First-principles study on the specific heat jump in the glass transition of silica glass and the Prigogine-Defay ratio

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Abstract
The most important characteristic of glass transition is a jump in the specific heat \( \Delta C_p \). Despite its significance, no standard theory exists to describe it. In this study, first-principles molecular-dynamics simulations are used to describe the glass transition of silica glass. The novel view that state variables are extended to include the equilibrium positions of atoms \( \{ \bar{R}_j \} \) is fully used in analyzing the simulation results. Decomposing the internal energy into three components (structural, phonon, and thermal expansion energies) reveals that the jump \( \Delta C_p \) of silica glass is entirely determined by the component of structural energy. The reason for the small \( \Delta C_p \) is its high glass-transition temperature, which makes the fluctuation in the structural energy insensitive to the temperature change. This significantly affects how the Prigogine-Defay ratio \( \Pi \) is interpreted, which was previously unknown. The ratio \( \Pi \) represents the ratio of the total energy change to the contribution of thermal expansion energy at the glass transition. The general property, \( \Pi > 1 \), of glasses indicates that glass transitions occur mainly via the change in the structural energy. Silica glass is an extreme case in that the transition occurs entirely through the change in internal structure, such as the distribution of the bending angle of Si–O–Si bonds.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Although silica glass (SiO\(_2\)) is an archetypal glass with a simplest chemical formula, it is a less-understood glass, as it is expressed by the word ‘a deceitful simplicity’ (chap. 5 of [1]). It exhibits several unusual properties, including its extremely large Prigogine-Defay (PD) ratio (larger than the usual by four orders of magnitude) [2] and its exceptional disparity between the thermodynamic and dynamic fragilities [3, 4]. Its thermal expansivity \( \alpha \) is exceptionally small, whereas its compressibility \( \kappa \) is normal. Further, its thermal expansion at high pressure is unusually large [5]. These, as well as other properties, are yet to be understood fully.

Experimentally, a limiting factor in studying the thermodynamic properties of silica glass is its large viscosity, which prevents the glass from achieving equilibrium. The contrast between the liquid and glass is relatively easy to discern in...
other glasses by measuring viscosity $\eta$. The temperature $T$ at which $\eta$ reaches about $10^{13}$ Poise agrees with the calorimetric transition temperature ($T_g$) obtained by specific-heat measurement. Alternatively, the viscosity of silica glass varies only gradually over a wide temperature range; no discernible characteristic temperature exists. Practically, the glass manufacturing process uses three characteristic temperatures: strain ($T_{s}$), annealing ($T_{an}$), and softening temperatures ($T_{st}$) [6]. This fact alone indicates that there is no sharp transition. This could explain why the viscosity of silica glass obeys the Arrhenius law.

The best method, notwithstanding existing objections, is the specific-heat measurement. Isobaric specific heat exhibits a jump of $\Delta C_p = C_{p}^{(0)} - C_{p}^{(g)}$, where $C_{p}^{(0)}$ and $C_{p}^{(g)}$ are the specific heat of the liquid and glass states, respectively. Using this method, the glass-transition temperature of silica glass is generally accepted as $T_g = 1480$ K [7]. Figure 1 shows the experimental data for $C_p$ as a function of $T$, compared with the three characteristic temperatures in the viscosity measurement [8, 9]. The figure shows consistency in $T_g$ between the two data; however, according to Brückner, the jump is not always observed [7]. Although the two data are consistent at the starting temperature at which the change in the slope in the $C_p-T$ curve occurs, the magnitude of jump $\Delta C_p$ in Sudo’s data is unclear due to the continuous increase in $C_{p}^{(g)}$. In this study, we accept the value $\Delta C_p = 8.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the jump, which is approximately 10% of the total specific heat at $T_g$ [10]. Throughout this study, the convention of the unit of per mole of average atoms is used for the gas constant $R$. With this convention, the above value of silica corresponds to 0.32$R$, which can be compared to the classical limit of isochoric specific heat, $C_v = 3R$. The value $\Delta C_p$ of silica glass may be the smallest among other glasses. It is considered that a correlation between the jump in $\Delta C_p$ and the glass fragility exists, which is a significant challenge in the current glass research [3, 11–21]. Although the jump implies an abrupt change, the glass-transition temperature has a finite width $\Delta T_g$, which is called the transition region [22]. In Sudo’s data, the width is unclear, whereas Richet et al.’s data show an abrupt change of less than 100 K in the width. Richet and Bottigia obtained the data shown in figure 1 by applying an involved analysis on $C_p(T)$ in the transition region in terms of the fictive temperature [23]. In addition, the specific heat of the liquid $C_{p}^{(l)}(T)$ differs between the aforementioned two data: one is nearly constant with respect to $T$, whereas the other increases; the increasing dependence is also observed in the review paper by Brückner [7]. The last two issues of the transition width $\Delta T_g$ and the $T$ dependence of the specific heat of liquid are noted but not investigated in the present study.

Theoretically, a nonempirical study on $\Delta C_p$ and $T_g$ for silica glass is lacking, primarily due to a lack of a rigorous theory of specific heat for liquids [24]. Instead, various models for the glass transition of oxide glasses were proposed. Some of them are reviewed by Ojovan [25]. A general consensus on why the jump $\Delta C_p$ of silica glass is so small has not yet been obtained. A recent study by Trachenko and Brazhkin calculated $\Delta C_p$ using an elastic model, and the result was consistent with experiments [26]. This model may convey some of the real properties of glasses. However, as will be discussed later, consistency with other properties is important for understanding the glass transition, and thus, a method without empirical parameters is required. This is the first purpose of this study. First-principles molecular dynamics (FPs-MD) simulations are used to investigate the glass transition of silica glass by calculating its thermodynamic properties. Particular attention is devoted to the specific-heat jump due to the importance of $\Delta C_p$ in the glass transition discussed above. (A study by Scheidler et al using the energy correlation method [27] is interesting, although model simulation. However, their result on specific heat was not enough to resolve $\Delta C_p$.) When studying the mechanism that determines $\Delta C_p$, it is crucial to know which state variables determine the internal energy of solids. This is the subject of the PD ratio, which has yet to be assigned a concrete interpretation. In this regard, the novel view on the state variables of solids, which was proposed by the first author of this paper [28, 29], has significant merit. Based on this view, the governing mechanism for $\Delta C_p$ can be identified at a microscopic level. The second purpose of this study is to describe this issue.

