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Molecular dynamics simulation of oxides with ionic–covalent bonds

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Abstract

A "semi-classical" method was developed for molecular dynamics simulation of a system with ionic–covalent bonds like silica. The ionic charges were calculated by minimization of the potential energy on each step of molecular dynamics simulation. Ionic–covalent potential was used in modeling of SiO_2 molecule, non-crystalline silica, and calcium metasilicate. The internal energy of a system includes energies of silicon ionization, affinity of oxygen to electrons, Coulomb interactions and repulsion of ions, and covalent Si–O energy. Calculated properties of glassy and liquid silica and SiO_2 molecule, such as density, internal energy, compressibility, distances between ions and vibration frequencies, are close to experimental values. Published by Elsevier Science B.V.

Keywords: Molecular dynamics; Simulation; Oxide; Ionic–covalent bonds; Thermodynamic properties; Structure

1. Introduction

On the basis of Pauling's electronegativity (ε), oxides can be characterized as systems with mixed, or ionic–covalent bonds. The larger difference between the electronegativity of an element forming oxide and the oxygen electronegativity, the higher contribution of ionic bond, and vice versa, oxides formed by elements with a relatively small difference in electronegativity with oxygen, are characterized as predominantly covalent oxides. Thus, difference in electronegativities of calcium ($\varepsilon_{Ca} = 1.0$) and oxygen ($\varepsilon_O = 3.5$) is 2.5. On this basis, CaO is considered as a basic oxide with 78% of ionic bonds. The electronegativity difference for oxygen and silicon ($\varepsilon_{Si} = 1.8$) atoms is equal to 1.7. Ionic bonds in silica are assigned only 51%. However, computer simulation of systems with mixed ionic–covalent bonds is a difficult problem due to constructing of adequate potentials and determination of electrons distribution between ions and bonding orbitals. Because of this, the simulation is conducted either in a pure ionic mode when an ionic charge of an element is taken in accordance with its valency, or in a pure covalent mode with a combination of pair and three-particle potentials. For oxides, including silica, the pure ionic approach is generally used [1]. In this case, the silicon charge is +4, and oxygen charge is −2. The Born-Mayer potential (Eq. (1)) is often used to describe interactions between ions.

In the pure covalent mode, the potential is generally includes two terms, which describe a direct interaction

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between two particles, and a three-particle interactions (Eq. (2)). The pair interaction in the potential is described by the Lennard-Jones, Morse or more sophisticated potentials; three-particle interactions are described by Keating, Stillinger-Weber, Aksilrod-Teller and other potentials [2]. This causes the necessity to introduce a number of adjustable parameters into the three-particle potential. The three-particle interactions are short acting.

In this paper, ionic–covalent nature of bonds is introduced by considering an effective charge of an ion in the molecular dynamics (MD) modeling of oxides. This approach is discussed in application to glassy and liquid silica, SiO_2 molecule, and liquid calcium silicates.

2. The choice of potentials for silica

In the case of pure ionic interactions, pair potentials in silica can be taken in the simple form of the Born-Mayer potential:

$$u_{ij}(r) = Z_i Z_j e^2/r + B_{ij}\exp(-r/R_{ij}), \tag{1}$$

where Z_i is the electric charge of the ith ion in units of the electron charge e, $Z_{Si} = +4, Z_O = -2$; B_{ij} and R_{ij} are the ionic cores repulsion parameters for ith and jth ions. The R_{ij} values can be taken 0.29 for all pairs [1,3]. In work [3], parameter B_{Si-Si} was equal to 2055.4 eV and $B_{Si-O} = 1729.5$ eV. Parameter B_{O-O} was taken to be equal to 1500.0 eV for silica and other oxides [1,4]. At these parameters, the density of molecular dynamics models was close to the experimental value, and the Si–O distance was equal to the value of 1.61 Å determined in structure studies [5,6].

