Self-diffusion of water molecules confined between quartz surfaces at elevated temperatures by molecular dynamics simulations

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Molecular dynamics (MD) simulations were performed to investigate the self-diffusion coefficients and density profiles of water confined between quartz (1010) surfaces at 298-573 K. The self-diffusion coefficient of water near the surface was lower than that of water far from the surface. The density profiles of H2O molecules showed several layered structures near the surface. In the thickness of 4.8 nm of H2O at 298 K, the thickness of layered structure was estimated to be 1.0 nm, and the self-diffusion coefficient was reduced in 1.0 nm distance from the surface. At 573 K, the thickness of reducing area could be larger than the thickness of layered structure of 1.5 nm. Even in higher temperature conditions such as 573 K, the self-diffusion coefficient of water near the surface was reduced.

Keywords: Interfacial water, Quartz, Molecular dynamics, Self-diffusion coefficient

INTRODUCTION

Water–Rock Interaction (WRI) has been realized as an essential process to understand Earth’s events such as volcanic eruption and earthquake. In general, WRI is controlled by partial and entire chemical reactions between fluid and solid materials and these reactions can be understood from micro- and nano-scale phenomena (Wissmeier and Barry, 2008; Hara and Tsuchiya, 2009).

Interfacial water, of which physicochemical properties were different from bulk water, was recognized in the vicinity of solid surface. Such characteristic properties of interfacial water should be revealed for understanding the WRI. There has been many studies about the interfacial water by both theoretical (Hassanali and Singer, 2007; Pertsin and Grunze, 2008) and experimental method (Yalamanchili et al., 1996; Asay and Kim, 2005; Abe et al., 2008; Anderson and Ashurst, 2009; Abe et al., 2012; Hamamoto et al., 2015). The physical properties on a solid surface show unique characteristics, for example the self-diffusion coefficient and viscosity (Ichikawa et al., 1999; Sakuma et al., 2003; Klein et al., 2004; Perkin et al., 2006; Siboulet et al., 2013), thermal expansion coefficient (Xu et al., 2009) and freezing point (Jähnert et al., 2008). On a silicon oxide surface, the ice–like infrared spectra was observed in 10 Å at 20.8 °C (Asay and Kim, 2005). While on a silica vapor–deposited silicon oxide surface, the thickness was 20 nm at room temperature (Anderson and Ashurst, 2009), and on a mesoporous silica surface, the thickness was estimated to be ~ 10 nm at 300 and 400 °C (Abe et al., 2012).

Quartz is an abundant rock-forming mineral, and quartz–water interface is one of the most common interfaces in the Earth’s crust. The interface has been previously studied for understanding the hydrogen bonding network (Aines and Rossman, 1984; Abe et al., 2008), interfacial structure (Schlegel et al., 2002), hydrolytic weakening (Griggs and Blacie, 1965; Kronenberg and Tullis, 1984) and quartz solubility (Akiniev and Diamond, 2009). The IR absorption peaks of thin film water on metal and on quartz were measured by FTIR up to 400 °C, 50 MPa, and these exhibited different trend (Abe et al., 2008). The density oscillation of water was observed at the interface by X-ray reflectivity and the thickness was ~ 3 Å (Schlegel et al., 2002).

Although the phenomena of quartz–water interface have been studied theoretically and experimentally, the dynamics of the interface at high temperature and pressure remains unclear. In this study, we performed the mo-
molecular dynamics (MD) simulations to understand the structure and dynamics of water confined between quartz surfaces at high temperatures and pressures.

**SIMULATION METHODOLOGY**

We prepared three systems of quartz/water interfaces for investigating the effect of water thickness as listed in Table 1. The thickness of H\textsubscript{2}O molecules between quartz ranges from 0.5 nm to 4.8 nm at 298 K. 2000 H\textsubscript{2}O molecules confined between quartz (10\textsubscript{1}/C\textsubscript{2}2\textsubscript{1}/0) surfaces are shown in Figure 1. The surface was characterized by the termination of silanol (Si–OH) group.

