Section 7. Other glass properties

Molecular dynamics study of temperature dependence of volume of amorphous silica

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Abstract

Vitreous silica (v-SiO₂) exhibits an unusual volume–temperature dependence; the volume has a maximum and minimum at certain temperatures, T* and Tp respectively. The origin of such an unusual thermal property was studied by molecular dynamics computer simulation. Four types of potentials were compared: pairwise additive potentials using exact the Coulomb term (E2) and screened Coulomb term (S2), and two potentials including a three-body term for reproducing the SiO₄ tetrahedral structure, one using the exact Coulomb term (E3), and the other one a screened Coulomb term (S3). The volume minimum could be reproduced by using the S2 and E2 potentials, but it could not be reproduced by using the E3 and S3 potentials; the three-body term acts repulsively at high temperatures to retain the O–Si–O bond angle at the tetrahedral angle in spite of many bonds being broken at such temperatures. Therefore, the three-body term is inappropriate for studying the properties and the structure of v-SiO₂ at high temperature. The origin of the volume–temperature dependence was discussed based on the analysis of the structure.

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1. Introduction

Vitreous silica (v-SiO₂) contains extremely low amount of metallic impurities and has high heat resistivity. [1,2] Therefore, this material is used as a container for heat treatment that is free from contaminants, e.g., the inner lining of a tube furnace used in the fabrication process of semiconductor devices [2]. Although the properties of v-SiO₂ at a high temperature are important both in industrial applications and scientific respects, the structure and the properties of this material have not been thoroughly clarified because this material does not have an ordered structure, unlike crystals. Properties of v-SiO₂ at high temperatures are important, because this material is used at a high temperature. However the experimental tools necessary for investigating the high-temperature properties are limited [3]. A complementary tool for studying the high-temperature properties of v-SiO₂ is molecular dynamics (MD) computer simulation [4]. Since the pioneering work of Woodcock et al. [5], a number of studies have been reported. Various kinds of potentials are used for different purposes. Woodcock et al. [5] used a Born–Mayer–Huggins (BMH) potential, which had originally been proposed for describing the interaction between ions. Tsuneyuki et al. [6] proposed a potential based on first-principles calculations for clusters using the Hartree–Fock approximation. Kawamura [7] proposed a potential, which contains a Morse term, to describe the attractive force in addition to the BMH potential term. Demiralp et al. [8] proposed a simpler potential which contains the Morse stretch potential combined with a semiempirical method for dealing with the effects of charge transfer between atoms, called the charge equilibration (QEeq) method.
These potentials contain Coulomb terms, which have long-range effects. Coulomb interactions cannot be calculated straightforwardly in MD simulation using the periodic boundary condition because the Coulomb force interacts far beyond the unit simulation cell. To overcome this problem, a technique called the Ewald method [9] is used. Since this method utilizes the three-dimensional periodicity of the simulation cell, this method cannot be applied straightforwardly to a system with two-dimensional periodicity such as a surface. To avoid this constraint, Garofalini [10] used a BMH-type potential with a screened Coulomb term. Since the charge density on the surface is different from that of the bulk [11,12], the screened Coulomb potential is not satisfactory for describing the surface properties and structures. However, this potential might be applicable for describing some bulk properties because the electric field caused by the charge at one atom is shielded by the other atoms and their charges.

On the surface, many dangling bonds exist. When using a pairwise additive potential, undercoordinated silicon at the surface tends to form a planar three-oxygen-coordinated structure because of the repulsion force between oxygen atoms [13]. However, some of the three-oxygen-coordinated silicon atoms retain part of the tetrahedral structure, which is a kind of radical structure \( \equiv Si \) called the E' center [13]. These structures exist on the surface of crushed silica powder, as observed by electron paramagnetic resonance (EPR) [14]. To reproduce such a structure, a three-body term is required, which constrains the O-Si-O bond angle to the tetrahedral angle of 109.47°. Feuston and Garofalini [15] proposed a potential containing such a three-body term in addition to their pairwise additive potential with the screened Coulomb term. Vashishta et al. [16] proposed a potential including the exact Coulomb potential and a three-body term similar to that proposed by Feuston and Garofalini [15].