In the case of pure covalent interactions, the potential energy of a system can be presented in the following form

$$U = \sum_{i<j} V_2(r_{ij}) + \sum_{i,j,k} V_3(r_{ij}, r_{ik}, r_{jk}) \tag{2}$$

were $V_2(r_{ij})$ is a potential of the direct i–j pair interaction, $V_3(r_{ij}, r_{ik}, r_{jk})$ is a three-particle term which depends not only on distances between ions, but also on angles in the triangle formed by i, j and k ions. Pair interactions can be described by Lennard-Jones, Morse or other potentials. The three-particle term includes such factors as $(\cos\theta_{jik} - \cos\theta^0_{jik})^2$, where $\cos\theta_{jik}$ and $\cos\theta^0_{jik}$ are the actual and equilibrium (109.5°) valence angles in the triangle j–i–k. This factor is essentially positive and describes the valence angles distortion energy. For silicon and germanium oxides particularly popular is the three-particle Stillinger-Weber potential [7]. In the modified form, this potential was used in simulation of amorphous silica in the MD model consisted of 41,472 particles [8].

Shortcoming of the pure ionic approximation to silica may be demonstrated in the simulation of models with different Born-Mayer potential parameters holding the Si–O distance near 1.61–1.63 Å. In these models, parameters B_{Si-O} and R_{Si-O} varied at constant $B_{Si-Si} = 2055.4$ eV, $B_{O-O} = 1500.0$ eV and $R_{Si-Si} = R_{O-O} = 0.29$ Å [1,3,4]. The results are shown in Table 1 for pure ionic models of the glass (246 ions in the basic cube) simulated at the experimental density 2.21 g/cm^3 and zero temperature using the continuous static relaxation (CSR) method. The

Table 1
Properties of pure ionic models of glassy SiO_2 at 0 K and density 2.21 g/cm^{3a}

Parameter, B_{Si-O} (eV)	Parameter, R_{Si-O} (Å)	Pressure (GPa)	U (kJ/mol)	U^* (kJ/mol)	R_1 (Å)		
					Si–Si	Si–O	O–O
1729.5	0.29	−0.92	−1238.3	−12488.3	3.16	1.61	2.45
2036.06	0.28	−1.62	−1327.1	−12577.2	3.17	1.62	2.45
2429.32	0.27	−2.32	−1416.6	−12666.6	3.17	1.61	2.45
2942.37	0.26	−2.77	−1506.6	−12756.7	3.15	1.62	2.45
3624.40	0.25	−3.35	−1598.4	−12848.4	3.16	1.62	2.42
4050.80	0.245	−3.66	−1643.2	−12893.2	3.16	1.62	2.44

[a] Potential energy, U is calculated with respect to free neutral atoms; potential energy, U^* is calculated with respect to free ions Si^{4+} and O^{2-}; $B_{Si-Si} = 2055.4$ eV; $B_{O-O} = 1500.0$ eV.

discrepancy with experiment is particular visible when the properties are calculated relatively free neutral atoms. It can be seen that models have either too low values of total energy, U relatively the experimental energy -1840.2 kJ/mole, or too large negative pressures, p. The compressibility module at 0 K is 129 and 132 GPa for the models with $B_{\mathrm{Si-O}} = 1729.5$ and 3624.4 eV what is much higher than the experimental value.

Bonds in real oxides are never pure ionic nor pure covalent, what is reflected in a partial transfer of the charge from one ion to another. Thus, silicon in silica does not have a charge equal exactly to $+4$, and the oxygen charge is not equal to -2. This means that potentials in silica have to include both Coulomb and covalent interactions. Moreover, ionic charges may depend on distance between ions. Therefore, in simulation of oxides with ionic–covalent bonds, ionic charges have to be calculated in the self-consistent manner at every simulation step, like in the ab initio simulation.

In this work, oxides with mixed ionic–covalent bonds were modeled using a "semi-classical" method. The potential energy of an oxide includes Coulomb and repulsion energies of ions, and covalent energy. Ions were considered as having variable charges. The ionic charges were calculated by minimization of the potential energy on each step of MD or CSR simulation. MD modeling of silica in a pure ionic bonds approximation showed [1,3,9] that this approximation gives correct O–Si–O and Si–O–Si angle distributions. On this basis, three-particle interactions which include valence angles can be neglected, what simplifies calculation of the covalent energy of a system.

The following procedure was employed to calculate the oxide energy, say calcium silicate, formed from silicon, oxygen and calcium atoms.

1. Valence electrons from free Ca and Si atoms are partly transferred to O atoms. Calcium, silicon and oxygen ions have charges which are generally different from their valencies, although the calcium charge can be assumed to be $+2$, and, therefore, Ca–O bonds can be considered as pure ionic.
2. Free ions having constant charges form a condensed system or stable molecules.