The remainder of the paper is organized as follows: A rigorous theory of specific heat for both solids and liquids is provided in section 2. A detailed explanation of the theory is can be found in [30], and here, only the essential components of the theory are described. The results of applying the theory to silica glass are described in section 3. Although we are mainly concerned with the behavior of the specific heat, structural analysis is also included. This is because it is found that the PD ratio is determined by the details of the structural change in the glass transition. The relation between the
structural change and the PD ratio is discussed in section 4. The last section presents the conclusion of this study.

2. Calculation method of specific heat

2.1 Theory

2.1.1 Specific heat. The study of glass transitions requires a thorough formulation of specific heat for liquids, which has recently been established [30]. The original paper [30] should be consulted for more information. The specific heat is defined as the change in internal energy $U$ with respect to a small change in temperature $T$. The internal energy of a material is defined at equilibrium and is given by the time average $E_{\text{tot}}(t) = \frac{1}{2} \sum_j M_j v_j(t)^2$. Thus, the internal energy $U$ is expressed as follows:

$$U = E_{\text{tot}}(t) = E_{\text{gs}}(\{\mathbf{R}_j(t)\}) + \frac{1}{2} \sum_j M_j v_j(t)^2. \quad (1)$$

We can determine the relationship between $U$ and $T$ by performing MD simulations as either $U$ or $T$ varies, with the volume $V$ fixed, thus deducing the isochoric specific heat $C_V = \langle \partial U/\partial T \rangle_V$. The formulation is quite generic up to this point. Because the total energy is well defined by DFT, $C_V$ can be directly calculated by DFT-based MD simulations, irrespective of whether a material is solid or liquid.

The harmonic approximation holds for solids at low temperatures. The instantaneous position of an atom is the sum of the equilibrium position $\mathbf{R}$ and a small displacement $\mathbf{u}$ from it, as $\mathbf{R}_j(t) = \mathbf{R}_j + \mathbf{u}_j(t)$. The ground-state energy $E_{\text{gs}}(\{\mathbf{R}_j(t)\})$ can be expanded with respect to the displacement; a part of time dependent term constitutes the phonon energy, $E_{\text{ph}} = \sum_q \hbar \omega_q (\alpha_j) \rho_q(t) / \omega_q$, where $\omega_q$ is the frequency of the $q$th phonon and $\rho_q(t)$ is its Bose–Einstein occupation number. Thus, the internal energy $U$ can be decomposed as follows:

$$U \equiv U(T, V, \{\mathbf{R}_j\}) = E_{\text{st}}(\{\mathbf{R}_j\}) + E_{\text{ph}}(T) + E_{\text{te}}(V). \quad (2)$$

In this study, two components, $C_{\text{st}}$ and $C_{\text{ph}}$, are obtained via MD simulation with a constant $V$, whereas $C_{\text{te}}$ is calculated from the experimental data of $\alpha$ and $\kappa$.

The following comments should be noted: First, for liquids, only the total energy $E_{\text{st}}$ and $C_{\text{ph}}$ (or $C_V$) are physically relevant; phonons are not real substances for liquids. However, the component $C_{\text{ph}}$ can be operationally obtained from the frequency spectra of time-dependent velocities, and appears to be effective. We can define the phonon contribution, $C_{\text{ph}}$, by applying the Bose–Einstein statistics to the frequency spectrum. In this case, $C_{\text{ph}}$ should be interpreted as a virtual quantity defined in an analogous manner to that of the solid case. Second, despite its practical utility, the virtual nature of the phonon picture should not be overlooked, particularly in terms of energy dissipation. This problem is particularly severe when the transition region is considered. This problem is solved by employing adiabatic MD simulations that automatically provide the correct relationship between $U$ and $T$. Finally, for liquids, a set of variables $\{\mathbf{R}_j\}$ loses its role as the arguments in equations (2) and (3). The equilibrium positions of atoms in liquids are indeterminate, and therefore, $U$ is a function of $V$ and $T$ only. We will show in section 4 that this property of variables has a significant impact on the thermodynamic relationships.

2.1.2. Adiabatic MD simulations. It is impossible to trace the entire glass transition process using computer simulations, even with classical MD simulations. Our idea is to simulate a glass transition through a series of adiabatic MD runs, by slightly changing the total energy $U$ from run to run. The internal energy $U$ is changed by adjusting the input velocities of atoms. In each run, a simulation is continued until reaching equilibrium under the constraint of a fixed $U$. The definition of equilibrium in this context is given in the next paragraph. This definition is underpinned from the fundamental view of thermodynamics (see [28]). The equilibrium positions of the previous run are used for the initial atom positions of the $k$th run: $\mathbf{R}_j^{(k)}(0) = \mathbf{R}_j^{(k-1)}$, where $\mathbf{R}_j^{(k)}$ are the atom positions of the $k$th run. Because an exact value of $T$ is unpredictable in adiabatic MD, the intended temperature of each run was obtained via trial and error. The rate of cooling/heating is irrelevant in this simulation because there is no way of knowing how much time is expanded between successive runs. However, a temperature interval, $\Delta T^{(k)}$, between subsequent runs mimics a fast
and slow rate of temperature change. Thus, fast and slow rates are used in this scenario. A pressure reservoir is also avoided for the same reason.