Vitreous silica exhibits an unusual volume–temperature (VT) dependence. At a temperature lower than a characteristic temperature \( T^* \), the volume expands with increasing temperature. Then in the temperature range of \( T^* < T < T_p \), \( r-SiO_2 \) shrinks. The volume has a minimum at temperature \( T_p \) and increases again for \( T_p < T \) [1]. Perchak and O’Reilly [17] studied the volume temperature dependence of \( r-SiO_2 \) by MD simulation using the pairwise additive potential proposed by Garofalini [10] and reproduced the ‘volume minimum’. In their result, however, the VT curve depended on the simulation conditions such as cooling and heating rates, and the parameter used for pressure control. They ascribed the volume minimum to the creation of five-oxygen-coordinated silicon atoms. Yamahara et al. [18] also reproduced the volume minimum using a pairwise additive potential. They ascribed the origin of the VT behavior to the densification associated with the formation of bridging oxygens during the cooling process and the rearrangement of the ring structure.

The VT behavior is sensitive to the potential that is used in the simulation. To discuss the effect of each term of the potential, we compare, in this study, the VT behavior of four potentials; pair-wise additive potentials using the exact Coulomb term (E2) and the screened Coulomb term (S2), and potentials including three-body terms for reproducing the \( SiO_4 \) tetrahedral structure, also using the exact Coulomb term (E3) and the screened Coulomb term (S3).

2. Simulation method

2.1. Potential

The potential energy for an \( N \)-body system can be expressed as

\[
U(r_1, r_2, \ldots, r_N) = \sum_{i<j} u_2(r_{ij}) + \sum_{i<j<k} u_3(r_{ijk}) + \cdots + u_N(r_1, r_2, \ldots, r_N).
\]

(1)

In most cases, the potential can be approximated as pairwise additive, i.e., including only the \( u_2 \) terms. In this work, we used potentials which include up to the three-body term \( u_3 \). The two-body term \( u_2 \) can be expressed as a function of the distance \( r_{ij} \) between particles \( i \) and \( j \), as \( u_2(r_{ij}) \). To reproduce the \( SiO_4 \) tetrahedral structures, the three-body term is expressed as

\[
u_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{ijk}) + h(r_{ik}, r_{ji}, \theta_{ijk}) + h(r_{kl}, r_{lk}, \theta_{kl}),
\]

(2)

where

\[
h(r_{ij}, r_{ik}, \theta_{ijk}) \equiv \lambda_i \exp \left( \frac{\gamma_i}{r_{ij} - r_i^C} + \frac{\gamma_i}{r_{ik} - r_i^C} \right) 
\times (\cos \theta_{ijk} - \cos \theta_{jk}^C)^2,
\]

(3)

with \( \theta_{ijk} \) being the angle formed by the particles \( i, k \) and \( j \). The details of the potentials and their parameters are shown in Tables 1 and 2, respectively.

Details of each potential are as follows. Potential S2 consists of only two-body terms using a screened Coulomb term.[10] The first term in \( u_2 \) is the screened Coulomb term and the second term represents the repulsive force. No three-body term is used in this potential. Potential E2 is a combination of the BMH potential and the Morse term. The first term is the exact Coulomb term, the second term is repulsive, the third term describes the van der Waals attraction, and the last term is the Morse potential term. Potential S3 includes three-body terms in addition to the same two-body term.
Potential \( u_2 \) is a repulsive term, the second term is the exact Coulomb term, and the third term is an attractive term. The three-body term in this potential has the same functional form as S3, but the parameters are different from those in the S2 potential. The potential term \( u_3 \) in E3 has a minimum at the Si–O–Si bond angle of 141°, whereas \( u_3 \) in the S3 potential term has a minimum at the tetrahedral angle of 109.47°. The magnitude of the prefactor \( k_{\text{Si–O–Si}} \) is greater than that of \( k_{\text{O–Si–O}} \). This is different from that in the S3 potential where the magnitude of \( k_{\text{Si–O–Si}} \) is 1/30 that of \( k_{\text{O–Si–O}} \). Such a strong potential term in E3 is introduced so as to reproduce the experimentally observed Si–O–Si bond angle.

