



# A new determination method of interatomic potential for sodium silicate glass simulations



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## ARTICLE INFO

### Article history:

Received 3 February 2017

Received in revised form 28 March 2017

Accepted 29 March 2017

Available online 21 April 2017

### Keywords:

Molecular dynamics simulation

Sodium silicate glasses

First-principles calculation

Material design

## ABSTRACT

An interatomic potential for the classical molecular dynamics (MD) simulation of sodium silicate glasses was proposed. The ionic charges for this interatomic potential were determined by Mulliken population analysis via the density functional theory (DFT) calculation of alkali silicate crystals. The Si—O interatomic potential energy curve was determined by molecular orbital (MO) calculation of  $\text{SiO}_2^{2+}$ . The results of classical MD simulations using the new interatomic potential were consistent with the experimental trends in interatomic distance, thermal expansion coefficient, molar volume, Si—O—Si bond angle distribution, and  $Q_n$  ratio with respect to the sodium composition of the silicate glass. The proposed interatomic potential improves the reproducibility of the ring size distribution in silicate glasses compared to conventional potentials.

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## 1. Introduction

The physical properties of glasses, including the self-diffusion coefficient of ions, electrical conductivity, thermal expansion, bulk modulus, specific heat, and glass transition temperature, are known to be related to the glass composition. For example, the thermal expansion coefficient of sodium silicate glasses increases with increasing  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio [1]. This effect is attributed to the change in atomic structure from a three-dimensional network structure to a two-dimensional flexible structure as the  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio increases [2]. Because the physical properties of glasses are closely related to the atomic structures of those glasses, the development of techniques to predict glass properties based on glass composition is important for the study of new functional glasses.

First-principles calculations have been widely used to investigate new functional crystals. However, simulations of glasses involve many nuclei and electrons, and the nonperiodic structures of glasses require large calculation models. In addition, the derivations of the self-diffusion and viscosity coefficients of glasses require calculations with long time scales [3]. Molecular dynamics (MD) simulations based on classical mechanics are suitable for the investigation of glasses because of their lower computational cost compared to first-principles calculations.

Interatomic potential function for application in classical MD simulations of oxide glasses have been developed using first-principles calculations. The interatomic potentials for Si—O, P—O, and Al—O pairs were determined from first-principles calculations of tetrahedron clusters [4–7]. These interatomic potentials were then applied to classical MD

simulations of silicate crystals/glasses, aluminophosphate crystals, and aluminosilicate crystals [4–7]. The development of these interatomic potentials has enhanced the reliability of classical MD simulations; however, this method, used to derive the above potentials, cannot necessarily be applied to generate the interatomic potentials needed to simulate all oxide glasses.

Silicate, aluminosilicate, and phosphate glasses essentially form only tetrahedral structural units, whereas borate glasses are formed by two structural units:  $\text{BO}_3$  and  $\text{BO}_4$ . In these cases, the interatomic potentials cannot be easily derived from first-principles cluster calculations. Cluster models for the first-principles calculation of glasses without experimental structural data are also difficult to obtain.

The Si—O bonds in  $\text{SiO}_2$  glass are weakened when network-modifying oxides (e.g.,  $\text{Li}_2\text{O}$  and  $\text{Na}_2\text{O}$ ) are introduced [8]. Noritake et al. [9] and Cormack et al. [10] used empirical formulae to determine the charges of silicon and oxide ions as functions of the  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio in sodium silicate melts/glasses for classical MD simulation. Sawaguchi et al. [11] also simulated lithium borate glasses/melts using classical MD with ionic charges determined by empirical equations depending on the  $\text{Li}_2\text{O}/\text{B}_2\text{O}_3$  ratio. However, no method to determine the optimal ionic charges based on glass composition for use in classical MD simulation has been established.

The target of this study is sodium silicate glass, which is a basic component of practical glasses. First, choosing a function as the interatomic potentials applying to classical MD simulations of the glasses, then we studied a method of finding an appropriate parameter values appeared in the potential function by first-principles calculations. The Si—O bond distance does not vary with glass composition [12–15], suggesting that the equilibrium distance of the Si—O interatomic potential must be fixed independent of the glass composition at ordinary temperature

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and pressure. In contrast, the charges of silicon and oxide ions are thought to depend on glass composition; this dependency is considered to contribute to the weakening of the Si—O bond with increasing alkali oxide ratio in silicate glasses [8]. This relationship must be reflected in the depth of the Si—O interatomic potential for each glass composition.

