the forces from a fully energy-minimized wavefunction as in Born-Oppenheimer MD. This was checked for several configurations throughout a run, up to 5 ps after the last Born-Oppenheimer wavefunction optimization.[47]

The above described methods and parameters have been used by the authors in earlier studies on the vibrational properties of silica species in aqueous fluids and hydrous silicate glasses.[48, 49]

2.2. Setup of Models

As the first step of this work, we obtained information on the volume-pressure relation at 3000 K to determine an appropriate density to be used in the following modeling steps. For this, we set up three 192-atom models at three densities between 1.4 and 2.05 g/cm\textsuperscript{3} (Table 1). These densities are based on literature data on pure SiO\textsubscript{2}, pure H\textsubscript{2}O and the partial molar volume of H\textsubscript{2}O in silicate melts.[50, 51, 52, 53] Initial
configurations were generated using an automated routine (referred to as R1 in Table 1) to exclude bias. For this, we used the final configuration of a classical 200 ps MD run of pure SiO$_2$ at 3000 K with the PIMAIM potential.[54] Randomly chosen silicon atoms were removed, and for each removed silicon atom four hydrogen atoms were inserted, each near to one of the four faces of a tetrahedron where a silicon atom had been removed. In addition to this first routine, a second automated routine (referred to as R2) is used in this study for the generation of unbiased initial configurations. A given cell volume is filled with atoms, under constraints regarding the minimal atomic distances, equal to the positions of the first maximum in the pairwise radial distribution functions from Pöhlmann et al.[22] The three models for the density-pressure relation started from the same initial configuration which was generated using the first routine (Table 1). They were run for 30 ps after initial equilibration of 11 ps. Pressure calculation of each of these models allowed us to obtain information on the volume-pressure relation as shown in Fig. 3. Due to lack of experimental data in the system of pure H$_2$O-SiO$_2$, apart from the Pulay-pressure, no additional pressure correction was used to account for systematic overestimation of silicate density by the PBE functional. The pressure fluctuation, calculated as mean absolute error (MAE), is indicated in Table 1.

In the following steps of this work, all models were run with constant molar volume of 20.7 cm$^3$/mol (density 1.88 g/cm$^3$). This density resulted in a pressure of 4.3 GPa at 3000 K (Table 1) and about 3.5 GPa at 2400 K as representative for upper mantle conditions.

As the next step, several mutually independent models of equimolar composition were set up: three large 192-atom models (models L1 to L3, 32 H$_2$O and 32 SiO$_2$ nominally, Table 2) and three medium-sized 96-atom models (M1 to M3, 16 H$_2$O and 16 SiO$_2$ nominally). The setup of separate, equally sized models allows us to obtain information on the variability of the structure at otherwise identical modeling conditions.[51, 34] two different model sizes yield information on the structural effect of system size. The temperature-cascade regime that we carried out on the models is given in Table 2. After runs at 3000 K, four models were quenched to 2400 K, two other models were run at an intermediate step at 2700 K before quench to 2400 K. Total run duration at 2400 K was between 100 and 200 ps (Table 2).
Table 1: The 192-atom models L-D1 to L-D3 (32 H$_2$O and 32 SiO$_2$) for an estimate of the density-pressure relation at 3000 K (Fig. 3). Molar volume refers to (H$_2$O)$_{0.5}$(SiO$_2$)$_{0.5}$.

<table>
<thead>
<tr>
<th>model label:</th>
<th>L-D1</th>
<th>L-D2</th>
<th>L-D3</th>
</tr>
</thead>
<tbody>
<tr>
<td>density (g/cm$^3$):</td>
<td>1.4</td>
<td>1.88</td>
<td>2.05</td>
</tr>
<tr>
<td>molar volume (cm$^3$/mol):</td>
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<td>20.7</td>
<td>19.0</td>
</tr>
<tr>
<td>model further used as:</td>
<td>–</td>
<td>L1</td>
<td>–</td>
</tr>
<tr>
<td>equilibration run (ps):</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>production run (ps):</td>
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<td>30</td>
<td>30</td>
</tr>
<tr>
<td>pressure at 3000 K(GPa):</td>
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<td>4.3</td>
<td>5.6</td>
</tr>
<tr>
<td>MAE of pressure (GPa):</td>
<td>0.8</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

For comparison and reference, we carried out a MD run of 20 ps for pure SiO$_2$ at 3000 K and molar volume of 45.8 Å$^3$/SiO$_2$, which is similar to the experimental volume of SiO$_2$ melt at the ambient conditions melting point.[55] The initial configuration of the SiO$_2$ model is the same as the seed that was used in routine 1 to construct models L-D1 to L-D3 (Table 1).

