Structural and dynamical properties of supercritical H₂O-SiO₂ fluids studied by ab initio molecular dynamics

Georg Spiekermann¹

GFZ German Research Centre for Geosciences, Section 3.3, Telegrafenberg, 14473 Potsdam, Germany

Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany

Max Wilke

GFZ German Research Centre for Geosciences, Section 3.3, Telegrafenberg, 14473 Potsdam, Germany

Sandro Jahn

GFZ German Research Centre for Geosciences, Section 3.3, Telegrafenberg, 14473 Potsdam, Germany

Institute of Geology and Mineralogy, University of Cologne, Greinstrasse 4-6, 50939 Cologne, Germany

Abstract

In this study we report the structure of supercritical H₂O-SiO₂ fluid composed of 50 mol% H₂O and 50 mol% SiO₂ 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/cm³, 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 $2 \text{SiOH} = \text{SiOSi} + \text{H}_2\text{O}$. The calculation of the reaction constant $K = [\text{OH}^-]^2 / [\text{H}_2\text{O}][\text{O}^{2-}]$ is carried out on the basis of the experimentally relevant Q^n 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 H₂O. 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 H₂O-silica interaction dynamics is described on the basis of the bond

¹corresponding author, georg.spiekermann@desy.de

autocorrelation function.

Keywords: fluid, SiO₂-H₂O, SiO₂, molecular dynamics, polymerization, DFT

1. Introduction

Geological processes such as mineral melting and magmatism are governed by the interplay of silicate matter with volatiles such as H₂O.[1, 2] The system H₂O-SiO₂ 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 H₂O-rich melt then become a question of semantics. Since large amounts of H₂O 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 H₂O-SiO₂ 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] H₂O in silicate melts exists predominantly in the form of SiOH hydroxy groups and of

28 molecular H_2O that fills voids in the silicate network or forms small clusters.[16, 17]
 29 These species mutually exchange in the network breaking reaction

Figure 1: Black and grey curves indicate the solubility of SiO_2 in H_2O as a function of temperature and pressure, according to the model of Hunt and Manning.[5] The composition, 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_2O and SiO_2 .

30 Therefore, oxygen atoms occur in three species in the system H_2O - SiO_2 : Molec-
 31 ular water (MWO), Bridging oxygen (BO) in the silica network, and non-bridging
 32 oxygen (NBO) in the form of hydroxy groups at its terminal branches. Structure, vis-
 33 cosity, self-diffusion coefficients and other properties of silica-rich supercritical fluid
 34 or of sub-critical hydrous silicate melt are governed by the extent to which reaction
 35 1 proceeds to either side. This reaction is particularly temperature-dependent and
 36 less affected by pressure. Considerable experimental effort has been dedicated to de-
 37 termine the temperature-dependent speciation of H_2O in hydrous silicate glasses and
 38 melts.[18, 19, 15] Fig. 2 shows an experimentally established temperature-dependence
 39 of the reaction constant $\ln K = [OH^-]^2/[H_2O][O^{2-}]$ for hydrous rhyolitic glasses,[20]
 40 with an extrapolation to the higher temperatures accessible to molecular dynamics
 41 (MD) modeling. This reaction constant is concentration-independent at low water con-
 42 tents, where dissociation of H_2O to $SiOH$ groups (NBO) is the predominant dissolution

43 mechanism.

44 At higher H₂O concentrations, the dissolution mechanism is assumed to shift from
45 the chemical dissolution via dissociation to physical dissolution via the accommoda-
46 tion of increasingly clustered H₂O molecules in the partially broken silica network.
47 Indications for a shift in the dissolution mechanism have been found in several studies.
48 Newton and Manning[4] predicted for 1350 K and 1 GPa a plateau of H₂O activity at
49 about 50 mol% H₂O. The content of molecular water, as opposed to hydroxy groups,
50 is expected to steeply increase in this compositional region. In related systems, such
51 as hydrous albitic melts, a similar change in the H₂O dissolution mechanism has been
52 assumed for about 30 mol% H₂O.[19, 21] Since the temperature and pressure condi-
53 tions make experimental investigation very challenging, computational data may be
54 insightful. Fig. 2 compares the extrapolated experimental reaction constant[20] to the
55 calculated K values for several computational studies. For the calculation of K , the
56 activity coefficients of all species are assumed unity, and the concentration values are
57 calculated assuming that the presence of oxygen species other than SiOH, H₂O and
58 SiOSi are negligible.