The time evolution of the averaged displacements, \( \langle R_j(t)^2 \rangle \), is used to determine whether equilibrium is reached; the bracket denotes the particle average. It is considered an equilibrium state of the solid phase when \( \langle R_j(t)^2 \rangle \) shows constant behavior with respect to \( t \). However, it is considered an equilibrium state of the liquid phase when the linearity between \( \langle R_j(t)^2 \rangle \) and \( t \) is observed over the entire simulation time \( t_{SM} \). The diffusion coefficient \( D \) is determined by the slope of the linear relationship. Examples for \( \langle R_j(t)^2 \rangle \) are shown in the supplemental materials.

### 2.2. Calculation method

The code used for FP-MD simulations is Phase/0 [32], which is a pseudopotential method. The oxygen atom is treated with an ultrasoft potential [33], whereas the silicon atom is treated with a norm-conserved potential [34]. The electron-correlation potential is calculated using the generalized gradient approximation of the Perdew–Burke–Ernzerhof type [35]. The cutoff energy of the plane-wave expansion is 30 Ry, and a one-point (\( R \) point) \( k \) mesh is used. Time steps from 0.72 to 1.2 fs are used in MD simulations. The total simulation time \( t_{SM} \) varies from 2 to 10 ps, depending on the relaxation time. When the presence/absence of diffusion is evident, 2 ps is considered sufficient, whereas long \( t_{SM} \) is used for the marginal case.

Structural models for the silica glass were prepared using crystal \( \alpha \)-quartz. The lattice system of \( \alpha \)-quartz is hexagonal, and the lattice parameters are \( a = 9.827 \), \( b = 9.827 \), and \( c = 10.809 \) Å. A supercell with dimensions of \( 2 \times 2 \times 2 \) was used, with 72 atoms in a cell. Two different cell sizes were prepared. One is the high-density cell, which has the original size of the lattice parameters of the crystal, whereas the other is obtained by slightly expanding the lattice parameters to have the same density as that of silica glass: the density of silica glass is smaller than that of the crystal by 16.9%. It is called the low-density cell. This low-density cell was used throughout, except for the calculation of the structural parameters during crystal melting (section 3).

### 3. Results of MD simulations

#### 3.1. Melting of crystal

In the beginning, the silica liquid was prepared by starting with \( \alpha \)-quartz crystals. Investigating the crystal melting process is not the goal of this study. However, understanding this process provides the basis for further analysis of the glass transition. The low-density cell was chosen for expectation of ease of melting; however, it was not as different as was expected.

Figure 2 shows variations of the diffusion coefficient \( D \) and structural energy \( E_a \) as functions of \( T \). \( D \) is presented in the units of \( \text{Å}^2/\text{ps} \) throughout this paper. \( E_a \) is virtually constant with respect to \( T \) until \( T = 4000 \) K, indicating that the crystal potential is approximately harmonic. Finite values of \( D \) appear around \( T = 4500 \) K, indicating the onset of melting. In accordance with the behavior of \( D \), the structural energy \( E_a \) abruptly increases. The estimated \( T_m = 4500 \) K is significantly greater than the experimental value (1600 K). The overestimation of melting temperature and similar quantities for silica are commonly observed in MD simulations, regardless of whether empirical [36–41] or FP potentials [42] are used. The reasons are discussed from several perspectives in [43–45]. Each reason may be correct from the respective perspectives. We hypothesize that the primary reason for the overestimation is the spurious energy barrier created by the periodic boundary condition with small supercell sizes, which eliminates long-wavelength phonons [30]. Appendix explains this effect. Presently, this overestimation due to the small size of supercells is unavoidable and is reserved as a future study. Readers should read the following description while bearing this overestimation in mind.

Figure 2 shows that a large fluctuation occurs around \( T_m \). A close inspection shows that the significance of this fluctuation is more than just a random variation. In the figure, the sequence of runs near \( T_m \) is indicated by connecting points using lines. In this region, the diffusion coefficient \( D \) decreases as \( T \) is slightly increased, and vice versa. This is the opposite of the normal behavior—an increase in \( T \) increases \( D \), implying instability. MD simulations are performed in finite-size cells. This causes a finite width in the energy distribution by \( \Delta T/T = 1/\sqrt{N} \). When the structure is changed, the energy distribution between the vibrational and translational motions becomes unbalanced. At temperatures slightly above \( T_m \), atoms with kinetic energy higher than the average kinetic energy, \( (E_K) \), begin to convert their motions to diffusing motions, decreasing \( (E_K) \) and increasing diffusion. Conversely, at temperatures slightly below \( T_m \), the low-energy part of atoms, which...
is absent when $\Delta T = 0$, is populated by absorbing energy from diffusing motions. Thus, an oscillatory behavior appears around $T_m$.

The step $\Delta E_{st}$ in the structural energy at $T_m$ corresponds to the latent heat, $H_m$. The $H_m$ value is blurred by the large fluctuation in $T$, ranging from 0.13 to 0.30 eV/atom. Even the calculated lower bound of $H_m$ is significantly higher than the experimental value 9.4 kJ mol$^{-1}$ (0.03 eV/atom) of $\alpha$-quartz [1]. This overestimation of the latent heat is likely to have the same origin as the overestimation in $T_m$. The spurious energy barrier created by periodic boundary conditions increases $H_m$ and $T_m$.

