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# Negative thermal expansion of quartz glass at low temperatures: An *ab initio* simulation study

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## ABSTRACT

Using a mixed classical Molecular dynamics (MD)/*ab initio* simulation scheme combined with a quasi-harmonic approximation, we calculate the linear thermal expansion coefficient  $\alpha_L(T)$  in vitreous silica glasses. The systems are first cooled down by classical MD simulations. Then they are structurally relaxed by *ab initio* DFT calculations. The vibrational properties are calculated employing the frozen phonon method, and these results are finally used to calculate the Helmholtz free energy as a function of volume. In agreement with experiments, our simulations predict that  $\alpha_L(T)$  is negative at low temperatures up to  $T \approx 150$  K. In this low-temperature regime, the simulation results are in quantitative agreement with experiments. To elucidate the origin of the negative thermal expansion, we analyze in detail the microscopic mode Grüneisen parameters in the system and show that the anomalous behavior of  $\alpha_L(T)$  can be related to the fact that the Grüneisen parameters for the lowest modes become negative at low temperatures – i.e., the lowest eigenfrequencies become stiffer with increasing volume.

## 1. Introduction

Oxide glasses are of great technical importance due to their optical and mechanical properties [1]. Especially, silicate glasses exhibit various peculiar properties that are interesting for applications. Among them is their low thermal expansion coefficient, as compared to, for example, typical metallic or polymeric materials [2]. Glasses with low thermal expansion coefficients are widely used for applications where temperature changes should not affect the mechanical properties of the material such as in laboratory glasses or in materials for cooking equipment. An example is Ti-doped fused silica which is used in microlithography applications for the structuring of semiconductors [3]. For this and other cases it is crucial to adjust the thermal expansion of glasses with an accuracy down to 1 ppb/K which requires the use of fused silica, i.e. SiO<sub>2</sub> with a high purity [4].

Apart from being very low, the thermal expansion coefficient of SiO<sub>2</sub> is also anomalous in that it becomes negative for temperatures below about 200 K [5,6]. This presents a challenge for the quantitative modeling of silica in terms of classical molecular dynamics (MD) computer simulations [7]. Such simulations describe the interactions between the atoms in terms of effective potentials that do not explicitly take into account the electronic degrees of freedom. Although effective

potentials [8,9] have been very successful in describing the structure and various dynamic properties of amorphous SiO<sub>2</sub> [10], in general, these models fail to correctly recover the thermal expansion and its low-temperature anomaly, at least on a quantitative level. This is partly due to the fact that the vibrational properties of amorphous silica are not reliably modeled in terms of effective potentials [9,11]. Here, *ab initio* calculations where the electronic degrees of freedom are explicitly taken into account in the framework of a density functional theory (DFT) approximation [12,13] have been proven to be very accurate with respect to the vibrational properties of amorphous SiO<sub>2</sub> [14–17]. Also, thermodynamic properties of  $\alpha$ -quartz have been accurately calculated by *ab initio* calculations [18]. This motivates to employ *ab initio* calculations to also investigate thermodynamic properties of amorphous SiO<sub>2</sub>. Indeed, this approach has been already successfully applied to calculate thermal expansion in silicates, for example of  $\beta$ -eucryptite [19]. In the present work we employ *ab initio* calculations to study the thermal expansion at low temperatures in SiO<sub>2</sub> glass in the framework of a quasi-harmonic approximation [20].

Compared to classical MD, *ab initio* MD simulations are very expensive and so they are typically restricted to system sizes of about 100–500 particles and to time scales in the picosecond range. As a consequence, *ab initio* MD simulations allow only to generate small

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glass samples by quenching equilibrated melts from very high temperatures to temperatures below the glass transition temperature with very high cooling rates of the order of  $10^{13}$  K/s. To overcome the latter restriction, we combine *ab initio* with classical MD calculations that allow to generate glass samples using a significantly lower cooling rate of  $10^{11}$  K/s. These glass samples are used as starting configurations for *ab initio* calculations from which the phonon modes are determined for systems at different densities (i.e. different systems with a fixed number of particles and a varying volume). From the phonon modes we then obtain the Helmholtz free energy for different temperatures and volumes and thus the temperature dependence of the thermal expansion coefficient as well as the mode Grüneisen parameters [21].

For the classical MD runs, we choose two different pairwise-additive potential models, namely the BKS [8] and the CHIK [9] model. Their use for generating glass samples is justified since previous studies have shown that these models provide a reliable description of the structure of amorphous silica [9,10]. In fact, as we shall see below, the *ab initio* calculations based on the refined classical configurations lead to a vibrational density of states which is in good agreement with neutron scattering experiments, in accordance with previous studies [14–17]. Here, we also demonstrate that *ab initio* calculations of the low-temperature thermal expansion are in good agreement with experiment; in particular we observe a negative thermal expansion coefficient at temperatures below about 160 K with a minimum at about 50 K. We show that this behavior is related to the fact that the microscopic mode Grüneisen parameters become negative at low phonon eigenfrequencies below 5 THz. This is in good agreement with previous observations and corresponding analysis of the vibrational modes in amorphous silicon [22].

The rest of the paper is organized as follows. In Section 2, the protocol for the generation of glass samples is described and the structural and vibrational properties are compared to experimental results. In Section 3, the theoretical background for calculating the thermal expansion coefficients and related properties in the framework of the quasi-harmonic approximation is given. Section 4 is devoted to the results, followed by a discussion and conclusions in Section 5.