59 In their ab initio MD study on SiO₂ with 11.8 mol% H₂O, Pöhlmann *et al.* observed
60 molecular water as low as 0.06 mol% at 3000 K and 0 bar.[22] Karki and Stixrude[23]
61 found by ab initio MD that in a silica melt with 23 mol% H₂O at 1.5 GPa and 3000 K,
62 only 8.3% of the nominal H₂O forms molecular water. Anderson *et al.*[24] found
63 in a Reverse Monte-Carlo study using the classical Garofalini-potential,[25] that in
64 a supercritical fluid of 40 mol% H₂O in SiO₂ at 3000 K and 1 GPa, only 1% of the
65 nominal water was molecular H₂O.

66 As described above, $\ln K$ is expected to be concentration-dependent at high H₂O
67 concentrations, and it is then expected to deviate downward from the shown linear
68 relation of the type $\ln K = a/T + b$. However, the agreement of the computational data
69 and the extrapolated experimental data in Fig. 2 is surprisingly good. In the inset in
70 Fig. 2, $\ln K$ is plotted for selected data points as a function of nominal H₂O content.
71 The $\ln K$ up to 40 mol% nominal H₂O content indicates only a weak downward trend.
72 This raises the question whether the downward trend (arrow in inset of Fig. 2) increases
73 when the H₂O concentration is increased to the level of 50 mol%, where Newton and

74 Manning[4] found a plateau of H_2O activity.

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

82 In the present study, we aim to investigate the structure of supercritical H_2O - SiO_2
83 fluid with 50% H_2O , and to explore whether the assumed change in dissolution mech-
84 anism at this high H_2O content can be evidenced in the model. At the same time, we
85 intend to establish, under which temperature conditions ab initio MD can contribute to
86 verifying thermodynamical predictions as those regarding the shift in solution mecha-
87 nism in supercritical H_2O - SiO_2 fluids.[4] Once these conditions are clarified, the pre-
88 dictive power of high-temperature $\ln K$ relations derived from ab initio MD models
89 would increase. This will eventually allow a hand-shake with experiments on the im-
90 portant relaxation processes in hydrous silicate melts,[26] for which ab initio modeling
91 accuracy is so important.

92 The structure of this study on the single-phase supercritical equimolar H_2O - SiO_2
93 fluid is as follows: The modeling approach is described in Section 2. Routines were
94 chosen to generate unbiased and mutually independent starting configurations (Section
95 2.2). In a first modeling step at 3000 K, we established a simple P-V relationship to
96 find a realistic and suitable density (Section 3.1). Then we set up several models of
97 two different sizes to evaluate the uncertainty due to finite size effects. The structure at
98 3000 K is described in terms of Q^n species and oxygen species in Subsections 3.2 and
99 3.4.

100 The smaller size models were then cooled in two successive steps to 2400 K to
101 explore the slowing-down of bond dynamics, which has to persist if structural equilib-
102 rium is to be sampled (Subsection 3.3). We found the Si-O bond dynamics to be high
103 enough, at least to observe structural adaptation after quenching all models to 2400 K.
104 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 5.15wt% H_2O [20]; large empty circle: model results of ab initio MD of 23 mol% H_2O in SiO_2 at 3000 K and 0.01 GPa[23]; empty squares: results of Reverse Monte Carlo for 40 mol% H_2O at 3000 K and 2.5 GPa[27]; small empty circles: for 40 mol% H_2O at 3000 K and 0.25 GPa[27]; triangles: values by Pöhlmann *et al.* for 11.8 mol% H_2O ; Inset: $\ln K$ values from inside the ellipse, plotted as a function of H_2O concentration. The arrow indicates a possible downward trend of $\ln K$, assumed on the basis of experimental observations[19, 21] and results of thermodynamic modeling.[4]

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

108 2. Methods

109 2.1. Modeling technique

110 We used density functional theory[28] in the plane wave pseudopotential approach
 111 as implemented in the CPMD code.[29] PBE was used as exchange-correlation functional.[30]
 112 Disordered network forming systems have been found to be better described by gener-
 113 alized gradient approximation functionals than by those functionals of the local density
 114 approximation type.[31, 32, 33, 34, 35] Martins-Troullier type pseudopotentials were
 115 used.[36] Spin polarization was not considered.[37] The Kohn-Sham wavefunctions
 116 were expanded at the Γ -point with a cutoff energy of 80 Ry. Dependence of elec-

117 tronic potential on more extended k-point sampling was found to be negligible. Forces
118 were within about 1% deviation compared to those obtained with larger plane wave
119 cutoffs of 140 Ry. All modeling runs were performed in the canonical (NVT) ensemble
120 in periodic boundary conditions. Temperature was controlled by a Nosé-Hoover
121 thermostat.[38] Pressure was calculated from the trace of the continuously calculated
122 stress tensor, which was corrected by the Pulay pressure for incompleteness of the basis
123 set.[39, 40, 41]