The value of $H_m = 0.03$ eV/atom of silica glass is very small among covalent crystals; for example, silicon crystal has $H_m = 0.5$ eV/atom despite a similar value of $T_m$. This implies that the melting of quartz is due to bond switching, rather than bond breaking [1]. This probably explains why silica glass has a high viscosity even in the melt. The energy barrier of glass transition, $E_b$, is expected to be of the same order as the latent heat, $E_b \sim H_m \sim RT_m$ (this relationship is discussed in [30]). However, the activation energy, $Q_a^*$, of silica glass is reported to be greater than 5 eV [4, 25, 46, 47]. This large discrepancy between expectation and experiment has remained an open question in glass physics. This magnitude of $Q_a^*$ is comparable to the energy of covalent bonds or the cohesive energy. In fact, it is occasionally interpreted that the activation energy for the glass transition of silica glass originates from bond breaking (for example, [48]). However, this interpretation is unrealistic on account of the fact that normally $H_m$ is much smaller than the cohesive energy. Therefore, there must be a mechanism through which the apparent activation energy experimentally obtained has a substantial overestimation. The mechanism was only recently disclosed by the first author of this study [49]. Experimentally, the activation energy is obtained by the Arrhenius plot. When the energy barrier varies rapidly as the temperature changes, this temperature dependence appears as a magnification factor, $k = T_g/\Delta T_g$, for the apparent activation energy.

Some structural parameters are plotted as a function of $T$ in figure 3. For calculating these parameters, another series of heating processes were performed using high-density cells to achieve the most accurate structural parameters feasible. The shown angles are the angle of O–Si–O (δ) in the tetrahedral unit, SiO$_4$, the bending angle of Si–O–Si ($\phi$), and the rotation angle of the O atom (£) about the Si–Si axis, which are the terminal atoms of the Si–O–Si bond. For clarity, these angles are shown in the Supplemental materials (p. 3). The bond length (r) of Si–O increases slightly with an increase in $T$. The rate of increase is $(1/r)d/dr = 7.3 \times 10^{-6}$ K$^{-1}$. This value is close to the linear thermal expansivity of $\alpha$-quartz, which is about $1.2 \times 10^{-5}$ K$^{-1}$ on the orientational average ( [50], p. 164), although the current value was obtained by constraining the volume constant. This is discussed in section 3.3. The tetrahedral angle δ does not change over a wide range of $T$. Therefore, the SiO$_4$ tetrahedron expands uniformly as the temperature increases.

At $T < 2000$ K, there is virtually no change in the bending angle $\theta$, although the distribution of $\theta$ broadens as $T$ increases in both directions of higher and lower angles. More bending would be expected due to the increase in bond length under the constraint of a fixed $V$. However, there are further freedoms in the parameters in order to allow uniform expansion of tetrahedra SiO$_4$ while maintaining a constant volume $V$. The tilt angle $\psi$ describes how two adjacent corner-shared tetrahedra can change their relative orientation. This tilt angle $\psi$ plays an important role in the $\alpha$–$\beta$ phase transition of quartz [51]. This angle can decouple the change in $V$ from the change in $\theta$. A relationship exists between $\psi$ and $\phi$. The change in $\phi$ is remarkable, as seen in figure 3. The angle $\phi$ rapidly increases as $T$ increases. The data displayed are the mean-square variation $\Delta \phi$, which has a large distribution; some are larger than 90°, implying virtually unrestricted rotation. The fact that the rotation of the bending bond Si–O–Si begins at temperatures significantly lower than $T_m$ explains why the $\alpha$–$\beta$ phase transition occurs at such a low temperature ($T = 846$ K).

3.2. Glass transition from liquid

3.2.1. Structural energy. The samples of liquid silica obtained in the preceding section were cooled to obtain the glass. Several cooling sequences are examined. The results are plotted in terms of $E_a$ and $D$ in figure 4. Two contrasting cooling sequences, among them, are chosen as the representatives, and are indicated using lines: (A) fast cooling—in the sense described in section 2—indicated using a blue
found to be in the range of $\Delta C_{st} = 0.50R$ to $0.68R$, depending on the cooling rate. Regarding the transition width $\Delta T_g$, our simulations have such large fluctuations that a clear $\Delta T_g$ could not be identified.

The structural energy $E_{st}$ decreases as the cooling rate decreases, implying increased stability. This is to be expected because slow cooling makes achieving the energy minimum easier. The difference in $E_{st}$ between samples (A) and (B) is approximately 800 K (0.07 eV/atom). The rate of cooling in the current MD simulations causes the energy difference to this extent: this may be an overestimation because the cooling rate in the calculation is outside the range accessible in the experiment. The energy difference $\Delta E_{gc}$ between the crystalline glass sample (B) is 1100 K (0.094 eV/atom), which is three times larger than the experimental value, 9.14 kJ mol$^{-1}$ (0.032 eV/atom), reported by Richet et al [9]. Notably, Ray previously reported that $\Delta E_{gc} = 29kJ mol^{-1}$ after accounting for the effect of sample grinding [52]. It is unclear why this significant difference in $\Delta E_{gc}$ occurs. We currently accept the value provided by Richet et al, which implies to accept a significant disparity between the calculation and the experiment.

The aforementioned difference in $E_{st}$ (0.07 eV/atom) between samples (A) and (B) must be attributed to the structural difference. Figure 5 shows a comparison of the radial-distribution function (RDF) between samples (A) and (B). There is no discernible difference in RDF. However, the distributions of angle $\theta$ are different for different structures. In contrast to the crystal case, $\theta$ has a broad distribution range. The maximum position of angle $\theta$ is about 10° times lower in sample (A) than that in sample (B). In addition, a small feature is observed in both samples around $\theta = 90^\circ$, which was observed in FP calculations by Kim et al [42]. The low-angle part increases from the sample (B) to sample (A). From the correlation between the energy and angle change, a decrease in $\theta$ (more bending) increases the structural energy $E_{st}$. In sample (B), structural analysis shows that in a unit cell, one oxygen atom out of 48 has a pair of bond angles with substantial bending around $\theta = 90^\circ$. If this pair of angle defects were removed, $E_{st}$ would be further reduced. We attempted to remove this defect by repeating the annealing and cooling processes without success. Perhaps the small size of the cell (72 atoms) is too restrictive to remove this defect.