In this study, an Si—O interatomic potential was developed based on the results of nonempirical molecular orbital (MO) calculations of an  $\text{SiO}_2^{2+}$  cluster. We selected this diatomic molecular cluster so that the coordination number of the polyhedron can correspond with changes due to temperature and pressure [16]. Based on these calculations, the shape of the Si—O interatomic potential function was fixed, with the exception of the potential depth, which changed with glass composition. The ion charges of silicate glasses were estimated from the results of density functional theory (DFT) calculations of alkali silicate crystals with related sodium silicate glass composition. The results of the two different calculations were combined to develop the complete Si—O interatomic potential function. Finally, a unique interatomic potential for the classical MD simulation of sodium silicate glass was obtained for each glass composition as described by the  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio. MD simulations of sodium silicate glasses with several compositions were then performed using the obtained interatomic potentials, and the results were evaluated using experimental results.

## 2. Determination method of interatomic potentials

### 2.1. Interatomic potential function

In this study, we applied the interatomic potential function reported by Sakuma et al. [17], which has been shown to accurately reproduce the physical properties and structures of oxide crystals. The interatomic potential,  $U_{ij}(r_{ij})$ , is shown in

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\epsilon_0 r_{ij}} + f_0(b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + \{D_{1ij} \exp(-\beta_{1ij} r_{ij}) - D_{2ij} \exp(-\beta_{2ij} r_{ij})\} \quad (1)$$

where  $r_{ij}$  is the distance between ions  $i$  and  $j$ . The first term is the Coulomb force term, where  $z$  is the ionic charge,  $\epsilon_0$  is the dielectric constant of vacuum, and  $e$  is the elementary charge. The second term is the short repulsive force term, where  $a_i$  and  $b_i$  are parameters, and the third term is the van der Waals force term with parameter  $c_i$ . The fourth term is added as a covalent force term to account for Si—O interactions, where  $D_{1ij}$ ,  $\beta_{1ij}$ ,  $D_{2ij}$ , and  $\beta_{2ij}$  are parameters. The constant  $f_0$  is  $4.185 \text{ kJ nm}^{-1} \text{ mol}^{-1}$ .

### 2.2. Determination of ionic charges

The ionic charges  $z_i$  were determined by DFT calculations of alkali silicate crystals using the CASTEP code [18]. A plane-wave basis and norm-conserving pseudopotential method with the GGA PBE exchange-correlation function [19] were applied. The target crystals [20–32] and applied  $k$ -point set are listed in Table 1. The charges of ions in crystals of lithium silicate and potassium silicate systems were also calculated for comparison. The following norm-conserving pseudopotentials were used: Li,  $2s^1$ ; Na,  $2s^2 2p^6 3s^1$ ; K,  $3s^2 3p^6 4s^1$ ; Si,  $3s^2 3p^2$ ; and O,  $2s^2 2p^4$ .

The crystal structures were optimized using a cutoff energy of 1500 eV and an SCF tolerance of  $5.0 \times 10^{-7} \text{ eV/atom}$ . The optimized lattice parameters are listed in Table 1 along with error based on the literature values [20–32]. The largest error was 2.88%. The ionic charges  $z_i$  in Eq. (1) for silicate crystals were calculated from Mulliken population analysis [33,34] for each crystal. The validity of this calculation method was confirmed by MD simulations of alkali silicate crystals and glasses in previous works [16,35]. The cutoff distance used to count electrons belonging to each nucleus was fixed to 0.3 nm for all target crystals. Fig. 1 shows the Mulliken charges of ions in alkali (A) silicate crystals with compositions of  $x\text{A}_2\text{O} \cdot (1-x)\text{SiO}_2$ . The charges of the silicon and alkali ions decrease with increasing  $x$ . The absolute values of Mulliken charges are recognized as having low reliability [33]. MD simulations of sodium silicate glasses using charges based on the Hirshfeld method [36], which is another charge analysis method, poorly reproduced the glass structures [16]. In contrast, the trends in Mulliken charge with chemical composition seem to be meaningful; thus, Mulliken charges were used in this study. The ionic charges  $z_{\text{Na}}$ ,  $z_{\text{Si}}$ , and  $z_{\text{O}}$  were given by Eqs. (2-1), (2-2), and (2-3), respectively, as functions of composition  $x$ :

$$z_{\text{Na}} = -0.25x + 1.0 \quad (0 < x \leq 1) \quad (2-1)$$

$$z_{\text{Si}} = -0.50x + 2.4 \quad (0 \leq x < 1) \quad (2-2)$$

$$z_{\text{O}} = -\frac{2x \cdot z_{\text{Na}} + (1-x) \cdot z_{\text{Si}}}{2-x} \quad (0 \leq x \leq 1) \quad (2-3)$$

The constants in Eqs. (2-1) and (2-2) were determined in consideration of the empirical values of  $z_{\text{Na}}$  and  $z_{\text{Si}}$  used in a previous study [11]. Eq. (2-3) for  $z_{\text{O}}$  was obtained from the charge neutrality of the crystals.