124 We used Car-Parrinello molecular dynamics[42] with a fictitious electronic mass
125 of 400 a.u. ($3.64 \cdot 10^{-28}$ kg) and an integration time step of 4 a.u. (0.097 fs).[43, 44,
126 45] The ratio of fictitious electronic mass to the mass of hydrogen is 0.22. It has
127 been shown that this reduces the effect of the electronic dynamics on the structure
128 H₂O at 300 K to a negligible level in comparison to Born-Oppenheimer molecular
129 dynamics.[44] This is also valid for dynamical properties. For instance, the effect
130 of Car-Parrinello molecular dynamics on the diffusion coefficient in H₂O at 300 K has
131 been found to be on the order of factor 2,[44] which is of the same magnitude as is the
132 effect of the choice of the exchange-correlation functional.[46]

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

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

141 2.2. *Setup of Models*

142 As the first step of this work, we obtained information on the volume-pressure
143 relation at 3000 K to determine an appropriate density to be used in the following mod-
144 eling steps. For this, we set up three 192-atom models at three densities between 1.4
145 and 2.05 g/cm³ (Table 1). These densities are based on literature data on pure SiO₂,
146 pure H₂O and the partial molar volume of H₂O in silicate melts.[50, 51, 52, 53] Initial

147 configurations were generated using an automated routine (referred to as R1 in table
 148 1) to exclude bias. For this, we used the final configuration of a classical 200 ps MD
 149 run of pure SiO₂ at 3000 K with the PIMAIM potential.[54] Randomly chosen silicon
 150 atoms were removed, and for each removed silicon atom four hydrogen atoms were
 151 inserted, each near to one of the four faces of a tetrahedron where a silicon atom had
 152 been removed. In addition to this first routine, a second automated routine (referred
 153 to as R2) is used in this study for the generation of unbiased initial configurations. A
 154 given cell volume is filled with atoms, under constraints regarding the minimal atomic
 155 distances, equal to the positions of the first maximum in the pairwise radial distribution
 156 functions from Pöhlmann *et al.*[22] The three models for the density-pressure relation
 157 started from the same initial configuration which was generated using the first routine
 158 (Table 1). They were run for 30 ps after initial equilibration of 11 ps. Pressure calcula-
 159 tion of each of these models allowed us to obtain information on the volume-pressure
 160 relation as shown in Fig. 3. Due to lack of experimental data in the system of pure
 161 H₂O-SiO₂, apart from the Pulay-pressure, no additional pressure correction was used
 162 to account for systematic overestimation of silicate density by the PBE functional. The
 163 pressure fluctuation, calculated as mean absolute error (MAE), is indicated in Table 1.
 164 In the following steps of this work, all models were run with constant molar volume
 165 of 20.7 cm³/mol (density 1.88 g/cm³). This density resulted in a pressure of 4.3 GPa
 166 at 3000 K (Table 1) and about 3.5 GPa at 2400 K as representative for upper mantle
 167 conditions.

168 As the next step, several mutually independent models of equimolar composition
 169 were set up: three large 192-atom models (models L1 to L3, 32 H₂O and 32 SiO₂
 170 nominally, Table 2) and three medium-sized 96-atom models (M1 to M3, 16 H₂O
 171 and 16 SiO₂ nominally). The setup of separate, equally sized models allows us to
 172 obtain information on the variability of the structure at otherwise identical modeling
 173 conditions,[51, 34] two different model sizes yield information on the structural effect
 174 of system size. The temperature-cascade regime that we carried out on the models is
 175 given in Table 2. After runs at 3000 K, four models were quenched to 2400 K, two other
 176 models were run at an intermediate step at 2700 K before quench to 2400 K. Total run
 177 duration at 2400 K was between 100 and 200 ps (Table 2).

Table 1: The 192-atom models L-D1 to L-D3 (32 H₂O and 32 SiO₂) for an estimate of the density-pressure relation at 3000 K (Fig. 3). Molar volume refers to (H₂O)_{0.5}(SiO₂)_{0.5}.

model label:	L-D1	L-D2	L-D3
density (g/cm ³):	1.4	1.88	2.05
molar volume (cm ³ /mol):	28.0	20.7	19.0
model further used as:	–	L1	–
equilibration run (ps):	11	11	11
production run (ps):	30	30	30
pressure at 3000 K(GPa):	0.7	4.3	5.6
MAE of pressure (GPa):	0.8	1.2	1.2

For comparison and reference, we carried out a MD run of 20 ps for pure SiO₂ at 3000 K and molar volume of 45.8 Å³/SiO₂, which is similar to the experimental volume of SiO₂ melt at the ambient conditions melting point.[55] The initial configuration of the SiO₂ 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 SiO₂ and of pure H₂O, and the partial molar volume of H₂O in silicate melts are shown for comparison.[51, 56, 53]. The density of 1.88 g/cm³ was chosen for further modeling.