### 3.2.2. Phonon contribution.

Next, we investigate the phonon contribution to the specific heat. Figure 6 shows the specific heat of the phonon part $C_{ph}$. The figure shows that $C_{ph}$ is close to the classical limit, 3R, at high temperatures $T > 2000$ K, and thus, the specific jump cannot be seen. If any jump is observed, it is less than the current resolution limit of about 0.01R.

This negligibly small value of $\Delta C_{ph}$ can be understood by examining the evolution of the phonon spectra. Figure 7 shows the evolution of phonon spectra throughout the melting and cooling processes. Readers may observe shifts in
Figure 5. Comparison of the radial-distribution-function (RDF) and the distribution of angle $\theta$ in samples (A) and (B). The intensity is plotted in arbitrary units, but the scales of the two samples are the same. The baseline of (B) is shifted upward for clarity.

Figure 6. Phonon contribution to specific heat $C_{ph}$ of silica glass. Blue: fast cooling sample (A), red: slow cooling sample (B).

Figure 7. Evolution of phonon spectra in the melting process of crystal $\alpha$-quartz and in the quenching process from silica melt. The intensity of crystal $\alpha$-quartz at $T = 160$ K is reduced by 2.5 for easy visibility.

the calculated spectra to lower frequencies if they compare the experimental spectra of crystal $\alpha$-quartz [53] and silica glass [54]. However, this is due to the TO–LO splitting for polar modes, which is not considered in the calculations. The phonon spectrum of crystal $\alpha$-quartz comprises multiple bands that are roughly divided into three groups: a high-frequency band at about 1100 cm$^{-1}$, a middle-frequency band at about 800 cm$^{-1}$, and a broad low-frequency band from 200 to 450 cm$^{-1}$. The fine structure of the crystal broadens as temperature increases, whereas these main features remain. We also observe traces of the main features even in the liquid. The phonon spectra shift to the low-frequency side, as $\alpha$-quartz is heated up to melt. On cooling the liquid to glass, the phonon spectra exhibit features similar to those of crystal $\alpha$-quartz. The phonon spectrum of silica glass has now been well characterized (see paper by McMillan et al for an overview of current knowledge [48]). An unusual behavior at the 440 cm$^{-1}$ band has been reported: the frequency increases as $T$ increases [48, 55]. This is interpreted to be due to the narrowing of the bending angle of the Si–O–Si bond [56, 57]. Unfortunately, this increase is not resolved in our simulation due to substantial fluctuations in phonon spectra. In any case, the details of the phonon spectra are irrelevant for the specific heat. This is because all the phonons are already thermally activated at high temperatures around $T_g$, a slight change in $T$ around $T_g$ does not affect the temperature dependence of $C_{ph}(T)$, and thus, there is no reason to expect any jump $\Delta C_{ph}$.

3.2.3. Effect of thermal expansion. The third contribution to the total specific heat is from the thermal expansion,
The contribution of thermal expansion is expressed by equation (4). Experimental data from the literature was used to evaluate this formula, and the values are tabulated in Table 1. Since we are interested in the change in $C_p$ around $T_g$, the values must be those just below and above $T_g$. Determining $C_p$ for silica glass involves several difficulties. First, on silica glass vary among studies. We adopted the cited values after a comparison of various data. Second, the changes in thermodynamic properties near $T_g$ are too small to be determined accurately. Third, since the width $\Delta T_g$ of the glass transition for silica glass is not well established, the changes in properties largely depend on the $\Delta T_g$ value used.

The reported data for volume expansivity $\alpha$ are rather well converged in a range of $1.3\text{–}2.1 \times 10^{-6} \text{K}^{-1}$ near room temperature [7, 58, 59]. However, there are few measurements of the $T$ dependence of $\alpha$ around $T_g$ and the reported data have substantially fluctuations, making it difficult to evaluate $\Delta \alpha$ [59]. Using $\Delta T_g = 100 \text{K}$ (see the data by Sudo in figure 1) and the expansivity data reported by Kuhn and Schadack [59], an amount of $\Delta \alpha / \alpha = 2\%$ was estimated. The compressibility $\kappa$ of silica glass is the most confusing quantity. The issue is the large disparity in $\kappa$ between the static and dynamic measurements—the static value is approximately four times larger than the dynamic value [62, 63]. Mysen and Richet reviewed previous data with appropriate interpretation [1]. In this study, we used recent values of Brillouin scattering measurement by Polian et al [60] and Guerette and Huang [61]. This is because the compressibility was measured over a wide range of $T$ covering near $T_g$. The compressibility $\kappa$ increases as $T$ increases. However, the increase is too small in the transition region to accurately determine the jump $\Delta \kappa$. The jump $\Delta \kappa / \kappa = -2\%$ has been estimated at most by assuming $\Delta T_g = 100 \text{K}$.

From these values listed in Table 1, the thermal expansion part of specific heat, $C_v$, is determined as $C_v^{(l)} = 2.3 \times 10^{-4} R$ and $C_v^{(l)} = 2.5 \times 10^{-4} R$ for glass and liquid, respectively, with a very small difference, $\Delta C_v = 2. \times 10^{-5} R$. Therefore, the contribution of thermal expansion to $C_p$ is negligible.