The energy of such a system includes ionization potentials of Ca and Si, affinity of oxygen to electrons, Coulomb interaction of charges, repulsion of ionic cores and covalent energy of Si–O bonds.

Coulomb energy of a system in the basic cube with periodic boundary conditions can be calculated by Ewald-Hansen method [4,10]. To calculate the covalent energy we must know the number of electrons, q_{ij} located on the bond between neighbors i and j. Then, the total potential energy of a system is calculated as:

$$\begin{aligned} U = \sum E_{\mathrm{trans}}(Z_i) + \sum_{i<j} \frac{Z_i Z_j e^2}{r} \\ + \sum B_{ij} \exp(-r/R_{ij})\, \psi(Z_i, Z_j) \\ + \sum_n f_{\mathrm{c}}(r_n) \varphi_{\mathrm{c}}(q_n) \end{aligned} \tag{3}$$

The first sum in RHS is the energy of converting of free atoms in free ions with charges Z_i. It is equal to the sum of ionization energy of Ca atoms to Ca^{+2}, Si atoms to ions with charges $Z(\mathrm{Si})$ and affinity energies of O atoms to Z(O) electrons. The second sum is the Coulomb energy of the system and can by calculated by the Ewald-Hansen method. The third sum is the repulsion energy of ion cores (see the second term in RHS of the Born-Mayer potential (1)). The factor $\psi(Z_i, Z_j)$ is introduced to take into account the change in the effective ion radius with its charge. The last sum in RHS is the covalent energy. Covalent interactions are considered along all n covalent bonds; they depend on a distance, r between ions, and number, q of electrons localized on the bond.

It is suggested that electrons are distributed between ions and valence bonds in such a way, that total energy of a system in a given state is at minimum (variational principle). Forces acting on a particle are found by differentiating the energy of a system with respect to coordinates of the given particle. In the differentiation of Eq. (3), the derivatives of ion charges and a number of bonding electrons, q appear. However, if q value minimizes the total energy, these derivatives and forces related to the change of Z_i and q with distance will be zero.

Charge transfer energies $E_{\mathrm{trans}}(Z_i)$ for intermediate values of charges, Z_i were calculated by interpolation of experimental data on ionization potentials (cumulative) of Si atom to states Si^{Z+} with $Z = 1$–4 [11].

This interpolation has the following form:

$$E_{\text{trans}}(Z_{\text{Si}}) = Z(10.6246 - 6.95938Z + 5.08292Z^2 - 0.599125Z^3)\,\text{eV} \tag{4}$$

Similarly was obtained the affinity energy of oxygen for Z electrons, using data [11] on the oxygen affinity for one and two electrons (2.33 and -6.76 eV, respectively). This energy as a function of Z can be approximated either by Eq. (5) or Eq. (6):

$$E_{\text{trans}}(Z_{\text{O}}) = 3.14571Z + 0.81571Z^4 \tag{5}$$

$$E_{\text{trans}}(Z_{\text{O}}) = 8.04Z + 5.71Z^2 \tag{6}$$

Affinity energy calculated by Eq. (5) is more close to the linear function in the interval $-1 < Z < 0$, than energy described by Eq. (6), and will be used in the MD modeling.

It was noticed above that repulsion of atomic cores, and therefore, a distance between ions depends on the ionic charges. Indeed, for example, the sum of ionic radii of Si^{4+} and O^{2-} is $0.39 + 1.36 = 1.75$ Å, while the distance in SiO molecule is 1.51 Å. This difference in distances may cause a visible difference in repulsion and covalent energies. This is taken into account by introducing functions $\psi(Z_i, Z_j)$, $f_c(r)$ and $\varphi_c(q)$ in Eq. (3), which are described by Eqs. (7)–(9):

$$\psi(Z_i, Z_j) = 1 - \beta(1 - Z_iZ_j/Z_{i0}Z_{j0}),$$

$$f_c(r) = \varepsilon\{\exp[-2\alpha(r/r_c - 1)] - 2\exp[-\alpha(r/r_c - 1)]\} \tag{8}$$