3.2. Radial distribution and coordination functions

The computation of the pairwise radial distribution function (RDF) 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 SiO₂ 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/cm³. 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).

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

195 structure of the silica network part of the system is close to that of SiO₂ melt, as can be
196 seen from the similarity of the Si-Si RDF to pure SiO₂.

197 We found it useful to describe the structure of the SiO₂-rich fluid in terms of
198 Qⁿ-speciation and its average value,[15] and in fractional amounts of bridging, non-
199 bridging and water-forming oxygen (BO, NBO, MWO, Subsection 3.4). The pairwise

Figure 3: Molar volume as a function of pressure, for three models with densities between 1.4 and 2.05 g/cm³ (black dots, Table 1). Error bars indicate the mean absolute error (MAE). Literature data of the molar volume of SiO₂ and of H₂O are shown for comparison. Dashed line: Pure H₂O at 3000 K[56]; grey crosses: modeled partial molar volume of H₂O in silicate melt[53]; solid grey line: experimental partial molar volume of H₂O in andesitic melt[57]; grey dots: pure SiO₂ at 3500 K[51]

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 SiO₂ at 3000 K are shown for comparison.

215 after time t , given that it existed at time zero. First, we determined at each time step
 216 of a trajectory, whether a pair of Si-O is bonded ($h=1$) or not ($h=0$). The criterion is
 217 the bond distance threshold of $2.4 \text{ \AA}$ for a Si-O pair considered to be bonded or not. At
 218 $2.4 \text{ \AA}$ is the center of the broad minimum of the Si-O RDF (Fig. 4). h changes with
 219 time according to whether the bond length is below or above the threshold distance.
 220 The time correlation function $c(t) = \langle h(0)h(t) \rangle / \langle h \rangle$, with $\langle h \rangle$ being the time average
 221 of h , is insensitive to short-lived (i.e., a few femtoseconds) interruptions in the bond's
 222 existence criterium due to strong thermal motion. From the BACF we derive a time
 223 constant by fitting a single exponentially decaying function as $Y = A_0 \exp(-t/\tau_{\text{Si-O}})$,
 224 where A_0 is a free parameter, and $\tau_{\text{Si-O}}$ is the time after which the probability of a Si-O
 225 bond existence has decayed to $1/e=0.37$. The decay is well approximated by a single
 226 exponential function (inset in Fig. 5).

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

Figure 5: Temperature dependence of the Si-O bond autocorrelation function (BACF) time constants, averaged over the three 96-atom models M1 to M3. Error bars indicate the mean absolute error. The solid line is a guide to the eye, the dashed line is an extrapolation to lower temperatures. Inset: example of a fit of a single exponential to the bond auto correlation function at 3000 K.

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 H_2O 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 H_2O 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

247 molecular water in the 192-atom models is on average 25% with little scatter between
 248 the three models. The models from the two different generation routines (Section 2.2)
 249 are structurally indistinguishable after a few picoseconds MD run at 3000 K.

Figure 6: Time evolution of the amount of molecular water as a fraction of the number of total nominal H_2O in the respective models. Left: 192-atom models L1 to L3 for 3000 K and 2400 K. Right: 96-atom models M1 to M3 for 3000 K, 2700 K and 2400 K, as marked by different shades of grey (Table 2).

250 Upon quenching of the 192-atom models from 3000 K to 2400 K, reaction 1 pro-
 251 ceeds to the left, and molecular water is released. In each of the 192-atom mod-
 252 els, the number of water molecules increases within 10 to 100 ps after the thermostat
 253 is switched to 2400 K. At 2400 K the period of fluctuations of the number of water
 254 molecules can no longer be established with certainty. Despite this uniform trend of
 255 increasing polymerization in all 192-atom models, they become structurally more di-
 256 verse at 2400 K than at 3000 K.

257 Contrary to the behavior of the 192-atom models, the 96-atom models do not re-
 258 lease molecular water upon quenching from 3000 K to 2400 K, but consume water

259 molecules (Fig. 6). At 3000 K, fluctuations of the amount of molecular water indi-
 260 cate a slightly larger period of about 30 ps, and we assume structural equilibrium is
 261 reached at 3000 K. The three 96-atom models agree in the amount of water molecules
 262 of 34% with little scatter, which is higher than in the case of the 192-atom models.
 263 After switching to 2700 K and later to 2400 K, the three 96-atom models show scatter
 264 in the amount of molecular water, but they agree qualitatively in their tendency to con-
 265 sume hitherto free molecular water. The amount of molecular water does not converge
 266 within the MD trajectory length of more than 200 ps after the thermostat is switched to
 267 2400 K.