### 3.2.4. Total specific heat

By analyzing the three components, we conclude that the contribution from the structural energy $E_{st}$ is responsible for the specific-heat jump of silica glass. Similar conclusions were reported in other studies on different glasses [30, 64, 65]. Although the degree of contribution of $\Delta C_{st}$ is different, the predominance of $\Delta C_{st}$ to $\Delta C_p$ may be regarded as a common property of glasses. The calculated value of $\Delta C_p$ of silica glass varies between $0.50R$ and $0.68R$, depending on the cooling rate. This is an overestimation of the experimental value of $0.32R$, which is probably due to the spurious energy barrier of the small-size supercell. The jump of $0.32R$ in silica glass is small compared to that of fragile glasses, which is of the order of $R$. This does not mean, however, that the change in the structural energy $E_s$ of silica glass is insignificant. In fact, the change $E_s$ of silica glass over the transition region is much larger than that of fragile glasses [30]. Specific heat, similar to entropy $S$, represents the fluctuation in the microscopic energy (Chap. 19 of Callen’s textbook [31]). Entropy becomes insensitive to the change in $T$ at high temperatures. Since the $T_g$ of silica glass is as high as $1480 \text{K}$, the small $\Delta C_p$ is a consequence of the insensitivity of entropy at high temperatures.

Finally, we check the specific heat of the liquid. The current simulations show that $E_{st}$ for the liquid is approximately linear, indicating constant $C_v^{(l)}$. The calculated value is $C_v^{(l)} = 0.73R$. By considering that the phonon contribution has already reached the classical limit, $3R$, and that thermal expansion is negligible, we conclude that the total specific heat of the liquid is constant, with $C_v^{(l)} = 3.73R$. Richet et al. reported a constant value, $C_v^{(l)} = 3.26R$, in a temperature range of $1480 < T < 2000 \text{K}$ [9]. Despite this overestimation, our result is consistent with theirs in terms of $C_v^{(l)}$ being a constant. However, we cannot assert that the calculation is correct simply because it agrees with Richet et al.’s experiment. Our simulations ignore the component of low-frequency phonons, whose frequency is less than $50 \text{cm}^{-1}$, due to the limited size of the supercell. These low-frequency phonons can be converted to purely translational motions as $T$ increases. Thus, contrary to being constant, a reduction in specific heat from $3R$ to $1.5R$ is expected if the temperature range is sufficiently large [66]. Alternatively, we do not have enough reason to rule out the experimental finding of an increase in $C_v^{(l)}$ with increasing $T$. Currently, we can only say that the thermodynamic properties of even the liquid of silica have hysteresis in the range of $1500 < T < 2000 \text{K}$, as suggested by researchers in the glass industry.

### 3.3. Reheating of glass

The obtained glasses (A) and (B) were heated again from low temperatures to examine the dependence on processes. Figure 8 shows variations in the diffusion coefficient $D$ and
structural energy $E_{st}$ when the glass is heated. The figure shows that the glass transition temperature is higher in this instance than in the cooling process: $T_g$ is about 1600 K for sample (A) and 3200 K for sample (B). This increase is expected because the barrier height is higher when measured from the low temperature side. Hence, we trust the $T_g$ values obtained in the cooling process. However, the hysteresis observed in the simulations between the cooling and reheating processes may be different from the experimentally observed one because the latter is caused by the grain boundaries, whereas the former is due to the artificial boundary condition. The results of the three processes of melting, cooling, and reheating, are superimposed in a figure, which is shown in Supplemental materials (p. 7).

Figure 9 shows the temperature dependence of the structural parameters, which is obtained for the slow-cooled sample (B). The change in bond length against $T$ is $(1/r)dr/dT = 7.9 \times 10^{-6} \text{ K}^{-1}$, which is close to that of $\alpha$-quartz obtained in the heating process. The fact that the crystal and glass have very different thermal expansivities despite the same $(1/r)dr/dT$ implies that the change in bond length is irrelevant to the small thermal expansivity of silica glass. The constancy in angles $\delta$ and $\theta$ with respect to $T$ before melting is the same for both crystal $\alpha$-quartz and silica glass. This constancy of $\theta$ is different from that obtained by model potentials [37–39], where $\theta$ decreases as $T$ increases. Although the mean value of $\theta$ is constant with respect to $T$, a notable difference of silica glass from the crystal case is its large mean-square variation. Figure 5 shows that the bending angle $\theta$ of the Si–O–Si bond has a wide range from 80 to 180$^\circ$. Similarly, the mean-square variation $\Delta \phi$ is also large even at room temperature. As mentioned in section 3.2.2, a decrease in $\theta$ from 140$^\circ$ increases the frequency of the bond stretching mode perpendicular to the Si–Si axis, whereas an increase from 140$^\circ$ results in an opposite outcome [56, 57]. This effect is observed in the shift in the 440-cm$^{-1}$ band of the Raman spectra of the crystal $\alpha$-quartz [48].

Both directions of expansion and contraction of the unit cell, which counterbalance each other, are caused by two parts of higher and lower angle $\theta$ relaxing thermal strains. This may explain why silica glass has a far lower thermal expansivity than crystal $\alpha$-quartz, despite their structural similarities. However, we would not comment further on this because several previous studies have already discussed it in detail.

When a silica glass melts, obviously changes in the structure occur, as seen in figure 9. Even below $T_g = 3200$ K, the average $\Delta \phi$ becomes indeterminate, which indicates free rotation. As $\theta$ indicates, the Si–O–Si bond is quickly bending as $T$ increases higher than 2200 K. In this way, the structural distinction between the glass and liquid is clear. By observing a similarity in the RDF of the glass and liquid, it is sometimes claimed that there is little difference in the structure between these two phases. However, RDF is the time average of the distance of two neighboring atoms. The diffusing motion is hidden in the measurement of RDF.
4. Interpretation of the PD relation

The preceding results provide useful insight on the PD relationship. The PD ratio \( \Pi \) has the following relation for glasses:

\[
\Pi = \frac{\Delta C_p \Delta \kappa}{TV(\Delta \alpha)^2} \geq 1. \tag{5}
\]

The formal confirmation of this relationship has been extensively studied [67–72], but the subtlety of this relationship is still up for debate [73–76]. Apart from these subtle problems, it is generally understood that the equality in equation (5) only holds when there is just one order parameter; otherwise, the inequality holds. The vast experimental data on glasses indicate that \( \Pi > 1 \), and in most cases, \( 2 < \Pi < 8 \), implying the presence of several (or more) order parameters. The abstract nature of the order parameters makes it difficult to derive physical meaning from them. The fact that there appears to be no general trend in \( \Pi \) among various glasses or correlation to other qualities such as fragility adds further difficulties.