$$\varphi_c(q) = q(1 - \gamma q), \tag{9}$$

where Z_{i0} is the ionic charge, which equal to the valency of i (+4 for Si and -2 for O). In the approximation of pure ionic bonds, $Z_i = Z_{i0}$ and $\psi(Z_i, Z_j) = 1$. In the approximation of pure covalent bonds $Z_i = 0$ and $\psi(Z_i, Z_j) = 1 - \beta$. Therefore, the parameter, β is related to the change in the distance between ions caused by covalent bond formation. It was found by trials and errors method to be equal to 0.2. Parameter, ε in the Morse potential (8) is the energy of the covalent bond with respect to one bonding electron, r_c is the bond length. Parameters, ε, r_c, β and γ were found from the analysis of simple and double Si–O bonds. Parameter, α characterizes the stiffness of the bond and can be determined using the vibration spectra.

In this work, potentials which describe both, free SiO_2 molecules and amorphous (liquid) silica were constructed using the following experimental data:

- dissociation energy of SiO molecule in gaseous phase, 7.2 eV [11];
- bond length Si–O in the molecule, 1.51 Å [11];
- vibration frequency, 37.23 THz [11];
- standard formation energy of glassy silica at 298 K, -901.4 kJ/mol [12];
- density of glassy silica at 298 K, 2.21 g/cm^3 [12];
- atomization energy of glassy SiO_2, 1840 kJ/mol;
- module of compressibility, 47.6 GPa;
- Si–O distance in the glass, 1.61 Å [6,13];
- compressibility of liquid silica, 0.067/GPa (for pure ionic model at 300 K the compressibility was calculated by MD method equal 0.128/GPa [3]).

To illustrate how parameters in Eq. (7)–(9) were assessed using these data, let us consider molecule SiO and crystal SiO_2. Considering bonds in SiO as double and pure covalent we obtain the bond energy per electron equal to $7.2/4 = 1.8$ eV. On other hand, the standard atomization energy of crystal SiO_2 is equal to 1849.5 kJ/mol. It consists of negative heat of formation of α-quartz (910.7 kJ/mol), sublimation energy of Si (445.2 kJ/mol) and dissociation energy of O_2 molecule (493.57 kJ/mol O_2) [12]. For glassy silica atomization energy is equal to 1840.2 kJ/mol. Would α-quartz be the oxide with purely covalent bonds, the energy of one bond will be equal to 4.792 eV, and therefore, the bond energy per electron will be $4.792/2 = 2.396$ eV/el. This value is 33% higher than in SiO molecule. Such values of energy for simple (two electrons) and double (four electrons) bonds may be obtained using parameters $\varepsilon = 3.00$ eV and $\gamma = 0.100$ in the Morse potential, Eq. (8) and in the $\varphi_c(q)$ function, Eq. (9). These values are very approximate and can be corrected by direct MD simulation.

As is was shown above, correct values of energy, density and inter-atomic distance could not be obtained in the approximation of pure ionic or pure covalent bonds. The energy of the model with ionic–covalent bonds must be lower than the pure ionic energy at the same density (variational principle). However, in construction of a model with mixed ionic–covalent bonds, the covalent energy should not be too low in comparison with ionic energy.

Otherwise, the fraction of ionic bonds will be negligible. Contribution of ionic bonds to the total potential energy of silica can be varied by varying $B_{\text{Si–O}}$ and $R_{\text{Si–O}}$ parameters. The potential energy of silica calculated in approximation of pure ionic bonds [3,4] with the use of parameters $B_{\text{Si-O}} = 1729.5$ eV, $R_{\text{Si-O}} = 0.29$ Å equal at 0 K to -1238.3 kJ/mol (relatively free atoms) was much higher than the experimental value of -1840.2 kJ/mol (See Table 1). To adjust the calculated values of the internal energy and density of silica to experimental data, the values of $B_{\text{Si–O}}$ and $R_{\text{Si–O}}$ parameters were taken to be equal $B_{\text{Si-O}} = 3482.30$ eV and $R_{12} = 0.25$ Å. These parameters were found by the trials and errors method.