268 3.5. Reaction constant derived from the Q^n species distribution

269 Knowledge of the evolution of relative amounts of MWO, NBO and WO, as pre-
 270 sented in the previous section, is necessary to calculate reaction constant

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

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

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

$$Q_{act}^{n,av} = 1.0 \cdot x^{Q1} + 2.0 \cdot x^{Q2} + 3.0 \cdot x^{Q3} + 4.0 \cdot x^{Q4}. \quad (3)$$

Figure 7: Snapshots showing the increase of molecular H₂O between 3000 K (top) and 2400 K (bottom) (model L1, Tables 2 and 3, and Fig. 6).

Figure 8: $\ln K$ calculated for the 192-atom models (black circles) and 96-atom models (grey circles), compared to the literature data as in Fig. 2. Note the good agreement of the 192-atom model to the extrapolation of experimental data (dashed line), [20] and the increasing $\ln K$ value of the 96-atom models with decreasing temperature, as also found in the 102-atom model by Pöhlmann *et al.* (triangle). [22] Inset: $\ln K$ as a function of water concentration.

284 Together with the total number of oxygen atoms, N_{oxygen}^{total} , (96 and 48 for 192- and
 285 96-atom models), the nominal number of oxygen in water molecules, N_{MWO}^{nom} (32 and
 286 16, respectively), and the nominal average degree of polymerization $Q_{nom}^{n,av} = 2.0$ in the
 287 ideal case of complete dissociation of all water molecules, the fraction of oxygen atoms
 288 in molecular water (MWO) is calculated as

$$x_{MWO}^{ox} = \frac{Q_{act}^{n,av} - Q_{nom}^{n,av}}{2} \cdot \frac{N_{MWO}^{nom}}{N_{oxygen}^{total}}, \quad (4)$$

289 the fraction of non-bridging oxygen atoms is calculated as

$$x_{NBO}^{ox} = 2 \cdot \left(1 - \frac{Q_{act}^{n,av} - Q_{nom}^{n,av}}{2} \right) \cdot \frac{N_{MWO}^{nom}}{N_{oxygen}^{total}}, \quad (5)$$

290 and the fraction of bridging oxygen atoms is calculated as

$$x_{BO}^{ox} = 1 - x_{MWO}^{ox} - x_{NBO}^{ox}. \quad (6)$$

291 These numbers agree with the directly calculated fractions of oxygen atoms (Sub-
 292 section 3.4 and Fig. 6) to within 2-3%. This deviation has its origin in the non-
 293 vanishing population density at the first minimum of the RDFs and in occasional and

294 short-lived untypical formation of steric configurations, such as oxygen-triclusters,
295 fivefold coordinated silicon, etc. These species range below 2% under the pressure
296 and temperature conditions of this study.

297 The stoichiometry of the present system of 50% SiO₂ and 50% H₂O with a oxygen-
298 to-silicon ratio of 3 imposes the mass balance constraint of

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

299 which is fulfilled to within 3% error (Table 3). This gives an estimate for the cor-
300 rectness of the Qⁿ species determination and the subsequent fractional oxygen species
301 calculation.

302 The average Qⁿ value of each model is plotted in Fig. 10. Q² and Q³ species are
303 most abundant in all models. The amount of Q⁰ is mostly below 1%, in some cases
304 below 2% and in one model (L3) at 5% (Table 3). By visual inspection we found that,
305 with the exception of model L3, the amount of Q⁰ is zero, and the values for Q⁰ in Table
306 3 correspond to fortuitous geometric situations where e.g. a Q¹ species is counted as
307 Q⁰ by the Qⁿ species recognition algorithm. At 3000 K, the Qⁿ distribution is similar
308 among the three separate 192-atom models. The fraction of Q⁴ species in the 96-atom
309 models is systematically higher, and the Q² content is on average lower than in the 192-
310 atom models. As a consequence, the 96-atom models show in each individual model a
311 higher degree of polymerization, with a total average Qⁿ value of 2.69.