## 2. Glass structures

In this section, the generation and validation of independent glass structures is described. This is done by employing a combination of classical molecular dynamics (MD) simulations with *ab initio* simulations. Details are presented in Subsection 2.1. Next, the quality of the glass structures is validated by comparing structural and vibrational properties with experimental results, namely the static structure factor and the vibrational density of states. This is described in detail in Subsection 2.2. A realistic description of the vibrational properties is of great importance as they are the basis for low temperature thermodynamics and for calculating the thermal expansion in the quasi-harmonic approximation.

### 2.1. Simulation details

All simulations are carried out at the experimental glass density [23] of  $\rho = 2.2$  g/cm<sup>3</sup> and in all cases the system size is restricted to 165 atoms. This implies a box size of  $L_{\text{Box}} = 13.5618$  Å and is a good compromise in that it minimizes finite size effects while still keeping the system size small enough that the system can be treated with *ab initio* simulations. The glass structures are generated in the following way: After a random initialization, the systems are equilibrated at 4300 K for 1.6 ns with a time step of 1.6 fs and then linearly cooled down to 300 K at a cooling rate of  $\Gamma = 1 \cdot 10^{11}$  K/s, using classical molecular dynamics (MD) simulations. After annealing at 300 K for 1.6 ns, the configurations are quenched down to 0 K. All classical MD simulations are conducted with the open source software package LAMMPS [24] using a chain of 3 Nosé-Hoover thermostats with a

damping parameter of 160 fs. Following this cooling scheme, 10 independent cooling runs are carried out with two different classical potentials, namely the BKS [8] potential and the CHIK [9] potential.

The BKS and the CHIK potentials only consist of pair interactions with the functional form of a Buckingham potential with Coulomb interactions

$$V^{\text{Buck+Coul}}(r) = V^{\text{Buck}}(r) + V^{\text{Coul}}(r) \\ = A_{\alpha\beta} \exp[-b_{\alpha\beta} r] - \frac{C_{\alpha\beta}}{r^6} + C_{\text{Coul}} \frac{q_{\alpha} q_{\beta}}{r}. \quad (\text{II.1})$$

The indices stand for the different atom types, namely  $\alpha, \beta \in \{\text{Si}, \text{O}\}$  and the different terms of the short-range part of the potential describe the Pauli repulsion energy  $A_{\alpha\beta} \exp[-b_{\alpha\beta} r]$  and the attractive van der Waals energy  $-\frac{C_{\alpha\beta}}{r^6}$  for non-bonded atoms. The interaction parameters are chosen according to the above-mentioned publications, Refs. [8,9]. To this end, the Coulomb interactions are divided into a short-range part evaluated in real space and a long-range part evaluated in Fourier space, computed with the standard routine for Ewald summations of the LAMMPS package with  $g_{\text{ew}} = 0.473375$  and  $|k| \leq 6 \cdot \frac{2\pi}{L_{\text{Box}}}$ . The Buckingham part of the potential, as well as the short-range Coulomb part, is truncated at  $r_c = r_c^{\text{ew}} = 6.5$  Å, shifted to zero and multiplied by a smoothing function of the form

$$G(r) = \exp\left[-\frac{d}{(r-r_c)^2}\right], \quad (\text{II.2})$$

with  $d = d^{\text{ew}} = 0.05 \text{Å}^2$ . The total short range potential, then, is substituted by a harmonic potential for atomic distances smaller than the positions of the first local maximum as the Buckingham potential has the unphysical property to diverge to minus infinity at small distances. As this modified version of the short-range potential is not implemented in the LAMMPS package, we used tabulated potentials of the so-called bitmap style [25]. In all cases, Verlet neighbor lists are employed [7]. They are updated when the first atom has moved more than half the skin distance of  $r_{\text{skin}} = 2 \text{Å}$ . During the cooling procedure, the systems fall out of equilibrium as soon as the relaxation time is of the order of the time scale of the cooling process. In our simulations, this happens at about 3000 K and 2700 K for the BKS and the CHIK potentials, respectively.

After the quench to 0 K, in each case, the configurations are structurally relaxed by means of a quantum mechanical DFT calculation employing a conjugate gradient algorithm [26]. The system volume is fixed and the relaxation is stopped when all forces on the atoms are smaller than  $5 \cdot 10^{-4}$  eV/Å. In this work, all DFT calculations are carried out using the Vienna Ab initio Simulation Package (VASP) [27,28]. A Perdew-Burke-Ernzerhof (PBE) type exchange-correlation functional of the generalized gradient approximation (GGA), revised for solids (PBEsol) [29], is chosen. Computations are conducted using a plane wave basis set and the projector augmented-wave method (PAW) [30,31]. A Gaussian smearing method is applied for the partial occupancies of the energy levels of the electronic states around the Fermi-level with a smearing width of  $\sigma = 0.02$  eV. Due to the large simulation box, only Gamma-point calculations are conducted with one  $k$ -point at the zone center of the Brillouin zone ( $\mathbf{k} = (0,0,0)^T$ ). Also, the projection operators of the PAW wave functions are evaluated in real space. In all cases, a plane-wave cutoff of  $E_{\text{cut}} = 500$  eV is chosen and the break condition for the electronic relaxation is a relative energy difference of  $10^{-8}$ .

It has been shown that different cooling rates  $\Gamma$  have effects on glass structures and thermodynamic properties [11,32]. To validate the reliability of our glass structures in terms of these effects, we conduct 10 additional cooling runs with each classical interaction potential in the exact same way as described above, changing the cooling rate to  $\Gamma = 1 \cdot 10^{12}$  K/s. To verify the combination of a classical MD quench and a subsequent quantum mechanical relaxation, we generate one additional glass structure by means of a full *ab initio* DFT quench. We cool the equilibrated system from 3600 K to 0 K with a cooling rate of

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