**Table 1**

The deviation denotes the difference of structural optimization by DFT.

Crystals	Ref.	Lattice parameter (deviation, %)						$k$ -Points	Number of ions in cell
		$a/\text{nm}$	$b/\text{nm}$	$c/\text{nm}$	$\alpha/\text{deg.}$	$\beta/\text{deg.}$	$\gamma/\text{deg.}$		
$\alpha$ - $\text{SiO}_2$	[20]	0.49134 (2.20)	0.49134 (2.20)	0.54052 (1.95)	90 (0)	90 (0)	120 (0)	$3 \times 3 \times 4$	9
$\text{Li}_2\text{Si}_2\text{O}_7$	[21]	1.9648 (1.27)	0.59969 (0.73)	0.48691 (1.37)	90 (0)	90 (0)	90 (0)	$1 \times 2 \times 3$	48
$\text{Li}_2\text{Si}_2\text{O}_5$	[22]	0.5807 (1.09)	1.4582 (1.30)	0.4773 (1.51)	90 (0)	90 (0)	90 (0)	$2 \times 1 \times 3$	36
$\text{Li}_2\text{SiO}_3$	[23]	0.9392 (0.47)	0.5397 (0.54)	0.466 (1.71)	90 (0)	90 (0)	90 (0)	$2 \times 3 \times 3$	24
$\text{Li}_6\text{Si}_2\text{O}_7$	[24]	0.7715 (0.67)	0.7715 (0.67)	0.488 (0.79)	90 (0)	90 (0)	90 (0)	$2 \times 2 \times 3$	30
$\text{Li}_4\text{SiO}_4$	[25]	0.7519 (0.74)	0.5648 (0.56)	0.5031 (0.61)	124.15 (0.05)	97.18 (0.21)	100.26 (0.34)	$2 \times 3 \times 3$	18
$\text{Li}_8\text{SiO}_6$	[26]	0.54243 (0.31)	0.54243 (0.31)	1.0626 (0.23)	90 (0)	90 (0)	120 (0)	$3 \times 3 \times 2$	30
$\text{Na}_2\text{Si}_2\text{O}_5$	[27]	0.6409 (1.35)	1.5422 (1.44)	0.4896 (1.40)	90 (0)	90 (0)	90 (0)	$2 \times 1 \times 3$	36
$\text{Na}_2\text{SiO}_3$	[28]	1.043 (2.11)	0.602 (2.63)	0.481 (1.50)	90 (0)	90 (0)	90 (0)	$1 \times 2 \times 3$	24
$\text{Na}_4\text{SiO}_4$	[29]	0.5576 (1.34)	0.5576 (1.47)	0.8393 (1.78)	80.92 (0.17)	71.84 (0.09)	67.44 (0.19)	$3 \times 3 \times 2$	18
$\text{K}_2\text{Si}_2\text{O}_5$	[22]	1.63224 (2.88)	1.1243 (1.25)	0.9919 (1.90)	90 (0)	115.97 (0.61)	90 (0)	$1 \times 1 \times 2$	108
$\text{K}_6\text{Si}_2\text{O}_7$	[30]	0.6458 (0.81)	0.8887 (0.75)	1.0879 (1.25)	90 (0)	125 (0.23)	90 (0)	$3 \times 2 \times 2$	30
$\text{K}_4\text{SiO}_4$	[31]	1.037 (0.74)	0.6392 (1.51)	1.0366 (0.88)	90 (0)	112.83 (0.63)	90 (0)	$1 \times 2 \times 1$	36
$\text{Li}_2\text{O}$	[32]	0.4628 (0.65)	0.4628 (0.65)	0.4628 (0.64)	90 (0)	90 (0)	90 (0)	$4 \times 4 \times 4$	12
$\text{Na}_2\text{O}$	[32]	0.555 (1.24)	0.555 (1.24)	0.555 (1.24)	90 (0)	90 (0)	90 (0)	$4 \times 4 \times 4$	12
$\text{K}_2\text{O}$	[32]	0.6436 (0.74)	0.6436 (0.74)	0.6436 (0.74)	90 (0)	90 (0)	90 (0)	$2 \times 2 \times 2$	12

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