312 At 2400 K, the average degree of polymerization of all 192-atom models increases,
313 but the individual average Qⁿ values of each model scatter between 2.60 and 2.86 (Fig.
314 10). The average Qⁿ value correlates well with an increase of Q³ species and anti-
315 correlates with Q² species. The amounts of Q¹- and Q⁴ species are still the same in
316 all 192-atom models. In the 96-atom models, the average degree of polymerization
317 decreases after quench to 2400 K, from the total average of 2.69 at 3000 K to 2.56 at
318 2400 K (Fig. 10). Their Qⁿ species distributions are higher in Q² species but lower in
319 Q³ and Q⁴ 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 30 ps in the 96-atom models. We interpret these oscillations as fluctuations of the thermally equilibrated structure. The Si-O bond time constant $\tau_{Si-O}=30$ 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_2O 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).

model name:	L1	L2	L3	L av.	M1	M2	M3	M av.
number of atoms:	192	192	192	192	96	96	96	96
3000 K:								
x^{Q0} :	0.01	0.01	0.05	0.02	0.02	0.01	0.00	0.01
x^{Q1} :	0.12	0.08	0.10	0.10	0.07	0.11	0.06	0.08
x^{Q2} :	0.38	0.35	0.26	0.33	0.27	0.30	0.32	0.29
x^{Q3} :	0.34	0.42	0.45	0.40	0.43	0.40	0.39	0.41
x^{Q4} :	0.13	0.13	0.14	0.13	0.20	0.18	0.21	0.20
sum:	0.98	0.99	0.99	0.99	0.99	1.00	0.99	0.99
$Q^{n,av.}$:	2.42	2.56	2.52	2.50	2.71	2.63	2.73	2.69
x_{MWO}^{ox} :	0.07	0.09	0.09	0.08	0.12	0.10	0.12	0.11
x_{NBO}^{ox} :	0.53	0.48	0.49	0.50	0.43	0.46	0.42	0.44
x_{BO}^{ox} :	0.40	0.43	0.42	0.42	0.45	0.44	0.46	0.45
$\ln K$:	2.29	1.76	1.90	1.99	1.25	1.52	1.17	1.31
mass bal. compl.:	0.36	0.35	0.35	0.35	0.33	0.34	0.33	0.33
2400 K:								
x^{Q0} :	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.01
x^{Q1} :	0.07	0.08	0.13	0.09	0.04	0.16	0.09	0.10
x^{Q2} :	0.18	0.29	0.33	0.27	0.40	0.36	0.27	0.34
x^{Q3} :	0.56	0.42	0.33	0.44	0.38	0.32	0.51	0.41
x^{Q4} :	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_{MWO}^{ox} :	0.14	0.12	0.10	0.12	0.10	0.07	0.11	0.09
x_{NBO}^{ox} :	0.38	0.42	0.47	0.42	0.47	0.53	0.44	0.48
x_{BO}^{ox} :	0.48	0.46	0.43	0.46	0.43	0.40	0.45	0.43
$\Delta x_{H_2O}^{ox}$ 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

336 results of our equimolar H_2O - SiO_2 models can be compared to results of other model-
 337 ing studies.[22, 23, 24] Comparing to the $\ln K$ of several studies, both as a function of
 338 temperature and as a function of H_2O concentration (Fig. 8) shows that our results with
 339 $\ln K = 1.99$ at 50 mol% H_2O are in good agreement to other modeling studies, given
 340 that conditions vary between all these studies.

341 As outlined in the introduction, we anticipated a decrease in $\ln K$ at 50 mol% H_2O
 342 based on the considerations of Newton and Manning[4]. This value was assumed as a
 343 turning point in the H_2O dissolution mechanism, from H_2O dissociation to clustering
 344 of molecular H_2O . However, the $\ln K$ of the 192-atom models does not indicate sig-
 345 nificant differences to those at lower H_2O concentration (inset in Fig. 8), including the
 346 extrapolation of experimental data by Nowak and Behrens to 3000 K.[20]

347 The agreement to the extrapolation of experimental data, and the almost constant
 348 value of $\ln K$ from low H_2O concentrations up to the 50 mol% H_2O , may indicate
 349 that reaction (1) is still not affected at these high water concentration. This would be
 350 at odds with the structural interpretation of the activity relationship by Newton and
 351 Manning.[4] and could mean that the activity-composition relationship is predomi-
 352 nantly controlled by other structural re-arrangements in this compositional range and
 353 not only by the reaction (1). On the other hand, the $\ln K$ found in the 192-atom model
 354 may still be affected by finite size effects. This model contains about twice the number
 355 of atoms compared to many other ab initio MD studies of silicate melts. In contrast to
 356 the other studies, it shows a T-dependence for $\ln K$ that would be expected. However,
 357 it may still be too small to allow for changes in structural incorporation, such as for-
 358 mation of clusters, as would be expected above a certain concentration for dissolution
 359 of H_2O in SiO_2 (and vice-versa). Clustering of cations (including hydrogen) in silicate
 360 glasses and melts is observed both in experiment[60] and in classical models of silicate
 361 glasses with thousands of atoms. The absence of this clustering suggests that there is
 362 a significant structural finite size effect on the structure of partly depolymerized silica
 363 networks, at least up to several hundreds of atoms.[61] Therefore, the structure of our
 364 192-atom models does not represent structures that are converged with respect to sys-
 365 tem size, and clusters cannot form. A final test requires modeling in a framework other
 366 than plane-wave DFT which becomes computationally prohibitively expensive beyond

367 two or three hundred atoms.