We refer to the systems simulated using these potentials as Samples S2, E2, S3 and E3. A system without the three-body term is referred to as a two-body system (2BS), and a system containing three-body terms as a three-body system (3BS).

### Table 1

<table>
<thead>
<tr>
<th>Potential</th>
<th>( u_2 )</th>
<th>( u_3 )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>( \frac{Z_i}{4} \text{erfc} \left( \frac{r_{ij}}{q_{ij}} \right) + A_{ij} \exp \left( \frac{r_{ij}}{b_{ij}} \right) )</td>
<td>0</td>
<td>[10]</td>
</tr>
<tr>
<td>E2</td>
<td>( \frac{Z_i}{4} \text{erfc} \left( \frac{r_{ij}}{q_{ij}} \right) + f_0(b_i + b_j) \exp \left( \frac{r_{ij}}{b_{ij}} \right) )</td>
<td>0</td>
<td>[7]</td>
</tr>
<tr>
<td>S3</td>
<td>The same as S2</td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td>E3</td>
<td>( H_{g_{ij}} + \frac{Z_i}{4} \text{erfc} \left( \frac{r_{ij}}{q_{ij}} \right) )</td>
<td></td>
<td>[16]</td>
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### Table 2

<table>
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<th>Potential</th>
<th>Parameter</th>
<th>Si</th>
<th>O</th>
<th>Si–Si</th>
<th>Si–O</th>
<th>O–O</th>
<th>O–Si–O</th>
<th>Si–O–Si</th>
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<td>S2</td>
<td>( \rho_i ) (nm)</td>
<td>4</td>
<td>-2</td>
<td>0.029</td>
<td>0.029</td>
<td>0.029</td>
<td>0.250</td>
<td>0.250</td>
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<td></td>
<td>( A_{ij} ) (J)</td>
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<td>2.962 \times 10^{-16}</td>
<td>0.7254 \times 10^{-16}</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>( \beta_{ij} ) (nm)</td>
<td>0.250</td>
<td>0.250</td>
<td>0.250</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>( \rho_i ) (nm)</td>
<td>2.4</td>
<td>-1.2</td>
<td>0.0945</td>
<td>0.1926</td>
<td>0.0090</td>
<td>0.0160</td>
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<td></td>
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<td>0.0409</td>
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<td></td>
<td>( b_i ) (nm)</td>
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<td>0.0160</td>
<td></td>
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<td></td>
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<td></td>
<td>( c_i ) (kJnm(^{1/2})mol(^{1/2}))</td>
<td>1.20</td>
<td>20</td>
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<td>( D_{ij} ) (J)</td>
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<td>( \rho' ) (nm(^{1/2}))</td>
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<td>S3</td>
<td>( \rho_i ) (nm)</td>
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<td>-2</td>
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<td>0.029</td>
<td>0.029</td>
<td>0.250</td>
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<td>( \beta_{ij} ) (nm)</td>
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<td>( \lambda_i ) (J)</td>
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<tr>
<td></td>
<td>( \gamma_i ) (nm)</td>
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<tr>
<td></td>
<td>( \theta_{ijk} ) (°)</td>
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<td>109.47</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td>( \rho_i ) (nm)</td>
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<td>0.00</td>
<td>2.40 \times 10^{-3}</td>
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<td></td>
<td>( H ) (Jnm(^3))</td>
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<td>2.625 \times 10^{-24}</td>
<td>1.190 \times 10^{-23}</td>
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<td>( \rho' ) (nm(^{1/2}))</td>
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<td></td>
<td>( \lambda_i ) (J)</td>
<td>8.07 \times 10^{-19}</td>
<td>3.23 \times 10^{-18}</td>
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<td>( \gamma_i ) (A˚)</td>
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<tr>
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<td>( \theta_{ijk} ) (°)</td>
<td>109.47</td>
<td>141.00</td>
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</table>