3. Simulation of non-crystalline silica using MD and CSR methods

In accordance with a procedure described in the previous section, on each simulation step the ionic charges were calculated by minimizing the total energy of oxide at given ions coordinates (adiabatic approximation). The calculation was conducted as follows:

1. about 250–500 ions (for silica 246 or 498) were confined into the basic cube with such edge length that the density of the model was equal to the experimental value;
2. the nearest neighbors of each silicon atom and possible valence bonds Si–O were recorded using the subroutine NEIGHBOR;
3. distances between all pairs of ions were calculated using the subroutine DISTANCE;
4. initial state of silica was either pure ionic model with $Z_{\text{Si}} = 4$, $Z_{\text{O}} = -2$, and $q = 0$ or pure covalent model with zero charges of all ions. This state was simulated using the subroutine SEED;
5. using Eqs. (3)–(5) and (7), a number of bonding electrons on each Si–O bond was calculated by the iteration method at each step of MD simulation (subroutine CHARGES). At these values of bonding electrons the total energy, U of the system was at minimum. If starting with a pure covalent model O=Si=O in which the number of covalent bonds is four, the number of bonding electrons on given bond decreased by Δ, then the oxygen ion charge was decreased by $\Delta/2$, and the silicon charge increased by $\Delta/2$. The limiting state is the pure ionic $O^{2-}Si^{4+}O^{2-}$ model. The number of bonding electrons on all bonds was calculated in the self-consistent manner. It took about 10 iterations for each bond to achieve the equilibrium distribution of bonding electrons. As the result the computing time goes up comparing with the pure ionic model;
6. forces acting on ions were calculated using the subroutine FORCES. They include Coulomb forces, repulsive forces between ion cores and covalent forces;
7. new coordinates of ions were calculated by molecular dynamics (L. Verlet) or continuous static relaxation algorithm;
8. the new list of nearest neighbors Si–O was recorded using the subroutine NEIGHBOR;
9. the new distances between atoms were calculated using the subroutine DISTANCES;
10. return to stage 5, etc.

Calculated ionic charges were slightly different for different initial states of a model in the subroutine SEED. This difference was due to a local energy minimums, which oppose to the free charge transfer between ions. Different initial states were tested to choose such of them, at which the total energy could be minimized. The ionic charges change continuously in the simulation process. Therefore, a displacement of particles in the MD experiment (stage 7) must be sufficiently small to minimize its effect on equilibrium charge distribution.

In the modeling of silica with ionic–covalent bonds, the initial state was the pure ionic model with 246 ions (82 silicon ions and 164 oxygen ions in the basic cube with the edge length 15.56 Å). Parameters of the potential Eq. (3) were as follows: $B_{\text{Si-Si}} = 2055.4$ eV, $B_{\text{Si-O}} = 3482.30$ eV, $B_{\text{O-O}} = 1500.0$ eV, $R_{\text{Si-Si}} = R_{\text{O-O}} = 0.29$ Å, $R_{\text{Si-O}} = 0.2489$ Å, $\varepsilon = 3.90$ eV, $r_c = 1.440$ Å, $\alpha = 3.500$, $\beta = 0.20$, $\gamma = 0.065$.

Results of simulation of silica with ionic–covalent bonds at 0 K obtained by the CSR method are shown in Table 2 in comparison with the pure ionic model and experimental data [12,13]. Calculated energy of ionic–covalent silica (with respect to free atoms) differs from experimental data only by 1.3%. Charges of silicon and oxygen ions were found to be 3.63 and

Table 2
Properties of models of non-crystalline SiO_2 at 0 K (246 particles in basic cube with the edge length 15.56 Å or 498 particles in cube with the edge length, 19.674 Å; density, 2.21 g/cm^3; temperature, 0 K)[a]

Property	Bond character			Experiment
	Ionic–covalent		Pure ionic at $B_{Si–O} = 1729.5$ eV	
	$N = 246$	$N = 498$		
p, GPa	−0.02	0.016	−0.92	∼0
U, kJ/mol	−1816.2	−1858.6	−1238.3	−1840.2
U^*, kJ/mol	−13066	−13109	−12488.3	
U_{Coul}, kJ/mol	−12588	−12588	−15232.7	
U_{rep}, kJ/mol	1952.1	1953.0	2244.2	
U_{cov}, kJ/mol	−215.0	−221.5	–	
U_{trans}, kJ/mol	9034.2	8996.8	11250.0	
K, GPa	107	70.8	132	47.6 (300 K)
Z_{si}	3.63 ± 0.51	3.62 ± 0.48	4.00	
Z_O	−1.81 ± 0.19	−1.81 ± 0.18	−2	
$\langle q \rangle$	0.374	0.374	–	
r_1 (Si–O), Å	1.61	1.61	1.61	1.616
r_1 (Si–Si), Å	3.15	3.15	3.16	3.099
r_1(O–O), A	2.55	2.57	2.45	2.637
θ (O–Si–O)	109.2 ± 14.6°	108.8 ± 14.0	108.8 ± 15.9°	109.5
θ (Si–O–Si)	155.0 ± 14.4°	152.7 ± 17.9	153.8 ± 17.8°	144–150°
ρ_1	0.885	0.891	0.882	0.900