3. Results

3.1. Density-pressure relation

The MD runs of models L-D1 to L-D3 yield three points in the P-V plane (Table 1 and Fig. 3). Literature pressure-volume data of pure SiO$_2$ and of pure H$_2$O, and the partial molar volume of H$_2$O in silicate melts are shown for comparison.[51, 56, 53]. The density of 1.88 g/cm$^3$ was chosen for further modeling.

3.2. Radial distribution and coordination functions

The computation of the pairwise radial distribution function (RDF) for for Si-O, O-H, O-O, Si-Si and H-H is the basis for further structural or dynamical evaluation of the structure. The RDFs from model L1 are shown for 3000 K in Fig. 4, pure SiO$_2$ is shown for comparison. The RDFs of O-H and Si-O are almost insensitive to temperature between 3000 K and 2400 K (not shown). The fundamental short-range
Table 2: Time-temperature regimes for all models. At each temperature, trajectories are separated in equilibration run and subsequent production run. All models are at density of 1.88 g/cm$^3$. The pressure in parenthesis refers to runs L-D1 to L-D3. Those pressures found in the individual runs are indicated separately, including the mean absolute error (MAE).

<table>
<thead>
<tr>
<th>model name:</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of atoms:</td>
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<td>192</td>
<td>192</td>
<td>96</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>initial setup routine:</td>
<td>R1</td>
<td>R2</td>
<td>R2</td>
<td>R2</td>
<td>R1</td>
<td>R1</td>
</tr>
<tr>
<td>cubic cell length (Å):</td>
<td>13.0</td>
<td>13.0</td>
<td>13.0</td>
<td>10.3</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>total trajectory (ps):</td>
<td>141</td>
<td>216</td>
<td>200</td>
<td>262</td>
<td>278</td>
<td>231</td>
</tr>
</tbody>
</table>

**3000 K: (4.3 GPa)**

| total MD time at 3000 K (ps): | 40 | 51 | 10 | 56 | 56 | 75 |
| equilibration run (ps): | 10 | 11 | 5 | 16 | 16 | 15 |
| production run (ps): | 30 | 40 | 5 | 40 | 40 | 60 |
| pressure (GPa): | 3.9 | 4.0 | 4.0 | 4.2 | 3.4 | 4.3 |
| MAE of pressure (GPa): | 0.9 | 1.1 | 1.0 | 1.6 | 1.6 | 1.6 |

**2700 K: (4.0 GPa)**

| total MD time at 2700 K (ps): | – | – | – | 52 | 52 | – |
| equilibration run (ps): | – | – | – | 12 | 12 | – |
| production run (ps): | – | – | – | 40 | 40 | – |
| pressure (GPa): | – | – | – | 3.4 | 3.5 | – |
| MAE of pressure (GPa): | – | – | – | 1.5 | 1.6 | – |

**2400 K: (3.6 GPa)**

| total MD time at 2400 K (ps): | 101 | 165 | 180 | 154 | 170 | 156 |
| equilibration run (ps): | 21 | 85 | 100 | 74 | 90 | 76 |
| production run (ps): | 80 | 80 | 80 | 80 | 80 | 80 |
| pressure (GPa): | 3.4 | 3.3 | 4.6 | 4.0 | 4.4 | 3.2 |
| MAE of pressure (GPa): | 1.0 | 1.0 | 1.2 | 1.7 | 1.8 | 1.4 |

structure of the silica network part of the system is close to that of SiO$_2$ melt, as can be seen from the similarity of the Si-Si RDF to pure SiO$_2$. We found it useful to describe the structure of the SiO$_2$-rich fluid in terms of $Q^n$-speciation and its average value,[15] and in fractional amounts of bridging, non-bridging and water-forming oxygen (BO, NBO, MWO, Subsection 3.4). The pairwise
coordination numbers, which are the basis for this, are calculated using the center of the broad minimum of the RDFs as the cutoff radius. The Si-O coordination distribution reflects the dominant tetrahedral coordination of silicon by oxygen, plus a small fraction of (short-lived) fivefold coordination. The O-Si coordination is distributed over zero-, one- and twofold coordination, thereby reflecting the three possible oxygen species MWO, NBO and BO. The O-H coordination distribution reflects the two possible hydrogen species SiOH and molecular H₂O.