The potential parameters for the simulation are shown in Table 2. The potential model of water was previously developed to well reproduce the physical properties of water and ice over the wide range of temperatures and pressures (Kawamura, 2008). The potential model of quartz originally was developed by K. Kawamura (personal communication) and was modified here to reproduce the experimentally determined OH–vibration spectrum of surface silanol group. Figure 2a shows OH–vibration spectrum of surface silanol groups in the MD simulation. Two peaks between 4000–2800 cm\textsuperscript{-1} were due to the presence of two different OH stretching bands. A sharp peak was present around 3800 cm\textsuperscript{-1}, and assigned to the OH stretching vibration of isolated non-hydrogen–bonded silanols. This peak was obtained around 3750 cm\textsuperscript{-1} (McDonald, 1958; Hair, 1975). A small peak was present around 3425 cm\textsuperscript{-1}, and assigned to hydrogen–bonded silanols. As shown in Figure 1, two types of silanol groups were confirmed. One is parallel to c axis and another makes hydrogen bonds with the oxygen of the former silanol group. The assignment of the vibrational bands is apparent from the analysis of c–component vibrational spectrum as shown in Figure 2b. The decreased peak at 3425 cm\textsuperscript{-1} indicates that the OH direc-

### Table 1. Details of simulation cells at 298 K

| No. | \(N_{\text{H}_2\text{O}}\) | \(W\) [nm] | \(a\) [Å] | \(b\) [Å] | \(c\) [Å] |
|-----|----------------|-----------|--------|--------|--------|
| 1   | 400           | 0.45      | 59.9   | 65.4   | 16.7   |
| 2   | 2000          | 1.75      | 59.9   | 65.4   | 29.4   |
| 3   | 6000          | 4.79      | 59.9   | 65.4   | 60.1   |

\(N_{\text{H}_2\text{O}}\) is the number of H\textsubscript{2}O molecules in the cell. 
\(W\) means the thickness of water layer, and \(a\), \(b\), \(c\) are the cell parameters. 
A snapshot of No. 2 cell is shown in Figure 1a.

### Table 2. Potential parameters of quartz and water

| Atom | Label | \(\epsilon\) [e] | Atomic weight [g/mol] | \(a\) [nm] | \(b\) [nm] | \(c\) [(kJ/mol)\(\textsuperscript{1/2}\) (nm)\(^2\)] |
|------|-------|------------------|-----------------------|--------|--------|----------------|
| Quartz | O     | -1.100           | 16.00                 | 0.1865 | 0.01460 | 0.06301 |
|       | Si    | 2.200            | 28.09                 | 0.0942 | 0.00720 | 0.00000 |
|       | H     | 0.550            | 1.01                  | 0.0101 | 0.00290 | 0.00000 |
| Water | O     | -0.920           | 16.00                 | 0.1728 | 0.01275 | 0.05606 |
|       | H     | 0.460            | 1.01                  | 0.0035 | 0.00440 | 0.00000 |

| Atom pairs | \(D_{1y}\) [kJ/mol] | \(\beta_{1y}\) [nm\(^2\)] | \(D_{2y}\) [kJ/mol] | \(\beta_{2y}\) [nm\(^2\)] | \(D_{3y}\) [kJ/mol] | \(\beta_{3y}\) [nm\(^2\)] | \(r_{3y}\) [nm] |
|------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|--------|
| O–Si       | -7036.75         | 19.50           | -                | -               | 44.37            | 660.0           | 0.1111 |
| O–H        | -3139.54         | 27.80           | -                | -               | -                | 1280.0          | 0.1283 |
| O\textsubscript{H}_2O–H\textsubscript{H}_2O | 57394.93 | 74.00 | -2189.30 | 31.30 | 34.74 | 1280.0 | 0.1283 |

| Atom pairs | \(f\) [10\(^{-22}\) kJ] | \(\theta\) [deg.] | \(r_\infty\) [nm] | \(g_\infty\) [nm\(^{-2}\)] |
|------------|-----------------|-----------------|--------|--------|
| H\textsubscript{2}O–O\textsubscript{H}_2O–H\textsubscript{H}_2O | 1.15 | 99.5 | 0.1430 | 92.0 |

The ‘-’ denotes that the parameter was not used.
tion has main component parallel to the surface.