[a] Note: potential energy, U is calculated with respect to free neutral atoms; potential energy U^* is calculated with respect to free ions Si^{4+} and O^{2-}; K is compressibility module.

−1.81, respectively. This means that the silica model is predominantly ionic, what can be attributed to strong Coulomb interactions between silicon and oxygen ions in the condensed phase. For the pure ionic model with $B_{Si-O} = 1729.5$ eV, the difference between the calculated and experimental atomization energies achieves 33%. The model with pure ionic bonds has higher internal energy than the model with ionic–covalent bonds by 578 kJ/mol and negative pressure. The normal density of this model is higher than the experimental value.

Distances between ions and valence angles for models are shown in Table 2 in comparison with experimental data for the glassy silica at 300 K [13]. The angle distributions in both models are close to the experimental data. The Si–O distance in the model with ionic–covalent bonds agrees well with the experimental value, but the distance between oxygen ions is shorter by 0.07 Å. It should be noticed that this distance is measured in diffraction experiments with low accuracy, because O–O pairs have small statistical weight and do not create the distinct peak in the total pair correlation function (see [6]). This also concerns the measurement of the Si–Si distance.

The compressibility module, K was calculated using data on the model volume as a function of pressure. The compressibility module of the model with ionic–covalent bonds was found to be 107 GPa, what is 2.2 times the experimental compressibility module at 300 K. The module of the model with pure ionic model is higher than the experimental one by factor 2.8. Therefore, the model with ionic–covalent bonds gives slightly better results on the compressibility module than the pure ionic model.

Silica models with ionic–covalent bonds were also constructed with 498 particles in the basic cube at 0 K using continuous static relaxation method. Calculated properties of these models are shown in Table 2. Increase in the model size improves results of calculation in comparison with experimental data for energy and particularly for compressibility module. The structure and ion charges change very little.

The structure of a non-crystalline system can be characterized by the topological parameter, ρ_1 which is determined by Eq. (10) [15]:

$$\rho_1 = \sum X_i X_j r_1(ij)/(V/N)^{1/3}, \tag{10}$$

where X_i is atomic fraction of particles i, $r_1(ij)$ the coordinate of the first peak of the partial pair correlation function for the ij pair, V/N the volume per one particle. Systems with dense non-crystalline structures (liquid and amorphous metals) have $\rho_1 = 1.08 \pm 0.02$, while for systems with loose structures $\rho_1 < 1.05$. Results obtained for both models show (Table 2) that silica models have the loose structure.

The potentials established above for systems with ionic–covalent interactions were also applied for MD simulation of glassy and liquid silica at 300 and 2000 K, using the L. Verlet algorithm. The results of calculations for models with 246 ions are shown in Table 3 in comparison with experimental data for the glassy silica at 300 K. It is seen that the structure of ionic–covalent models agrees well with experimental results and changes little with temperature. It was very difficult to evaluate the compressibility modules of models due to strong pressure fluctuations and a long equilibration time. Roughly, the compressibility module at 2000 K was assessed to be 34 GPa.

To examine the effect of model size on its properties, models of liquid silica at 2000 K were constructed with 246 and 498 particles in the basic cube. At $N = 498$ the energy was found to be -1711.0 kJ/mol, what is by 1.2% lower than the energy -1690.5 kJ/mol of the model with 246 particles. The charge of the silicon ion in the larger model was 3.59 ± 0.52, while in the model with 246 ions it was 3.39 ± 0.61. Therefore, the growth of model in size leads to some increase in the ionic bond contribution. However, it does not have a visible effect on results of calculation of properties of silica.