3.3. Reaction dynamics as a function of temperature

Reaching and sampling structural equilibrium within a given trajectory length requires that reaction 1 takes place sufficiently often during the MD run, continuously breaking and creating Si-O bonds. Here, we investigate the question of how the dynamics of reaction 1 slows down when the system is quenched from 3000 K to 2400 K.

A precise description of the bond dynamics (i.e., the relaxation dynamics) is given by the bond autocorrelation function (BACF, also termed bond population correlation function).[58, 59] This function expresses the existence probability of an Si-O bond.
Figure 4: Pairwise radial distribution functions (RDF) from model L1 for 3000 K. The results for pure SiO$_2$ at 3000 K are shown for comparison.

after time $t$, given that it existed at time zero. First, we determined at each time step of a trajectory, whether a pair of Si-O is bonded ($h=1$) or not ($h=0$). The criterion is the bond distance threshold of 2.4 Å for a Si-O pair considered to be bonded or not. At 2.4 Å is the center of the broad minimum of the Si-O RDF (Fig. 4). $h$ changes with time according to whether the bond length is below or above the threshold distance. The time correlation function $c(t) = \langle h(0) h(t) \rangle / \langle h \rangle$, with $\langle h \rangle$ being the time average of $h$, is insensitive to short-lived (i.e., a few femtoseconds) interruptions in the bond’s existence criterion due to strong thermal motion. From the BACF we derive a time constant by fitting a single exponentially decaying function as $Y = A_0 \exp(-t/\tau_{Si-O})$, where $A_0$ is a free parameter, and $\tau_{Si-O}$ is the time after which the probability of a Si-O bond existence has decayed to $1/e=0.37$. The decay is well approximated by a single exponential function (inset in Fig. 5).

The Si-O BACF time constants are plotted against temperature in Fig. 5. The scatter between different models is small, as indicated by the error bars. No model size effect can be observed on the bond stability. At 3000 K, $\tau_{Si-O}$ is about 30 ps, at 2700 K 70 ps, and at 2400 K $\tau_{Si-O}$ is about 230 ps.
3.4. Reaction dynamics as a function of model size

In the prior section, we have established how the rate of reaction 1 is affected by temperature. In this section, we investigate how the direction of the network modifying reaction 1 is affected by the model size.

Structural changes involving reaction 1 are necessarily reflected in changes in the relative amounts of molecular water. Fig. 6 shows the amount of molecular water of the 192-atom and 96-atoms models, as a fraction to the total nominal H2O content. We calculated the number of water molecules at every timestep. Those oxygen atoms are counted as MWO that have at least two hydrogen atoms in the first neighbor shell, but no silicon atom. Bridging oxygen (BO) and non-bridging oxygen atoms are treated in analogy. This calculation was executed for every single timestep without any consideration of the stability of a water molecule over time, which explains the short-lived oscillations of the number of water molecules.

At 3000 K, the number of H2O molecules fluctuates in all models around an average value with a period of about 15 ps for the 192-atom models, and of about 30 ps for the 96-atom models. Fig. 7 shows for a snapshot of model M3-1 at 3000 K. The fraction of
molecular water in the 192-atom models is on average 25% with little scatter between the three models. The models from the two different generation routines (Section 2.2) are structurally indistinguishable after a few picoseconds MD run at 3000 K.

Upon quenching of the 192-atom models from 3000 K to 2400 K, reaction 1 proceeds to the left, and molecular water is released. In each of the 192-atom models, the number of water molecules increases within 10 to 100 ps after the thermostat is switched to 2400 K. At 2400 K the period of fluctuations of the number of water molecules can no longer be established with certainty. Despite this uniform trend of increasing polymerization in all 192-atom models, they become structurally more diverse at 2400 K than at 3000 K.

Contrary to the behavior of the 192-atom models, the 96-atom models do not release molecular water upon quenching from 3000 K to 2400 K, but consume water.
molecules (Fig. 6). At 3000 K, fluctuations of the amount of molecular water indicate a slightly larger period of about 30 ps, and we assume structural equilibrium is reached at 3000 K. The three 96-atom models agree in the amount of water molecules of 34% with little scatter, which is higher than in the case of the 192-atom models. After switching to 2700 K and later to 2400 K, the three 96-atom models show scatter in the amount of molecular water, but they agree qualitatively in their tendency to consume hitherto free molecular water. The amount of molecular water does not converge within the MD trajectory length of more than 200 ps after the thermostat is switched to 2400 K.