Temperature and pressure were controlled by a scaling method. Four pressure-temperature conditions \((P = 10.0 \text{ MPa at } T = 298, 373, 473, \text{ and } 573 \text{ K})\) were simulated for investigating the effect of temperature. The equation of motion of atoms was approximated by the difference equation using the velocity Verlet algorithm. The time increment for the difference equation is 0.4 fs.

Constant number of atoms, pressure and temperature (NPT) ensemble was performed to obtain the density at equilibrium state. Subsequent canonical (NVT) ensemble simulations for 250000 calculation steps (100 ps) were performed for analyzing the structure and dynamics of water. All MD simulations were performed using in-house program based on MXDORTO (Sakuma and Kawamura, 2011).

In this study, the self-diffusion coefficients \((D)\) of \(\text{H}_2\text{O}\) molecules were calculated as the \(D\) of oxygen atoms in \(\text{H}_2\text{O}\) molecules using Green-Kubo relation:

\[
D = \frac{1}{nN} \sum_{j=1}^{N} \left\langle \sum_{j=1}^{N} \mathbf{v}_j(t) \cdot \mathbf{v}_j(0) \right\rangle dt
\]

where \(n\) is the dimension of the system (3 or 2), \(N\) is the number of \(\text{H}_2\text{O}\) molecules, \(t\) is the simulation time and \(\mathbf{v}\) is the velocity vector of \(j\)th \(\text{H}_2\text{O}\) molecule. \(\mathbf{v}_j(t)\mathbf{v}_j(0)\) is \(j\)th \(\text{H}_2\text{O}\) molecule’s velocity autocorrelation function. Representative velocity autocorrelation functions and convergence of the integration for bulk water were shown in Figure 3. The \(D\) in this study was obtained by the integration from 0 to 2-5 ps because of the good convergence of the values greater than 2 ps as shown in Figure 3.

Here, we calculated two-dimensional self-diffusion coefficient \((D_{xy}; n = 2)\) parallel to the quartz surface. The two-dimensional self-diffusion coefficient of \(j\)th \(\text{H}_2\text{O}\) molecule \(D_{xy}(j)\) was calculated as

\[
D_{xy}(j) = \frac{1}{2 \rho_j} \left\langle \mathbf{v}_{oy}(t) \cdot \mathbf{v}_{oy}(0) \right\rangle dt
\]

This \(D_{xy}(j)\) was used for calculating the mean value \(D_{xy}\) of all \(\text{H}_2\text{O}\) molecule. This \(D_{xy}(j)\) was also used to determine the self-diffusion coefficient at each distance \(z\) from quartz surfaces \(D_{xy}\) as follows.

\[
D_{xy} = \frac{\sum_{j=1}^{N} D_{xy}(j) \cdot \rho(j,z)}{\sum_{j=1}^{N} \rho(j,z)}
\]

where \(\rho(j,z)\) is the existence probability of \(j\)th \(\text{H}_2\text{O}\) molecule at \(z\). In a long time calculation, \(\text{H}_2\text{O}\) molecules can be located at various positions between quartz surfaces, and therefore the self-diffusion coefficient of one \(\text{H}_2\text{O}\) molecule reflects the averaged diffusion coefficient at various positions. In order to derive the self-diffusion coefficient as a function of the distance from the quartz surface, the trajectory data of 100 ps were divided into 20 ps segment, and the segments were used for calculation of (2) and (3). The results of all segments were averaged, and shown in Figure 4.

**RESULTS AND DISCUSSION**

**Self-diffusion coefficients of bulk water**

Self-diffusion coefficients of bulk water were calculated for confirming the reliability of employed velocity-scaling method and water model. A cubic cell including 1500 \(\text{H}_2\text{O}\) was used and the cell size was fixed by using the averaged density depending on the simulated temperature and pressure. The self-diffusion coefficient calculated by Nosé-Hoover chain method (Martyna et al., 1992) with the time increment of 0.1 fs was compared with the results by temperature-scaling method as summarized in

![Figure 3](image-url) Normalized velocity auto-correlation function (VAC, solid lines) and integrated VAC (dash lines). \(T = 298\) K (black lines) and \(T = 573\) K (gray lines).