In this regard, the novel perspective of state variables of solids proposed by Shirai [28, 29] has significant advantages from which the inequality of (5) is reasonably understood. In the following, we present an exposition of the PD ratio from this perspective. Shirai demonstrated that the thermodynamic state variables (thermodynamic coordinates) of a solid are the equilibrium positions \( \{ \mathbf{R}_j \} \) of the atoms comprising the solid [28]. In fact, the set of \( \{ \mathbf{R}_j \} \), in addition to \( T \) and \( V \), forms the arguments of the function \( U \) in equation (2). This conclusion was deduced from the basic requirements for state variables: first, a state variable must have a definite value in equilibrium; second, an equilibrium state must be uniquely specified by a set of state variables [29]. The first requirement differentiates solid states from gas states. The atoms of solids maintain their own and unique positions in any of their equilibrium states, whereas atom positions for gases are indeterminate on time averaging and therefore cannot be state variables. The second requirement guarantees that thermodynamic states are independent of the history in which the current state was obtained. We consider two samples (A) and (B) in section 3.2. If the state variables of glass were only \( T \) and \( V \), it would be concluded that the obtained glass is in a nonequilibrium state because it is impossible to describe the difference between these two samples by any function of the form \( U(T, V) \). If the state were in nonequilibrium, work could be extracted from it without harming the environment. This conflicts with the second law of thermodynamics. Accordingly, the glass state must be in an equilibrium state. Affirmatively, we can use \( U = U(T, V, \{ \mathbf{R}_j \}) \) to describe the difference in the thermodynamic properties of samples (A) and (B), irrespective of the history. (The authors recognize that many readers are reluctant to accept the present view, because of the prevailed tenet of thermodynamics that the states must be described by a few state variables. In this case, we suggest readers to interpret the state variables simply as parameters instead. Then, the relation \( U = U(T, V, \{ \mathbf{R}_j \}) \) can be read as a function of parameters \( \{ \mathbf{R}_j \} \) in addition to \( T \) and \( V \).

Order parameters in phase transitions are variables having nonvanishing and definite values in equilibrium, and thus, they satisfy the first requirement for state variables. It is assumed that they are something characterizing the structure of a state of matter [77]. The structure is best described by a complete set of atom positions \( \{ \mathbf{R}_j \} \). Therefore, any property that is uniquely determined by \( \mathbf{R}_j \), or the entire set \( \{ \mathbf{R}_j \} \) can be used for order parameters. We will select the latter choice as our order parameters. This choice satisfies the second requirement for state variables. Thus, the order parameters become equivalent to the state variables of a solid. This implies that the number of order parameters for glass equals the number of atoms in the glass. From this viewpoint, inequality is a natural consequence of order parameters in glasses.

The PD ratio contains further information. Silica glass is a special case in that its \( \Pi \) value is extremely high, ranging from \( 10^5 \) to \( 10^6 \) [2]. This large uncertainty of the \( \Pi \) value is due to the extremely small thermal expansivity of silica glass—the smallest of all materials on earth. It is difficult to resolve small changes in the volume of silica glass; the materials of the apparatus in which expansivity measurement of silica is performed change the volumes more. By combining equations (4) with (5), we obtain the following:

\[
\Pi = \frac{\Delta C_p/C_v}{(\Delta \alpha/\alpha)^2/(\Delta \kappa/\kappa)}. \tag{6}
\]

A simple formula for thermal expansivity \( \alpha = \alpha C_v/V \), where \( \gamma \) is the Grüneisen parameter, which indicates the magnitude of anharmonicity of atom potentials; see, for example, equation (25.19) of [78]. In this formula, \( \gamma C \) is an averaged value across all phonon modes, assuming that all phonon modes contribute equally to thermal expansion. However, we must investigate this assumption. Since the thermal expansion is an isotropic response to heat injection, modes that preserve the cell volume do not contribute to thermal expansivity; some angle-bending modes are examples of this. An illustrative example is the librational mode of \( \alpha \)-boron [79]. Despite the angle-bending forces in \( \alpha \)-boron having large anharmonicity, the frequency of the librational mode does not exhibit pressure dependency, which is usually considered evidence for small anharmonicity. Therefore, in the formula for \( \alpha \), the specific heat \( C \) should be replaced with \( C_v(V) \), which is contributed to only by those phonons whose frequencies depend only on the isotropic volume change.

\[
\alpha = \frac{\gamma_{in}(V)C_v(V)}{V} \kappa, \tag{7}
\]

where \( \gamma_{in}(V) \) is the corresponding mode-grüneisen parameter. Notably, the isothermal compressibility \( \kappa \) of silica glass is not as small as is expected from the small thermal expansivity \( \alpha \). This apparent conflict between the \( \kappa \) and \( \alpha \) behavior is due to the unusually small isotropic-Grüneisen parameter \( \gamma_{in} \) of silica glass—it is smaller than usual by one order of magnitude [80]. The small value of the average Grüneisen parameter is due to the counterbalance between positive and negative mode-Grüneisen parameters \( \{ \gamma_q \} \), as described in section 3.3.
When the factor, $\gamma_2 C_\alpha/V$, is constant with respect to $T$, the change in $\alpha$ is solely determined by $\kappa$, and their relative changes are the same.