3.5. Reaction constant derived from the $Q^n$ species distribution

Knowledge of the evolution of relative amounts of MWO, NBO and WO, as presented in the previous section, is necessary to calculate reaction constant

$$K = [OH^-]^2/[H_2O][O_2^-]. \quad (2)$$

However, the relative amounts of MWO, NBO and WO are often estimated indirectly from experimental insight into the degree of polymerization of the silicate network part of the hydrous glass or melt. For this reason, we here evaluate the $Q^n$ species distribution, which is obtained from the analysis of all tetrahedra present in a model (Fig. 9). Calculation of $Q^n$ species occurs on the basis of geometric criteria derived from the partial RDFs (see subsection 3.2). The Si-Si partial RDF shows a clearly defined first coordination shell within the cutoff radius of 3.6 Å. This allows us in most cases to unambiguously determine of the number of Si neighbors to an individual Si atom, and hence the degree of polymerization of the tetrahedron under investigation. This analysis is carried out with an algorithm that averages over the time interval of the production run (Table 2). The results for each model are given in Table 3.

From the $Q^n$ species distribution, the actual average degree of polymerization $Q_{av}^{n,act}$ is calculated via

$$Q_{av}^{n,act} = 1.0 \cdot x_{O^1} + 2.0 \cdot x_{O^2} + 3.0 \cdot x_{O^3} + 4.0 \cdot x_{O^4}. \quad (3)$$
Figure 7: Snapshots showing the increase of molecular H\textsubscript{2}O between 3000 K (top) and 2400 K (bottom) (model L1, Tables 2 and 3, and Fig. 6).
Together with the total number of oxygen atoms, \(N_{\text{oxygen}}^{\text{total}}\), (96 and 48 for 192- and 96-atom models), the nominal number of oxygen in water molecules, \(N_{\text{MWO}}^{\text{nom}}\) (32 and 16, respectively), and the nominal average degree of polymerization \(Q_{\text{av}}^{\text{nom}} = 2.0\) in the ideal case of complete dissociation of all water molecules, the fraction of oxygen atoms in molecular water (MWO) is calculated as

\[
\lambda_{\text{MWO}}^{o} = \frac{Q_{\text{av}}^{o} - Q_{\text{av}}^{\text{nom}}}{2} \frac{N_{\text{MWO}}^{\text{nom}}}{N_{\text{oxygen}}^{\text{total}}}, \tag{4}
\]

the fraction of non-bridging oxygen atoms is calculated as

\[
\lambda_{\text{NBO}}^{o} = 2 \left( 1 - \frac{Q_{\text{av}}^{o} - Q_{\text{av}}^{\text{nom}}}{2} \right) \frac{N_{\text{MWO}}^{\text{nom}}}{N_{\text{oxygen}}^{\text{total}}}, \tag{5}
\]

and the fraction of bridging oxygen atoms is calculated as

\[
\lambda_{\text{BO}}^{o} = 1 - \lambda_{\text{MWO}}^{o} - \lambda_{\text{NBO}}^{o}. \tag{6}
\]

These numbers agree with the directly calculated fractions of oxygen atoms (Subsection 3.4 and Fig. 6) to within 2-3%. This deviation has its origin in the non-vanishing population density at the first minimum of the RDFs and in occasional and
short-lived untypical formation of steric configurations, such as oxygen-triclusters, fivefold coordinated silicon, etc. These species range below 2% under the pressure and temperature conditions of this study.

The stoichiometry of the present system of 50% SiO$_2$ and 50% H$_2$O with a oxygen-to-silicon ratio of 3 imposes the mass balance constraint of

$$\frac{1}{4}x_{NBO}^{ox} + \frac{1}{2}x_{BO}^{ox} = 1/3, \quad (7)$$

which is fulfilled to within 3% error (Table 3). This gives an estimate for the correctness of the $Q^n$ species determination and the subsequent fractional oxygen species calculation.

The average $Q^n$ value of each model is plotted in Fig. 10. $Q^2$ and $Q^3$ species are most abundant in all models. The amount of $Q^0$ is mostly below 1%, in some cases below 2% and in one model (L3) at 5% (Table 3). By visual inspection we found that, with the exception of model L3, the amount of $Q^0$ is zero, and the values for $Q^0$ in Table 3 correspond to fortuitous geometric situations where e.g. a $Q^1$ species is counted as $Q^0$ by the $Q^n$ species recognition algorithm. At 3000 K, the $Q^n$ distribution is similar among the three separate 192-atom models. The fraction of $Q^3$ species in the 96-atom models is systematically higher, and the $Q^2$ content is on average lower than in the 192-atom models. As a consequence, the 96-atom models show in each individual model a higher degree of polymerization, with a total average $Q^n$ value of 2.69.