### 2.2. Simulation method

Cubic simulation cells with 648 particles were used for all samples. The equations of motion were integrated by the velocity Verlet method with a time step of 0.1 fs. Temperature and pressure were controlled by the scaling method. Starting from the β-cristobalite structure at 500 K, the systems were heated stepwise at a heating rate of 200 K/0.1 ns to the maximum temperatures. The maximum temperatures for S2, E2, S3 and E3 potentials were 9000, 7000, 9000, and 6000 K, respectively. After holding these temperatures for 0.1 ns, the systems were...
cooled to 400 K at a cooling rate of 200 K/0.1 ns, keeping the pressure at 10^5 Pa (≈1 atm). After cooling to 400 K, the systems were heated again at a heating rate of 200 K/0.1 ns.

3. Results

3.1. Volume–temperature curve

Fig. 1 shows the temperature dependence of specific volume (volume per unit mass). For Samples S2 and E2 at 10^5 Pa, each VT curve shows the minimum at temperature \( T_p \) and the cooling and the heating curves coincide with each other. In these figures, characteristic temperatures \( T^* \) and \( T_p \) are indicated: \( T^* = 4400 \) K and \( T_p = 4700 \) K in Sample S2, and \( T^* = 3300 \) K and \( T_p = 7300 \) K in Sample E2. At temperatures lower than \( T^* \), the specific volume depends linearly on temperature; the slope for Sample S2 is negative, whereas that for Sample E2 is positive.

For the 3BS, the VT behavior is different. For Sample S3, the system did not condense during the cooling process; the system remained in the gas phase even when it was cooled to 400 K. At a high pressure of 10^10 Pa, the system condensed and the VT curve shows the volume minimum, as in the case of the 2BS. In this case, \( T^* = 2700 \) K and \( T_p = 7600 \) K. Hereafter, this sample is adopted for comparison with the other systems at 10^5 Pa. In Sample E3, the system condensed upon cooling and, the heating curve was the same as the cooling curve. The volume decreased monotonically with decreasing temperature at both 10^5 and 10^10 Pa; the curve did not exhibit the volume minimum, regardless of pressure.

For 2BS, the VT curves at 10^10 Pa in the cooling process were also calculated. In these curves, however, no volume minimum was apparent.

3.2. Radial distribution function

Fig. 2 shows the radial distribution function (RDF) \( g(r) \) at various temperatures. Characteristic temperatures \( T^* \) and \( T_p \) are indicated by the horizontal dashed lines as a guide for comparison between the structure and the VT dependence. (The position of the line is the interior division point assuming that the position of \( g(0) \) corresponds to each temperature.) At temperatures higher than \( T^* \), the first peak becomes broader and the third peak becomes weaker and the third peak is buried in the tails of the second and third peaks. This is due to the destruction of the short- and intermediate-

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Fig. 1. Temperature dependence of the specific volume at 10^5 and 10^10 Pa. The S3 system was vaporized at 10^5 Pa.
range orders. The short-range order, i.e., the SiO$_4$ tetrahedral structure, was also destroyed. This is seen in the broadening and decrement of the first and second peaks. The destruction of the short-range order can be seen more directly in the coordination number.

### 3.3. Coordination number

Fig. 3 shows the temperature dependence of the coordination number. The coordination number of an atom is calculated from the numbers of atoms existing within the Si–O distance that is less than the length at which the RDF is minimum. Here, SiO$_n$ indicates the $n$-oxygen-atom-coordinated silicon atom, and OSi$_m$ indicates the $m$-silicon-atoms-coordinated oxygen atom. At temperatures lower than $T^*$, most silicon atoms are coordinated with four oxygen atoms, and most oxygen atoms are coordinated with two silicon atoms. This indicates that most atoms contribute to the SiO$_4$ tetrahedral structure. At a temperature higher than $T^*$, the fraction of four-oxygen-coordinated silicon atoms decreases in each sample, and the fraction reaches 60–80% at $T_p$. In the 2BS, five-oxygen-coordinated silicon atoms appeared at temperatures higher than $T^*$. The population of this structure in Sample S2 is greater than that in Sample E2.