$$\frac{\Delta \alpha}{\alpha} = \frac{\Delta \kappa}{\kappa}. \quad (8)$$

This relationship holds for crystals on the same order in anharmonic perturbations $[81]$. Similarly, from equation (4), the part of thermal expansion, $C_{\alpha}$, changes as follows:

$$\frac{\Delta C_{\alpha}}{C_{\alpha}} = \frac{\Delta \alpha}{\alpha}. \quad (9)$$

From equations (8) and (9), equation (6) can be rewritten as

$$II = \frac{\Delta C_p}{\Delta C_{\alpha}} = \frac{(\text{Change in the total energy})}{(\text{Contribution of isotropic volume change})}. \quad (10)$$

Since $II > 1$ (mostly > 2), the glass transition occurs mainly due to a change in the internal structure that determines $E_{st}$; the contributions of thermal expansion and phonons are small. Section 3 shows that the jump $\Delta C_p$ for silica glass is almost entirely determined by $\Delta C_{\alpha}$, leading to $II \gg 1$. As noted in section 3.2.4, the specific heat as well as entropy reflect energy fluctuations, as $(\overline{E^2} - \overline{E}^2)/\overline{kB^2}$. In this sense, $II$ is better than $C_{st}$ itself for assessing how largely the structural energy contributes to the internal energy change because the insensitivity to temperature change is eliminated by taking the ratio $\Delta C_p/\Delta C_{\alpha}$. As stated in Introduction, the apparent properties of silica do not seem to change so much between the glass and liquid states. However, the difference is clearer by looking at $II$, indicating the significant change in the internal structure.

Using a suitable model potential, Filipovich had attributed $\Delta C_p$ of silica glass to the contribution of structural parameters more than three decades ago [82]. In addition to the volume change, he modeled the $\Delta C_p$ of silica glass by introducing the distribution of angle Si–O–Si. These two types of changes were described by two independent force constants. From this model, he showed that $\Delta C_p$ and $\Delta \alpha$ change independently, resulting in $II > 1$. His model is essentially correct, with reducing the entire set of state variables $\{R\}$ to only two variables.

By contrast, if $\Delta C_p$ is caused by only the contribution of thermal expansion $\Delta C_{\alpha}$, $II = 1$ is deduced. This occurs when the changes in thermodynamic properties of the glass are described by elastic models with single parameters, such as the volume change $\Delta V$. A simple model, such as the free-volume model, is often used in the glass literature. The free-volume model describes the energy change by the effective volume of a ‘hole’—the disordered structure is represented by holes. In this case, the equality $II = 1$ is necessarily deduced. Starting with a simple model is suitable; however, it may not be sufficiently accurate.

5. Summary

The glass transition of silica glass was investigated using FP-MD simulations by calculating the specific heat. The current simulations are severely limited due to the small size of the cells. The periodic boundary condition with small cell sizes yields a spurious energy barrier for atom motions, resulting in overestimations in melting temperature, glass-transition temperature, and other similar properties. Despite these shortages, this study provides new information on the thermodynamic properties of silica glass.

The glass-transition temperature $T_g$ was obtained in the range of 1600–2600 K, with a jump in the specific heat, $\Delta C_p = 0.50$ to 0.68$R$. Although these values are higher than the experimental values, the obtained values are within a reasonable range when the aforementioned uncertainties are considered. Decomposing the internal energy into three components (structural, phonon, and thermal expansion energies) according to state variables reveals that the jump $\Delta C_p$ of silica glass is entirely determined by the structural energy $E_{st}$. The change in $E_{st}$ is controlled primarily by the distribution of the bending angle of the Si–O–Si bond. The reason for the small $\Delta C_p$ is the high $T_g$ of silica glass, which makes the fluctuation in $E_{st}$ insensitive to the temperature change.

One outcome of this study is finding a physical interpretation for the PD ratio $II$. It represents the ratio of the total energy change in the glass transition to the thermal expansion contribution. The experimental fact that $II > 1$ implies that the glass transition is mostly caused by the change in $E_{st}$, which is controlled by the internal structure. An extreme example is the current case of silica glass, where the glass transition occurs without assistance from the change in thermal expansion or phonons. Despite the apparent similarities between the glass and liquid states, the two states of silica glass are very distinct in their internal structures, which is reflected in the large value of $II$.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Appendix. Effects of periodic boundary condition

The effect of using periodic boundary conditions on atom motions is investigated here. The periodic boundary condition is used in all MD simulations. This introduces spurious
reflections of atom motion at the boundaries. The length $a$ of the supercell limits the lowest wavelength of phonons in phonon spectra. The absence of phonons with wavelength $\lambda$ longer than $a$ can be looked upon as the formation of virtual potential acting on atoms, which eliminates these long-wavelength phonons. This effect becomes severe when $a$ is small. We estimate the effect of cell size on atom motions. A virtual periodic potential $V_p$ is introduced to reproduce this effect. A simple form is assumed as follows:

$$V_p(x) = \frac{V_0}{2} \left[ 1 - \cos \left( 2\pi \frac{x}{a} \right) \right], \quad (A.1)$$

We use this virtual potential as a real one near the equilibrium position, $x = 0$. Around $x = 0$, this potential has a harmonic form with the force constant, $f' = (V_0/2)(2\pi/a)^2$. This yields the lowest frequency of the used cell, $\omega = \sqrt{2f'/M}$. The lowest frequency obtained in the current cell size $2 \times 2 \times 2$ for crystal α-quartz was approximately 50 cm$^{-1}$. Using the mass of oxygen for $M$, we obtain $f' = 23$ µdyn Å$^{-1}$, and thus, a potential barrier of $V_0 = 0.37$ eV. This magnitude is sufficient to raise the melting temperature by a few thousands of degrees K.

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