368 4.2. Structural changes after quench to 2400 K

369 The 192-atom models show a remarkable structural rearrangement within 10 to
 370 100 picoseconds after quench to 2400 K. The degree of polymerization increases, and
 371 the SiO₂ network releases molecular H₂O, which was priorly bound as SiOH hydroxy
 372 groups (Fig. 6, and snapshots in Fig. 7). The fractional amount of molecular water in-
 373 creases on average by 41% between 3000 K and 2400 K. Based on the increased bond
 374 stability (Section 4.4), structural equilibrium has not been reached in the MD runs at
 375 2400 K. Therefore, the process of water release could continue if the MD runs were
 376 longer. Reaching structural equilibrium at 2400 K is however beyond the aim of this
 377 study. The observed formation of molecular water is rather an effect of decreasing tem-
 378 perature than of the concomitant drop of pressure. We infer this from the insensitivity
 379 of silicate melt structure with respect to pressure in the investigated range of about
 380 3.5 to 4.3 GPa.[53, 23] At 2400 K, the average degree of polymerization has increased
 381 in all 192-atom models, however, the uniform structural picture at 3000 K has been
 382 replaced by a variety of average Qⁿ values and Qⁿ species distributions (Fig. 9).

Figure 10: The average Qⁿ 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.

383 The formation of molecular H₂O, which may be also considered as release of wa-

384 ter from the network, after lowering the temperature is expected on the basis of the
 385 phase diagram of the system $\text{H}_2\text{O}-\text{SiO}_2$ (Fig. 1).[5] Below 2000 K and 1 GPa, a wide
 386 miscibility gap opens over a narrow temperature interval. Above these conditions, a
 387 single $\text{H}_2\text{O}-\text{SiO}_2$ phase exists. Within this single phase, the ratio of H_2O to SiOH is
 388 expected to increase with decreasing temperature.[19, 4, 5] Clustering on the nano-
 389 scale is observed in various chemical systems such as silicate glasses and aqueous
 390 solution.[62, 61, 17, 63] There is evidence that critical fluctuations in hydrous melt
 391 may even be larger than for any other network modifier.[64] We therefore consider the
 392 possibility that the observed release of molecular water at 2400 K as a precursor of the
 393 formation of water clusters in a polymerizing silica network, a process that eventually
 394 leads to phase separation occurring at lower temperatures.

395 4.3. Finite size effects in partly broken silica network

396 The three 192-atom models L1 to L3 give consistent structural results with an aver-
 397 age Q^n value of 2.5 at 3000 K, and an increase to 2.75 on average at 2400 K (Fig. 10). In
 398 contrast, each of the 96-atom models shows an opposite trend. At 2400 K, the 96-atom
 399 models show individual Q^n values that are higher than any of the 192-atom models, al-
 400 though a decrease of the Q^n value with temperature would be expected. This abnormal
 401 behavior is also reflected in the corresponding $\ln K$ values in Fig. 8. The same increase
 402 in water molecules and therefore in $\ln K$ has been observed previously in a 102-atom
 403 model (see triangles in Fig. 2),[22]. This suspicious behavior of smaller models may
 404 not necessarily be true in the long-time limit of several hundreds of picoseconds. We
 405 prefer to address this as a retarding, transient finite size effect. It reflects the inability
 406 of the smaller models for formation of molecular H_2O as demonstrated by comparison
 407 to the larger 192-atom models on the timescale of hundred picoseconds (Fig. 10).

408 This finite size effect especially affects the structural results of partially broken
 409 silica networks from ab initio models of typically about 100 atoms. In the case of pure
 410 SiO_2 , it has been shown by Van Ginhoven *et al.*[34] that it is possible to obtain a good
 411 structural description of SiO_2 from the average of several small models with less than
 412 100 atoms.[34] According to their results, each small SiO_2 model can be thought of as
 413 a small region in a larger system. We consider that this observation may be less valid

414 in the case of partially depolymerized hydrous silica network, because partially broken
415 silicate networks show more variability in their intermediate range structure.[34, 51]

416 Therefore, partially depolymerized silicate networks are especially sensitive to the
417 model size. This probably applies especially to the system $\text{SiO}_2\text{-H}_2\text{O}$ where the struc-
418 tural adaptation by reaction 1 not only requires large translational movements, but large
419 energetic barriers to be overcome.[65] These barriers are less pronounced in the case
420 of silicate melts with 'truly ionic' cations such as alkaline and Earth-alkaline cations
421 are present.