### 3.4. Bond angle distribution

Figs. 4 and 5 show the O–Si–O and Si–O–Si bond angle distributions, respectively. The O–Si–O bond angle distribution curve has a peak at the tetrahedral angle of 109° at temperatures lower than $T^*$. The peak begins broadening at temperatures above $T^*$. The peak position in the 2BS shifts to lower angles with increasing temperature at temperatures higher than $T^*$. The peak shift in 2BS must reflect the appearance of the five-oxygen-coordinated silicon atoms. For the 3BS, on the other hand, the peak positions remain at the tetrahedral angle due to the three-body term.

The Si–O–Si bond angle distribution below $T^*$ has a peak at 160°, except for E3. The peak position is...
different from the value of 141° experimentally observed using X-ray diffraction [19] and nuclear magnetic resonance (NMR) [20]. In Sample E3 at 400K, peaks at 135° and 160° were observed. This is because the three-body term forces the bond angle to be 141°, while the bond angles are around 160° in the simulated system. The relative intensity of the 160° peak of Sample E3 increases with increasing temperature and the distribution becomes broader compared with those of other samples. This explains the increase in volume with temperature. In addition to the strong peaks at 135° and 160°, a very weak peak at 84° was also observed.

3.5. Mean square displacement and diffusion constant

To clarify the dynamic properties, the mean square displacements (MSDs), defined by

\[ G(t) = \lim_{T \to \infty} \frac{1}{T} \int_0^T \left( \vec{r}(t + \tau) \cdot \vec{r}(\tau) \right)^2 d\tau, \]

were calculated. MSDs at various temperatures are shown in Fig. 6. As seen from this figure, MSD begins to show the Markov process at \( T \gtrsim T^* \). At these temperatures, \( G(t) \sim 6Dt \) for a sufficiently long time, \( D \) being the diffusion constant. This suggests that temperature \( T^* \) corresponds to the glass transition temperature \( T_g \). The temperature dependence of the diffusion constant is shown in Fig. 7. The diffusion constant at \( T^* \) is \( \sim 10^{-7} \text{ cm}^2 \text{ s}^{-1} \) in Samples S2, E2 and S3. The diffusion constant in the 2BS at \( 10^{10} \text{ Pa} \) is greater than that at \( 10^5 \text{ Pa} \). This indicates that the pressure induced melting, as in the case of H₂O [21]; the diffusion constant becomes lower with the increment of pressure.

4. Discussion

4.1. Effect of the three-body term

Before discussing the origin of the volume minimum, we will discuss the effect of the three-body term.
Most of the crystalline and vitreous silica is constructed of corner-sharing SiO$_4$ tetrahedra. The three-body term was introduced to reproduce the tetrahedral structure. In particular, at the silica surface, this term is effective for reproducing a structure with dangling bonds, such as the $E^0$ center. At a high temperature, however, the three-body term is inappropriate because the structure is forced to retain the tetrahedral O–Si–O bond angle even when some bonds have been broken. Three-oxygen-coordinated silicon sometimes tends to form a planar structure by sp hybridization [13]. If the bond angle deviates from the tetrahedral angle due to thermal agitation, the three-body term acts as a repulsive force. Therefore, as in the case of Sample S3, the system might be vaporized when the temperature increases. Since the only attractive force of the S3 potential is the screened Coulomb interaction, the system cannot condense again even when it is cooled to a sufficiently low temperature; once the distance between the particles exceeds the range of the screened Coulomb potential, attractive force will no longer be effective.