![Figure 4](image-url) \(D_{xy}\) (broken lines) and density (solid lines) of water in (a) 400 \(\text{H}_2\text{O}\), (b) 2000 \(\text{H}_2\text{O}\) and (c) 6000 \(\text{H}_2\text{O}\) confined between quartz surfaces as a function of distance from quartz surface. The structure and dynamics was symmetric, therefore one sides were shown here.
Table 3. Self-diffusion coefficient of bulk water (1500 H2O) at 298 K

| Method        | dt [fs] | \(D_{\text{bulk}} \times 10^9 \text{m}^2/\text{s}\) |
|---------------|---------|-----------------------------------------------|
| Nose-Hoover chain | 0.1     | 1.612 ± 0.081                                 |
| Velocity scaling    | 0.1     | 1.593 ± 0.041                                 |

Calculated by two temperature controlling methods. The calculations were performed with \(NVT\) ensemble (\(\rho = 0.998\ \text{g/cm}^3\)) and for 20 ps (200000 or 50000 steps). Three-dimensional self-diffusion coefficient \(D_{\text{bulk}}\) and the standard deviation of 10 independent runs were described in the table.

Table 4. Self-diffusion coefficients of bulk water

| Method        | 298 K | 373 K | 473 K | 573 K |
|---------------|-------|-------|-------|-------|
| \(D_{\text{bulk}} \times 10^9 \text{m}^2/\text{s}\) | 1.585 | 6.961 | 18.44 | 35.798 |
| \(D_{\text{MM}} \times 10^9 \text{m}^2/\text{s}\) | ±0.060 | ±0.164 | ±0.198 | ±0.528 |
| \(D_{\text{NN}} \times 10^9 \text{m}^2/\text{s}\) | 2.929 |

Calculated \(D_{\text{bulk}}\) and the standard deviation of 10 independent runs were described in the table. \(D_{\text{NN}}\) is the experimental result summarized in the literatures.

* Yoshida et al., 2005; ** Holz et al., 2000.

Table 3. Since three dimensional self-diffusion coefficients \((D_{\text{bulk}}; n = 3)\) have no difference within the error, the velocity-scaling method with a time increment of 0.4 fs was employed in the following sections.

Calculated \(D_{\text{bulk}}\) at four pressure \((P)\)-temperature \((T)\) conditions \((P = 0.1 \text{ MPa at } T = 298 \text{ K and } P = 10.0 \text{ MPa at } T = 373, 473, \text{ and } 573 \text{ K})\) were listed in Table 4. The value underestimated at 298 K, though the values at elevated temperature agreed with the experimental results presented in Holz et al. (2000) and Yoshida et al. (2005).

Two-dimensional self-diffusion coefficients of water confined between quartz surfaces

To investigate the relationship between interfacial structure and local mobility of H2O, self-diffusion coefficient \(D_{\text{xy}}\) and density profile of water at each distance from surfaces were calculated as shown in Figure 4. Figure 4a shows the results of 400 H2O confined between quartz surfaces. The density was characterized by a single peak, and this peak seems to be composed by adsorbed H2O molecules on the quartz surface. The self-diffusion coefficients were significantly lower than the bulk value.

Figure 4b shows the results of 2000 H2O molecules confined between quartz surfaces. At 298 and 373 K, no flat density area was observed. A shoulder and a large peak were observed at \(z \approx 0.1\) to 0.2 nm indicating the presence of two different types of adsorbed water near the surface. Two different types of adsorbed water correspond to two types of water bonding to two types of silanol groups by hydrogen bonding. This quartz surface has two types of silanol group on the surface as shown in Figure 1a. One is located near the bulk crystal and another is located near the film water. The shoulder of the density profiles near quartz surface observed at \(T < 373 \text{ K}\) corresponds to H2O molecules making hydrogen bonds with silanol groups near the bulk crystal. This shoulder peak disappear at elevated temperatures because there is no significant difference among silanol group at these temperatures as shown in Figure 1b. Subsequent peaks observed at \(z \approx 0.5\) and 0.8 nm gradually decayed with increasing the distance from quartz surface. The periodicity corresponds to the size of a H2O molecule (~0.3 nm) and this indicates the presence of five water layers between quartz surfaces. The peaks of the density at \(z \approx 0.5\) and 0.8 nm were less significant at 473 and 573 K. Figure 4c shows the results of 6000 H2O system. The structure of 6000 H2O system was similar to those of 2000 H2O systems. Three peaks at \(z = 0.15, 0.5, \text{ and } 0.8 \text{ nm}\) can be distinguished at 298 and 373 K. The third peak disappeared at higher temperatures. Previous experimental study shows the ice-like infrared spectra in three monolayers on silicon oxide surface at 20.8 °C (Asay and Kim, 2005) and this is consistent with our results.