4. Simulation of isolated SiO_2 molecule

SiO_2 molecule was isolated in the basic cube with a rather large edge length (20 Å) to neglect interactions with molecules in neighboring cubes. Models with ionic–covalent and pure ionic bonds were constructed using the procedure described above. The binding energy for the model with ionic–covalent bonds was found to be dependent on the choice of the initial state. When the initial state was the model with pure ionic bonds (with charge +4 for silicon ion and −2 for oxygen ion) the equilibrium binding energy was

Table 3
Properties of ionic–covalent models of glassy and liquid SiO_2 at temperatures 300 and 2000 K and density 2.21 g/cm^3 [a]

Property	300 K	2000 K	Experiment 300 K
p, GPa	0.53 ± 0.05	1.12 ± 0.95	~0
H, kJ/mol	−1822.8	−1690.5	−1829 [11,13]
U, kJ/mol	−1834.0	−1765.3	−1840 [11,13]
U^*, kJ/mol	−13084.1	−13015.3	−13090
U_{Coul}, kJ/mol	−11789.9	−10760.8	
U_{rep}, kJ/mol	1850.3	1710.0	
U_{cov}, kJ/mol	−286.1	−358.5	
U_{trans}, kJ/mol	8391.6	7644.0	
K, GPa		~34	47.6
Z_{Si}	3.51 ± 0.56	3.34 ± 0.65	
Z_O	-1.76 ± 0.27	-1.67 ± 0.35	
R_1 (Si–Si), Å	3.15	3.17	3.1
R_1 (Si–O), Å	1.62	1.64	1.63
R_1 (O–O), Å	2.53	2.63	2.6
θ (O–Si–O)	109.1 ± 13.8°	108.9 ± 14.0°	109.5° [12]
θ (Si–O–Si)	153.0 ± 17.2°	151.5 ± 16.5°	147° [12]
ρ_1	0.884	0.906	?

[a] Total energy, H and potential energy, U are calculated with respect to free neutral atoms; potential energy, U^* is calculated with respect to free ions Si^{4+} and O^{2-}.

Table 4
Properties of models of SiO_2 molecule[a]

Property	Bond character	
	Ionic–covalent	Pure ionic
U, eV	−14.30	0.245
U^*, eV	−130.90	−116.36
U_{Coul}, eV	−34.20	−147.68
U_{rep}, eV	8.87	31.31
U_{cov}, eV	−11.35	
U_{trans}, eV	22.38	116.6
Z_{Si}	2.114	4.00
Z_O	−1.057	−2
q	1.886	
r_1 (Si–O), Å	1.60	1.36
r_1 (O–O), Å	3.20	2.72
ν, THz	38.7	47.7

[a] Potential energy, U is calculated with respect to free neutral atoms; potential energy, U^* is calculated with respect to free ions Si^{4+} and O^{2-}.

14.30 eV. When the model with pure covalent bonds was chosen as the initial state, the binding energy after a relaxation was 12.04 eV. The model with pure ionic bonds was used as the initial state in the simulation of SiO_2 molecule. Results of modeling are shown in Table 4. It is remarkable that the calculated frequency of longitudinal vibrations of the Si–O bond in the model with ionic–covalent bonds (38.7 THz) is almost equal to experimentally determined frequency in SiO molecule (37.23 THz).

The oxygen charge is very close to -1 (the simple valence bond). The fraction of ionic bonds in the molecule is 0.53, what coincides with Pauling value 0.51.

In the SiO_2 molecule with pure ionic bonds, the equilibrium molecule length (the O–O distance of 2.72 Å) is shorter than in the model with ionic–covalent bonds (3.20 Å, see Table 4) and the frequency of longitudinal vibrations is higher. The SiO_2 model with pure ionic bonds has higher energy than the model with ionic–covalent bonds. Moreover, it dissociates to free atoms with the dissociation energy of 0.245 eV.