The application of pressure confines the system to within the effective range of the screened Coulomb potential. In potential E3, on the other hand, an attractive force is effective because the exact Coulomb interaction is used. Therefore, this system condenses with decreasing temperature. The three-body term acts as a repulsive force that increases with rising the temperature due to the increasing thermal agitation. As a result, the atoms can diffuse even at a temperature as low as 2400 K, as seen from Figs. 5(d) and 6(d). In this potential, no volume minimum appears even when a pressure of 10$^{10}$ Pa is applied, as shown in Fig. 1(d). In Sample E2, applying a pressure of 10$^{10}$ Pa also does not produce a volume minimum. Therefore, there might be an optimal pressure for reproducing the volume minimum. The volume minimum in Sample S3 can be reproduced by loading to a pressure of 10$^{10}$ Pa. Although, this system contains a three-body term to shape the SiO$_4$ tetrahedra, the connection between the corner-shared tetrahedra is rather flexible because the value of $\lambda_{\text{Si–O–Si}}$, which represents the magnitude of the three-body term,
Fig. 5. Distribution function $f(\theta_{\text{Si-O-Si}})$ of Si–O–Si bond angle $\theta_{\text{Si-O-Si}}$ at various temperatures.

Fig. 6. Mean square displacement (MSD) of at various temperatures.
is one-thirtieth that of $k_{\text{O-Si-O}}$, as shown in Table 1. Therefore, the effect of the three-body term on the Si–O–Si bond angle is negligible in spite of the minimum of this term being at the tetrahedral angle.

The force derived from the term for the Si–O–Si bonds in Sample E3 could be more serious compared to that for the O–Si–O bond because the magnitude of the potential term related to Si–O–Si bond angle is greater than that for the O–Si–O bond angle, i.e., $k_{\text{Si-O-Si}} = 4k_{\text{O-Si-O}}$. The mean value of the O–Si–O bond angle is the tetrahedral angle even when no three-body term exists, as shown in Fig. 4(a) and (b). The Si–O–Si term, on the other hand, makes the bonds unstable because the peak of the bond angle distribution is at 160°, which is different from the minimum of this term of 141°. Thus this term promotes bond breakage even at a low temperature. As a result, the atoms begin to diffuse at a lower temperature ($\approx$2000 K) compared with the other samples. As a result, the fraction of four coordinated silicon atoms decreases above $\approx$2000 K, as shown in Fig. 3(c). It is noted that the absolute value of $k_{\text{O-Si-O}}$ in S3 $1.8 \times 10^{-17}$ J is approximately twenty times larger than that of E3, i.e., $8.07 \times 10^{-19}$ J. The weaker value of $k_{\text{O-Si-O}}$ in E3 could be another reason why Sample E3 condenses at a low temperature at $10^5$ Pa while Sample S3 condenses only when pressure is loaded.

4.2. Origin of volume minimum

Perchak and O’Reilly [17] showed the volume minimum using the S2 potential. They used a system with 648 particles. The randomly distributed system was heated rapidly to 10000 K and cooled stepwise at 200 K/4ps to 300 K and heated again at a heating rate of 200 K/4ps. Although they showed the volume
minimum, the VT curve showed hysteresis, i.e., the cooling curve and the heating curve were different. The curves also depended on the cooling rates and the pressure controlling conditions. This result is quite different from the present result for S2, where the cooling and heating curves are the same. This is because our holding time at each temperature is much longer (0.1 ns), and our system is better equilibrated.

Yamahara et al. [18] calculated the temperature dependence of the density using the E2 potential for a system with 3000 atoms. Although the density–temperature curve is similar to the present result, the density of the present system is slightly less than theirs. This may be due to the difference in the cooling rate. The cooling rate used in their study is 25 K/ps higher than that in the present study, 200 K/100 ps. Another difference between the present and their work is the number of particles in a simulation cell; the number of particles in the present study, 648, is less than the 3000 used in their work [18]. This difference may affect the accuracy of the simulation, but must not greatly affect the average volume.

In the present simulation, the volume minimum was observed in both Samples S2 and E2. Perchack and O’Reilly [17] pointed out that the volume minimum is due to the creation of five-oxygen-coordinated silicon atoms (SiO₅). In fact, as shown in Fig. 3(a) and (b), SiO₅ is induced at temperatures higher than T*. However, S3 at a pressure of 10¹⁰ Pa also shows a volume minimum in spite of the fact that SiO₅ did not appear, as shown in Fig. 3(c). Therefore another reason should be considered.