At 2400 K, the average degree of polymerization of all 192-atom models increases, but the individual average $Q^n$ values of each model scatter between 2.60 and 2.86 (Fig. 10). The average $Q^n$ value correlates well with an increase of $Q^3$ species and anti-correlates with $Q^2$ species. The amounts of $Q^1$- and $Q^4$ species are still the same in all 192-atom models. In the 96-atom models, the average degree of polymerization decreases after quench to 2400 K, from the total average of 2.69 at 3000 K to 2.56 at 2400 K (Fig. 10). Their $Q^n$ species distributions are higher in $Q^2$ species but lower in $Q^3$ and $Q^4$ species than the 192-atom models.
Figure 9: The Q^n species distribution at 3000 K (top) and 2400 K (bottom), averaged over the 192- and 96-atom models, respectively (Table 2). Error bars indicate the mean absolute error. Thin lines are a guide to the eye. The vertical dashed lines indicate the average Q^n-speciation of the 192- and 96-atoms models, respectively.

4. Discussion

4.1. Structure at 3000 K

At 3000 K, the structure of the three mutually independent 192-atom models is relatively uniform regarding the average Q^n value and the Q^n species distribution (Figs. 9 and 10). This shows that the methods to generate the initial configurations (Table 2) do not have a measurable influence on the structure after few picoseconds. The oscillations of the total number of molecular water have a period of about 15 in the 192-atom and and 30 ps in the 96-atom models. We interpret these oscillations as fluctuations of the thermally equilibrated structure. The Si-O bond time constant $t_{Si-O}=30$ ps is considerably smaller than most run durations at 3000 K. This also applies to the 96-atom models. However, the 96-atom models systematically yield a degree of polymerization that is larger than the one of the 192-atom models (Fig. 10).

The fraction of H$_2$O present as molecular water in the 192-atom models at 3000 K is 25% on average (Fig. 10), which leads to a reaction constant of $\ln K = 1.99$, in remarkable agreement with the extrapolated value of the experimentally determined reaction constants determined in hydrous silicate melts[20] (Fig. 8). In addition, the
Table 3: Distribution of $Q^n$ species, average $Q^n$ value, and $\ln K$ for all models at 3000 K and 2400 K. Important average values for the 192- and 96-atom models are bold. For calculation procedure see equations 3 to 6 in Subsection 3.5. Mass balance compliance refers to the silicon mass balance requirement (Eqn. 7).

<table>
<thead>
<tr>
<th>model name</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>L av.</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M av.</th>
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<tr>
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<td>192</td>
<td>96</td>
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<tr>
<td>$x^{Q^0}$</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>$x^{Q^1}$</td>
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<td>0.08</td>
<td>0.10</td>
<td>0.10</td>
<td>0.07</td>
<td>0.11</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>$x^{Q^2}$</td>
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<td>0.26</td>
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<td>0.27</td>
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<td>$x^{Q^3}$</td>
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<td>0.42</td>
<td>0.45</td>
<td>0.40</td>
<td>0.43</td>
<td>0.40</td>
<td>0.39</td>
<td>0.41</td>
</tr>
<tr>
<td>$x^{Q^4}$</td>
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<td>0.13</td>
<td>0.14</td>
<td>0.13</td>
<td>0.20</td>
<td>0.18</td>
<td>0.21</td>
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<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>1.00</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$Q^n, av.$</td>
<td>2.42</td>
<td>2.56</td>
<td>2.52</td>
<td>2.50</td>
<td>2.71</td>
<td>2.63</td>
<td>2.73</td>
<td>2.69</td>
</tr>
<tr>
<td>$x^{ox_{MWO}}$</td>
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<td>0.09</td>
<td>0.09</td>
<td>0.08</td>
<td>0.12</td>
<td>0.10</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>$x^{ox_{NBO}}$</td>
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<td>0.48</td>
<td>0.49</td>
<td>0.50</td>
<td>0.43</td>
<td>0.46</td>
<td>0.42</td>
<td>0.44</td>
</tr>
<tr>
<td>$x^{ox_{BO}}$</td>
<td>0.40</td>
<td>0.43</td>
<td>0.42</td>
<td>0.42</td>
<td>0.45</td>
<td>0.44</td>
<td>0.46</td>
<td>0.45</td>
</tr>
<tr>
<td>$\ln K$</td>
<td>2.29</td>
<td>1.76</td>
<td>1.90</td>
<td>1.99</td>
<td>1.25</td>
<td>1.52</td>
<td>1.17</td>
<td>1.31</td>
</tr>
<tr>
<td>mass bal. compl.:</td>
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<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.33</td>
<td>0.34</td>
<td>0.33</td>
<td>0.33</td>
</tr>
</tbody>
</table>