The self-diffusion coefficients changed as the distance from surfaces. All results show that \(D_{\text{xy}}\) was reduced near the surface, and was almost a constant value at far from surface. In 6000 H2O system (Fig. 4c), \(D_{\text{xy}}\) of the center (1.5-3.0 nm) was almost same as bulk value. At 298 K, the thickness of layered structure was estimated to be 1.0 nm. \(D_{\text{xy}}\) of the same system reduced in 1.0 nm near the surfaces. The thickness of small \(D_{\text{xy}}\) area seems to be larger than the thickness of layered structure at elevated temperatures. Although this might be caused by the calculation method of \(D_{\text{xy}}\), since the large movement of H2O molecules in the cell at elevated temperatures reduces the resolution in space in this method. The reduction of \(D_{\text{xy}}\) value was not so large, but the effect of the presence of surface could affect the dynamics of water more than the effects on the structuring of water near the quartz surfaces.

Arrhenius plots of the \(D\), which is the averaged value of \(D_{\text{xy}}\), were shown in Figure 5. The calculated \(D\) seem to be approximated by a straight line in this plot and therefore the data were fitted to the following equation,

\[
\ln(D) = \ln(D_0) - \frac{E_a}{RT}
\]

where \(D_0\) is the frequency factor, \(R\) is gas constant \((R = 8.31 \text{ J K}^{-1}\text{mol}^{-1})\) and \(E_a\) is the activation energy for the
diffusion process. These parameters are summarized in Table 5. The self-diffusion coefficient of H₂O molecules in confined geometry can be fitted by the Arrhenius equation as shown in Figure 5. No significant deviation from the Arrhenius equation indicates that the structural change of two types of hydrogen bonded water molecules at elevated temperature (Fig. 4) has not significantly affected on the diffusion mechanism. Note that this discussion was based on four points at 298, 373, 473, and 573 K in the Arrhenius plot; therefore, this results do not rule out the possibility that the structural change has a small effect on the diffusion mechanism. The activation energies $E_a$ of three different systems including 400, 2000, and 6000 H₂O confined between quartz surfaces can be obtained $\sim 16-17$ kJ/mol. These values were close to $E_a$ of bulk water of 17.6 kJ/mol (Mills, 1973). As discussed in the $E_a$ of bulk water (Mills, 1973), the data show a gentle curvature and therefore the diffusion mechanism cannot be solely explained by the activation energy. However, this activation energy theory should be useful for understanding the diffusion mechanism. The similar values of $E_a$ of H₂O between bulk state and in confined geometry implied that the diffusion mechanism is similar and the activation energy may be interpreted by the dissociation energy of hydrogen bond.

CONCLUSIONS

We investigated self-diffusion coefficients and density profiles of H₂O molecules confined between quartz surfaces by using MD simulations from 298 to 573 K. The self-diffusion coefficient of water with the thickness of 1 nm showed significantly lower value compared with that of bulk water. Even in higher temperature conditions such as 573 K, the self-diffusion coefficient of water near the surface was reduced. The density profiles of H₂O molecules showed several layered structures near the surface, and the third peak from the surface disappeared at higher temperatures. The thickness of small self-diffusion coefficient area seems to be larger than the thickness of layered structure at elevated temperatures. The activation energies of the diffusion process in confined geometries were calculated based on the Arrhenius theory, and these values were close to that of bulk water. This implied that the diffusion mechanism in confined geometries is similar that in bulk and the activation energy may be interpreted by the dissociation energy of hydrogen bond.

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