As seen in Fig. 6, the atoms begin to diffuse at ≈T*. At temperatures below T*, the Si–O–Si bond angle distribution does not change markedly (Fig. 5). Above T*, on the other hand, the peak of the distribution shifts to lower angles and becomes broader because the distribution expands to lower bond angels. This causes the decrement of the distance between the nearest Si atoms because the Si–O bond length remains almost constant, as seen from the first peak position of the RDF in Fig. 2. Thermal expansion coefficients of quartz and cristobalite change from positive to negative above the phase transition temperature from the α to β phase. Yamahara et al. [18] pointed out that the average bond angle, and therefore the mean distance, between the nearest Si atoms in β-cristobalite decreases with increasing temperature. The sign of the thermal expansion of β-cristobalite is depends sensitively on the potential. Huang and Kieffer [22] studied the α–β transition of cristobalite using a charge-transfer three-body potential. They showed almost no thermal expansion for β-cristobalite but that the nearest Si–Si distance increases with increasing temperature, even for β-cristobalite. This must be caused by the effect of the three-body term. The transverse vibration of the Si–O–Si bond must cause a reduction of the nearest Si–Si distance, as in the case of the thermal shrinkage of the polymer chain network in rubber [23]. During the decrease of the Si–Si distance with increasing temperature, the population of dangling bonds increases, as seen in Fig. 3. The creation of defects causes the dilatation of the material. In the temperature range between T* and Tp, the effect of shrinkage due to decreasing the Si–Si distance exceeds the effect of the dilatation due to the creation of defects.

In Sample S2, the peak shift and broadening at temperatures between T* and Tp are drastic. This suggests that the effect of the reduction of the Si–Si distance on volume reduction exceeds the effect of dilatation by bond breakage, and causes the drastic decrease of the volume in this temperature range. For Samples E3 and S3, on the other hand, the peak shift and the broadening in this temperature range is not so apparent as in the case of Sample S2. Therefore, the change of the volume in this temperature range is also not as apparent as in the case of S2. One might suspect that the effect of dilatation due to breaking bonds exceeds that of the reduction of Si–Si distance and that shrinkage is caused by other mechanisms because the change of coordination number cannot be neglected in this temperature range. A possible origin of the shrinkage is the creation of the SiO₅ structure, as pointed out by Perchak and O’Reilly [17] who used the S2 potential. Since the proportions of the SiO₅ structure in Samples E2 and S3 at temperatures between T* and Tp are quite small, this mechanism must not be the main mechanism of the volume shrinkage. Therefore, we consider that the effect of the reduction of the Si–Si distance on volume shrinkage exceeds the effect of dilatation due to the defect creation in this temperature range.

At temperatures higher than Tp, the Si–O–Si bond angle distribution becomes independent of the temperature. In this temperature region, only the effect of the increase of defects determines the VT dependence. This feature can be applied to all systems that exhibit the volume minimum.

Sample E3 did not show the volume minimum at either pressure of 10⁵ or 10¹⁰ Pa. In Sample E3 at 400 K, peaks of the Si–O–Si bond angle distribution were observed at 135° and 160°. The three body term forced a bond angle of 141°, but this angle is inappropriate for the simulated system. The relative intensity of the 160° peak increases with increasing temperature and the distribution becomes broader compared with other samples. The broadening corresponds to the increment of the volume with rising temperature. In addition to the strong peaks at 135 and 160°, a very weak peak at 84° is observed. This could be due to the existence of two SiO₅ tetrahedra sharing one edge. If the O–Si–O angle is exactly the tetrahedral angle, the angle must be 70°. The peak angle of 84° could be caused by distortion of the structure.
4.3. Thermal expansion at temperatures lower than $T^*$

At temperatures lower than $T^*$, the volume depends almost linearly on temperature in samples S2, E2 and S3. The linear thermal expansion factors of samples S2, E2 and E3 are $-1.5 \times 10^{-6}$, $3.2 \times 10^{-6}$ and $6.8 \times 10^{-7}\text{ K}^{-1}$, respectively. Thermal expansion coefficient of Sample S2 is negative, whereas those in the other samples are positive. The experimental value of the thermal expansion coefficient of $\nu$-SiO$_2$ is $5-8 \times 10^{-7}\text{ K}^{-1}$ [24].