**3000 K:**

| $x^{Q^0}$   | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.00 | 0.01  |
| $x^{Q^1}$   | 0.07 | 0.08 | 0.13 | 0.09 | 0.04 | 0.16 | 0.09 | 0.10  |
| $x^{Q^2}$   | 0.18 | 0.29 | 0.33 | 0.27 | 0.40 | 0.36 | 0.27 | 0.34  |
| $x^{Q^3}$   | 0.56 | 0.42 | 0.33 | 0.44 | 0.38 | 0.32 | 0.51 | 0.41  |
| $x^{Q^4}$   | 0.19 | 0.21 | 0.21 | 0.20 | 0.14 | 0.14 | 0.13 | 0.14  |
| sum         | 1.00 | 0.99 | 1.00 | 1.00 | 0.99 | 1.00 | 1.00 | 1.00  |
| $Q^n, av.$  | 2.86 | 2.74 | 2.60 | 2.73 | 2.58 | 2.41 | 2.68 | 2.56  |
| $x^{ox_{MWO}}$ | 0.14 | 0.12 | 0.10 | 0.12 | 0.10 | 0.07 | 0.11 | 0.09  |
| $x^{ox_{NBO}}$ | 0.38 | 0.42 | 0.47 | 0.42 | 0.47 | 0.53 | 0.44 | 0.48  |
| $x^{ox_{BO}}$ | 0.48 | 0.46 | 0.43 | 0.46 | 0.43 | 0.40 | 0.45 | 0.43  |
| $\Delta x^{ox_{H_2O}}$ w.r.t. 3000 K: | +107% | +33% | +15% | +50% | -19% | -34% | -7%  | -20%  |
| $\ln K$    | 0.74 | 1.14 | 1.62 | 1.16 | 1.70 | 2.32 | 1.34 | 1.79  |
| mass bal. compl.: | 0.31 | 0.32 | 0.34 | 0.32 | 0.34 | 0.37 | 0.33 | 0.35  |

**2400 K:**
results of our equimolar H$_2$O-SiO$_2$ models can be compared to results of other modeling studies.[22, 23, 24] Comparing to the ln $K$ of several studies, both as a function of temperature and as a function of H$_2$O concentration (Fig. 8) shows that our results with ln $K = 1.99$ at 50 mol% H$_2$O are in good agreement to other modeling studies, given that conditions vary between all these studies.

As outlined in the introduction, we anticipated a decrease in ln $K$ at 50 mol% H$_2$O based on the considerations of Newton and Manning.[4] This value was assumed as a turning point in the H$_2$O dissolution mechanism, from H$_2$O dissociation to clustering of molecular H$_2$O. However, the ln $K$ of the 192-atom models does not indicate significant differences to those at lower H$_2$O concentration (inset in Fig. 8), including the extrapolation of experimental data by Nowak and Behrens to 3000 K.[20]

The agreement to the extrapolation of experimental data, and the almost constant value of ln $K$ from low H$_2$O concentrations up to the 50 mol% H$_2$O, may indicate that reaction (1) is still not affected at these high water concentration. This would be at odds with the structural interpretation of the activity relationship by Newton and Manning.[4] and could mean that the activity-composition relationship is predominantly controlled by other structural re-arrangements in this compositional range and not only by the reaction (1). On the other hand, the ln $K$ found in the 192-atom model may still be affected by finite size effects. This model contains about twice the number of atoms compared to many other ab initio MD studies of silicate melts. In contrast to the other studies, it shows a T-dependence for ln $K$ that would be expected. However, it may still be too small to allow for changes in structural incorporation, such as formation of clusters, as would be expected above a certain concentration for dissolution of H$_2$O in SiO$_2$ (and vice-versa). Clustering of cations (including hydrogen) in silicate glasses and melts is observed both in experiment[60] and in classical models of silicate glasses with thousands of atoms. The absence of this clustering suggests that there is a significant structural finite size effect on the structure of partly depolymerized silica networks, at least up to several hundreds of atoms.[61] Therefore, the structure of our 192-atom models does not represent structures that are converged with respect to system size, and clusters cannot form. A final test requires modeling in a framework other than plane-wave DFT which becomes computationally prohibitively expensive beyond
two or three hundred atoms.