5. Simulation of non-crystalline metasilicate $CaO{\cdot}SiO_2$

Models of non-crystalline metasilicate with 255 particles in the basic cube were constructed at

Table 5
Properties of models of non-crystalline $CaO{\cdot}SiO_2$ at 1873 K (density 2.48 g/cm^3; 255 particles in basic cube with edge length 15.815 Å)[a]

Property	Bond character		Experiment
	Ionic–covalent	Pure ionic	
p, GPa	0.02 ± 0.58	0.38 ± 0.89	~0
U, kJ/mol	−1439.2	−1417.2	−1429.4
U^*, kJ/mol	−8257.8	−8235.8	
U_{Coul}, kJ/mol	−9101.2	−9650.9	
U_{rep}, kJ/mol	1317.6	1415.0	
U_{cov}, kJ/mol	−14.0	–	
U_{trans}, kJ/mol	6358.3	6818.6	
Z_{Si}	3.86 ± 0.37	4.00	
Z_O	−1.95 ± 0.11	−2	
r_1 (Si–Si), Å	3.17	3.18	3.23 [16]
r_1 (Si–O), Å	1.60	1.59	1.62 [16]
r_1 (O–O), Å	2.57	2.56	2.66 [16]
r_1 (Ca–O), Å	2.31	2.31	2.41 [16]
r_1 (Ca–Si), Å	3.42	3.44	
r_1 (Ca–Ca), Å	3.42	3.59	
θ (O–Si–O)	108.5 ± 15.6°	108.9 ± 14.9°	
θ (Si–O–Si)	151.0 ± 14.3°	154.8 ± 12.3°	
ρ_1	0.961	0.983	

[a] Potential energy, U is calculated with respect to free neutral atoms; potential energy, U^* is calculated with respect to free ions Si^{4+} and O^{2-}.

Table 6
Coordination numbers distribution in models of non-crystalline $CaO{\cdot}SiO_2$ at 1973 K (density, 2.61 g/cm^3; 255 particles in the basic cube with the edge length 15.56 Å)

Ion pairs	Number of ions with Z neighbors							
	$Z = 0$	1	2	3	4	5	6	7
Ionic–covalent bonds								
O around Si	–	–	–	–	41	10	–	–
Si around O	4	84	65	–	–	–	–	–
Pure ionic bonds								
O around Si	–	–	–	–	43	8	–	–
Si around O	4	86	63	–	–	–	–	–

1873 K. The algorithm accounted for the influence of ion charges on the interaction parameters for Ca–Si and Ca–O core repulsion. Therefore, Eqs. (3) and (7) were used for all ion pairs in calculations.

Parameters, ε and r_c in Eq. (3) were adjusted to fit the calculated energy of metasilicate formation from oxides CaO and SiO_2 to its experimental value equal about -40 kJ/mol at 1873 K [14]. This energy was obtained at $\varepsilon = 1.40$ eV and $r_c = 1.43$ Å.

The structure of models with ionic–covalent bonds changes very slowly with time what causes the hysteresis of density of the system. Generally, the pressure exhibited very strong fluctuations and depended on the model treatment (heating or cooling, expansion or contraction and so on). The models were examined in contraction and expansion processes to find the volume of the system at which the pressure was near zero.

Calcium metasilicate was modeled in the approximations of ionic–covalent and pure ionic bonds. Results of modeling are shown in Table 5. Si–O bonds are predominantly ionic, the fraction of ionic bonds is $3.86/4 \cong 0.96$, what is slightly higher than in pure silica (see above). The energy of the model with ionic–covalent bonds is closer to the experimental value than the energy of the model with pure ionic bonds.

Structure properties of models with ionic–covalent and ionic bonds are very close to one another. In Table 6, distributions of coordination numbers for ion pairs Si–O and O–Si are shown for models with ionic–covalent and pure ionic bonds. In both models, silicon atoms are predominantly surrounded by four oxygen atoms (41–43 silicon atoms out off 51 have four oxygen atoms in the first coordination sphere), and one or two silicon atoms are the closest neighbors of the oxygen atom. Type of bonds has very slight effect on structure properties of models of calcium metasilicate.

6. Conclusions

A model with ionic–covalent bonds is more adequate for computer simulation of silica and other oxides than a model with pure ionic bonds. Ionic–covalent potential suggested in this work was used in modeling of non-crystalline silica and SiO_2 molecule. Calculated properties of glassy and liquid silica and SiO_2 molecule, such as density, internal energy, compressibility, distances between ions and vibration frequencies, are close to experimental values.

This model was also applied for calcium metasilicate. Structure characteristics of the $CaO{\cdot}SiO_2$ model in the approximation of the ionic–covalent bonds and pure ionic model are rather close to one another, and are in a good accord with experimental data.

In non-crystalline silica and calcium metasilicate, ionic bonds dominate over covalent bonds, due to strong Coulomb interactions between silicon and oxygen ions in condensed phases.

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