A probable origin of the thermal expansion is the change in the Si-O bond length. However, the position of the first peak in the Si-O RDF shifts to slightly shorter length with increasing temperature (Fig. 2). As mentioned in the previous subsection, $\beta$-cristobalite exhibits negative thermal expansion when using pairwise additive potential. Silica glass might also have the tendency to shrink with increasing temperature via the broadening of the Si–O–Si bond angle distribution. In fact, broadening of the Si–O–Si bond angle distribution is observed even at temperatures lower than $T^*$ in Sample S2, as seen in Fig. 5(a). This must be the origin of the negative thermal expansion in Sample S2. In Samples E2 and S3, on the other hand, little change was observed for the Si–O–Si distribution. As seen in Fig. 2(b) and (c), there is slight broadening of the first peak of the RDF. This might be the cause of the dilatation of the network of positive thermal expansion. Another effect is the increment of the population of the defects. As seen in Fig. 3(a)–(c) some defect structures are induced by the increment of the temperature even at a temperatures lower than $T^*$. The sign of the thermal expansion is determined by the balance of these two factors which are sensitive to the details of the potential. The reason why the thermal expansion coefficient of $\nu$-SiO$_2$ is smaller than those of the other materials is related to the balance between these two effects.

5. Summary and conclusion

The minimum of the VT curve in $\nu$-SiO$_2$ is studied by classical MD simulation. The volume of $\nu$-SiO$_2$ increases linearly with increasing temperature for $T < T^*$, and shrinks for $T < T < T_p$. The volume takes a minimum at $T = T_p$ and then increases again for $T_p < T$. To examine the effect of the potential on the VT dependence, four types of potentials were compared: pair additive potentials using an exact Coulomb term (E2) and a screened Coulomb term (S2), and potentials including a three-body term for reproducing the SiO$_4$ tetrahedral structure, again using an exact Coulomb term (E3) and a screened Coulomb term (S3). When using pair additive potentials, S2 and E2, the volume minimum can be reproduced. When using the S3 potential, the volume minimum was reproduced by applying a high pressure of $10^{10}\text{ Pa}$. Analysis of the RDF, coordination number, bond angle distribution and diffusion phenomena showed that the shrinkage in the temperature region $T^* < T < T_p$ is caused by the decrease of the distance between the nearest Si–Si atoms, and the dilatation at $T_p < T$ is caused by the increment of the population of defects.

For $T < T^*$, the volume depends linearly on the temperature, and the sign of the thermal expansion coefficient was dependent on the potential. This could be caused by the balance between the reduction of the nearest Si–Si distance and the increment of the number of the defects. The low thermal expansivity of $\nu$-SiO$_2$ is due to the balance between these two factors.

When using the E3 potential, the volume minimum could not be reproduced; the volume of sample E3 increased monotonically with increasing temperature. This must be due to the effect of the three-body term which acts as repulsive force at a high temperature. Therefore, this three-body term is inappropriate for studying the properties and the structure of $\nu$-SiO$_2$ at a high temperature. Potential E2 would be most appropriate for studying the $\nu$-SiO$_2$ structure at high temperatures among the four potentials because this potential uses the exact Coulomb potential term and can reproduce a positive thermal expansion coefficient at temperatures lower than $T^*$.

From the temperature dependence of the coordination number and the bond angle distribution, the negative thermal expansion at $T^* < T < T_p$ is caused by the decrease of the mean distance between the nearest Si–Si, which is inferred from the decrease of the mean Si–O–Si bond angle. The positive expansion coefficient for $T_p < T$ is due to increase of the population of the dangling bonds.

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References