4.2. Structural changes after quench to 2400 K

The 192-atom models show a remarkable structural rearrangement within 10 to 100 picoseconds after quench to 2400 K. The degree of polymerization increases, and the SiO$_2$ network releases molecular H$_2$O, which was priorly bound as SiOH hydroxy groups (Fig. 6, and snapshots in Fig. 7). The fractional amount of molecular water increases on average by 41% between 3000 K and 2400 K. Based on the increased bond stability (Section 4.4), structural equilibrium has not been reached in the MD runs at 2400 K. Therefore, the process of water release could continue if the MD runs were longer. Reaching structural equilibrium at 2400 K is however beyond the aim of this study. The observed formation of molecular water is rather an effect of decreasing temperature than of the concomitant drop of pressure. We infer this from the insensitivity of silicate melt structure with respect to pressure in the investigated range of about 3.5 to 4.3 GPa.[53, 23] At 2400 K, the average degree of polymerization has increased in all 192-atom models, however, the uniform structural picture at 3000 K has been replaced by a variety of average Q$^\circ$ values and Q$^\circ$ species distributions (Fig. 9).

![Figure 10: The average Q$^\circ$ speciation individually for all models for 3000 K and 2400 K (right side), and separately averaged over the 192- and 96-atoms models, respectively (left). Error bars indicate the mean absolute error. Lines are a guide to the eye.](image)

The formation of molecular H$_2$O, which may be also considered as release of wa-
ter from the network, after lowering the temperature is expected on the basis of the phase diagram of the system H$_2$O-SiO$_2$ (Fig. 1).[5] Below 2000 K and 1 GPa, a wide miscibility gap opens over a narrow temperature interval. Above these conditions, a single H$_2$O-SiO$_2$ phase exists. Within this single phase, the ratio of H$_2$O to SiOH is expected to increase with decreasing temperature.[19, 4, 5] Clustering on the nanoscale is observed in various chemical systems such as silicate glasses and aqueous solution.[62, 61, 17, 63] There is evidence that critical fluctuations in hydrous melt may even be larger than for any other network modifier.[64] We therefore consider the possibility that the observed release of molecular water at 2400 K as a precursor of the formation of water clusters in a polymerizing silica network, a process that eventually leads to phase separation occurring at lower temperatures.

4.3. Finite size effects in partly broken silica network

The three 192-atom models L1 to L3 give consistent structural results with an average Q$^n$ value of 2.5 at 3000 K, and an increase to 2.75 on average at 2400 K (Fig. 10). In contrast, each of the 96-atom models shows an opposite trend. At 2400 K, the 96-atom models show individual Q$^n$ values that are higher than any of the 192-atom models, although a decrease of the Q$^n$ value with temperature would be expected. This abnormal behavior is also reflected in the corresponding ln $K$ values in Fig. 8. The same increase in water molecules and therefore in ln $K$ has been observed previously in a 102-atom model (see triangles in Fig. 2).[22] This suspicious behavior of smaller models may not necessarily be true in the long-time limit of several hundreds of picoseconds. We prefer to address this as a retarding, transient finite size effect. It reflects the inability of the smaller models for formation of molecular H$_2$O as demonstrated by comparison to the larger 192-atom models on the timescale of hundred picoseconds (Fig. 10).

This finite size effect especially affects the structural results of partially broken silica networks from ab initio models of typically about 100 atoms. In the case of pure SiO$_2$, it has been shown by Van Ginhoven et al.[34] that it is possible to obtain a good structural description of SiO$_2$ from the average of several small models with less than 100 atoms.[34] According to their results, each small SiO$_2$ model can be thought of as a small region in a larger system. We consider that this observation may be less valid...
in the case of partially depolymerized hydrous silica network, because partially broken silicate networks show more variability in their intermediate range structure.[34, 51]

Therefore, partially depolymerized silicate networks are especially sensitive to the model size. This probably applies especially to the system SiO$_2$-H$_2$O where the structural adaptation by reaction 1 not only requires large translational movements, but large energetic barriers to be overcome.[65] These barriers are less pronounced in the case of silicate melts with ‘truly ionic’ cations such as alkaline and Earth-alkaline cations are present.