422 4.4. Bond dynamics as a function of temperature

423 In MD models of silicates, a system can achieve structural equilibration probably
424 only if the MD trajectory length exceeds the average Si-O bond lifetime. In the case
425 of 3000 K, this criterium is fulfilled, as can be judged by the Si-O bond time constant
426 $\tau_{\text{Si-O}}$ of about 30 ps (Fig. 5). Another criterium is the observation of multiple os-
427 cillations in the number of water molecules (Figs. 6 and 5). At 2400 K, with a Si-O
428 bond time constant of about 230 ps, this criterium is clearly not fulfilled. Therefore, we
429 cannot assume that structural equilibrium is reached in our MD runs at 2400 K. Based
430 on this number, we consider that reaching structural equilibrium at 2400 K in terms of
431 Q^n species and water molecules would require at least 500 ps as a first approximation.
432 Moreover, the BACF time constants calculated here represent a *lower limit* estimate
433 for the time necessary for structural equilibration. This is because the equimolar com-
434 position under investigation here ensures a maximum of interaction between the SiO_2
435 network and H_2O molecules. In addition to that, the limited size of the models in-
436 hibits the formation of H_2O clusters that are assumed to occur on the nanometer scale
437 in reality.[5, 60] In clusters, the H_2O molecules would be "passivized" with respect to
438 breaking of the silicate network.

439 The bond time constants seem system-specific and we expect that in other, more
440 ionic systems, such as $\text{Na}_2\text{O-SiO}_2$ and MgO-SiO_2 , or in systems with a built-in charge-
441 coordination disequilibrium as in the case of Al_2O_3 , the energy barriers (and therefore
442 the time constants) may be smaller. Then, structural equilibrium of the silica network
443 can be at lower temperatures, eventually down to 2200 K or so.

444 A relation between bond stability and temperature, as the one established here with
445 ab initio accuracy, could be a benchmark for the reliability of classical potentials at high
446 temperatures. Atomic-scale modeling of systems that involve the H₂O-SiO₂ interaction
447 reaction 1 crucially depends on the correct reproduction of its reaction energy and its
448 energetic reaction barriers.

449 5. Conclusions

450 We have investigated supercritical equimolar H₂O-SiO₂ fluid at three temperatures
451 and two different model sizes under the aspects of structure and structural changes after
452 temperature is decreased. We draw three main conclusions.

453 1) We found at 3000 K an average Q^n value of 2.5 and a fraction of molecular H₂O
454 of about 25%. The $\ln K$ plots only slightly below extrapolated experimental data of
455 dilute H₂O in a silicate melt. Larger downward deviation from this extrapolation would
456 be expected based on the predicted change in H₂O solution mechanism in silicate melts
457 above about 30 mol% H₂O.[4] A reason could be, that the 192-atom cells are too small
458 to allow for proper modeling of the clustering on the nanometer-scale expected in other
459 studies. After quench from 3000 K to 2400 K, the supercritical H₂O-SiO₂ fluid releases
460 molecular H₂O on a timescale of tens to hundreds of picoseconds, in agreement with
461 the temperature dependence of reaction constant K .

462 2) In this ab initio modeling study, we have used models that are about double in
463 number of atoms (192 atoms), compared to what is commonly used. This allowed
464 us to observe a peculiar difference in behavior between 192-atom and 96-atom mod-
465 els. First, at 3000 K, the 192-atom models show consistently a higher average degree
466 of polymerization than the 96-atom models. Second, after quench from 3000 K to
467 2400 K, the 192-atom release water molecules, in agreement with experiment, but the
468 96-atom models all consume water molecules after quench from 3000 K to 2400 K.
469 This cross-over in behavior points to a structural finite size effect, which possibly acts
470 even stronger on partially depolymerized silicate networks than on pure SiO₂. As a
471 finite size effect, smaller models are stabilized in their structure, rendering lower prob-
472 ability for structural change within a given MD run duration. This affects the reliability

473 of ab initio MD modeling of silicate melts and glasses in a general way.

474 3) We analyzed the Si-O bond stability by means of the bond autocorrelation func-
475 tion, to investigate the temperature dependence of the dynamics of the dissociation
476 reaction $\text{H}_2\text{O} + \text{SiOSi} = 2 \text{SiOH}$. The calculated Si-O bond time constants show, that
477 within a MD trajectory of 200 ps length, reaching structural equilibrium is assured for
478 3000 K, but not for 2400 K. Knowledge of the relation between temperature and Si-
479 O bond stability is important for future modeling in the system $\text{H}_2\text{O-SiO}_2$, but also
480 for modeling of chemical compositions closer to naturally occurring hydrous silicate
481 melts.

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

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