4.4. Bond dynamics as a function of temperature

In MD models of silicates, a system can achieve structural equilibration probably only if the MD trajectory length exceeds the average Si-O bond lifetime. In the case of 3000 K, this criterium is fulfilled, as can be judged by the Si-O bond time constant $\tau_{\text{Si-O}}$ of about 30 ps (Fig. 5). Another criterium is the observation of multiple oscillations in the number of water molecules (Figs. 6 and 5). At 2400 K, with a Si-O bond time constant of about 230 ps, this criterium is clearly not fulfilled. Therefore, we cannot assume that structural equilibrium is reached in our MD runs at 2400 K. Based on this number, we consider that reaching structural equilibrium at 2400 K in terms of Q$^n$ species and water molecules would require at least 500 ps as a first approximation. Moreover, the BACF time constants calculated here represent a lower limit estimate for the time necessary for structural equilibration. This is because the equimolar composition under investigation here ensures a maximum of interaction between the SiO$_2$ network and H$_2$O molecules. In addition to that, the limited size of the models inhibits the formation of H$_2$O clusters that are assumed to occur on the nanometer scale in reality.[5, 60] In clusters, the H$_2$O molecules would be “passivated” with respect to breaking of the silicate network.

The bond time constants seem system-specific and we expect that in other, more ionic systems, such as Na$_2$O-SiO$_2$ and MgO-SiO$_2$, or in systems with a built-in charge-coordination disequilibrium as in the case of Al$_2$O$_3$, the energy barriers (and therefore the time constants) may be smaller. Then, structural equilibrium of the silica network can be at lower temperatures, eventually down to 2200 K or so.
A relation between bond stability and temperature, as the one established here with ab initio accuracy, could be a benchmark for the reliability of classical potentials at high temperatures. Atomic-scale modeling of systems that involve the H$_2$O-SiO$_2$ interaction reaction 1 crucially depends on the correct reproduction of its reaction energy and its energetic reaction barriers.

5. Conclusions

We have investigated supercritical equimolar H$_2$O-SiO$_2$ fluid at three temperatures and two different model sizes under the aspects of structure and structural changes after temperature is decreased. We draw three main conclusions.

1) We found at 3000 K an average $Q^n$ value of 2.5 and a fraction of molecular H$_2$O of about 25%. The ln $K$ plots only slightly below extrapolated experimental data of dilute H$_2$O in a silicate melt. Larger downward deviation from this extrapolation would be expected based on the predicted change in H$_2$O solution mechanism in silicate melts above about 30 mol% H$_2$O.[4] A reason could be, that the 192-atom cells are too small to allow for proper modeling of the clustering on the nanometer-scale expected in other studies. After quench from 3000 K to 2400 K, the supercritical H$_2$O-SiO$_2$ fluid releases molecular H$_2$O on a timescale of tens to hundreds of picoseconds, in agreement with the temperature dependence of reaction constant $K$.

2) In this ab initio modeling study, we have used models that are about double in number of atoms (192 atoms), compared to what is commonly used. This allowed us to observe a peculiar difference in behavior between 192-atom and 96-atom models. First, at 3000 K, the 192-atom models show consistently a higher average degree of polymerization than the 96-atom models. Second, after quench from 3000 K to 2400 K, the 192-atom release water molecules, in agreement with experiment, but the 96-atom models all consume water molecules after quench from 3000 K to 2400 K. This cross-over in behavior points to a structural finite size effect, which possibly acts even stronger on partially depolymerized silicate networks than on pure SiO$_2$. As a finite size effect, smaller models are stabilized in their structure, rendering lower probability for structural change within a given MD run duration. This affects the reliability
of ab initio MD modeling of silicate melts and glasses in a general way.

3) We analyzed the Si-O bond stability by means of the bond autocorrelation function, to investigate the temperature dependence of the dynamics of the dissociation reaction $\text{H}_2\text{O} + \text{SiOSi} = 2\text{SiOH}$. The calculated Si-O bond time constants show, that within a MD trajectory of 200 ps length, reaching structural equilibrium is assured for 3000 K, but not for 2400 K. Knowledge of the relation between temperature and Si-O bond stability is important for future modeling in the system $\text{H}_2\text{O}-\text{SiO}_2$, but also for modeling of chemical compositions closer to naturally occurring hydrous silicate melts.

The limitation in the number of atoms to commonly far less than 200 atoms is a speciality of the plane wave approach to DFT, other basis set formalisms allow larger models, with a varying degree of accuracy. However, the temperature-dependence of the Si-O bond dynamics is a general limitation to ab initio MD of silicate melts. In order to close the gap to experimental work on atomic-scale relaxation processes in silicate melts such as the Si-O bond dynamics,[26] classical potentials will remain a valuable tool. Their reliability can be increased by comparing Si-O bond time constants derived from a autocorrelation function, as proposed here.

6. Acknowledgments

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[12] H. Bureau, H. Keppler, Complete miscibility between silicate melts and hydrous


