

A. A. Raskovalov*The Institute of High-Temperature Electrochemistry,
Ural Branch of the Russian Academy of Sciences,
20 Akademicheskaya St., Yekaterinburg, 620137, Russian Federation
e-mail: other@e1.ru*

Simulation of borosilicate glasses with non-constant force field molecular dynamics

In this study the simulation of microscopical behavior of borosilicate glasses was conducted with non-constant force field molecular dynamics. The suggested model consists of classical pair potentials in the Buckingham form, long range Coulomb interaction, intramolecular bonded interactions and possibility of bond breaking and formation. The latter effects are accompanied by changes in the types of the bond-forming particles. The simulated system corresponds to the structure of borosilicate glasses with predominantly four-coordinated boron atoms. Different structure groups are formed due to the dissociation/formation of intramolecular bonds, and the processes of the glass network rearrangement intensifies with temperature increasing.

Keywords: molecular dynamics; non-constant force field; glass; borate; silicate.

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Introduction

Borosilicate glasses are materials with a wide range of applications. They can be used for nuclear waste utilization [1], as implants for tissue repair [2], in electrochemical devices as ionic conductors [3–5], as sealants for solid oxide fuel cells [6] and in many other areas of human activity. From this point of view, microscopical behavior of these glasses comes to researchers' attention. Glasses consisting of several network former oxides (B_2O_3 , SiO_2 , P_2O_5 and some others) can contain a colossal amount of possible structure groups and their combinations. For this reason numerical simulations of mixed glasses are very promoting because it can "view" glass structure at molecular level. To date, a molecular dynamics (MD) simula-

tion of silicate, borate and mixed borosilicate glasses was conducted in series of papers [1–5, 7–19]. Most of these works deal with classical MD, except researches [2, 17] performed with Car-Parinello (MD) [20] and reax force field [21] (ReaxFF), correspondingly. The Car-Parinello method brings quantum mechanical calculation into MD simulation. The ReaxFF is constructed to provide chemical reactivity during MD simulation. The last two methods are used to include effects of chemical bonds dissociation and recombination to the simulation. These effects are needed to be considered for correct simulation of glass behavior. To perform such calculations with classical MD is an ambiguous and complicated, if not impossible, task.

In the present paper I demonstrate how one can perform MD simulation of borosilicate glass with non-constant force field methodology. This approximation consists

Simulation details

MD simulations were performed with an original program written in C in canonical (NVT) ensemble. Newton's equations of motion were integrated by Velocity Verlet algorithm [22] with timestep of 0.5 fs during 100'000 steps. Equilibration time was 0.5 ps (1000 timesteps). Electrostatic interactions were accounted using the Ewald summation. Nosé-Hoover thermostat [23] with relaxation time of 0.02 ps was used for maintaining the temperature around desired temperature. There was tested three temperatures: 298, 500 and 1000 K. The considered system consists of 94 Si atoms, 80 B atoms, 429 O atoms and 242 alkaline metal (Me) atoms (the total number of particles is 845). The oxygen atoms were divided into bridging (O_c) and non-bridging (O_n) species. Bridging oxygen connects with two atoms of glass-forming element (Si/B) and non-bridging — with only one. Initial configuration of the system was generated with own special code. The box was cubic with the edge length of 20.4 Å to match an approximate density of glassy silicates. Van der Waals interactions in the system were given by Buckingham pair potential:

$$U_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}, \quad (1)$$

where U_{ij} is the potential energy between the i -th and the j -th atoms, r_{ij} is the distance between them, and A_{ij} , ρ_{ij} and C_{ij} are empirical parameters. Besides the Van der Waals short-range interactions, covalent bonds between oxygen and silicon/boron

of possibility of bond breaking and formation (including changing in particle types of bond forming atoms) runtime.

were set in the form of an intramolecular harmonic potential:

$$U_{ij} = \frac{k_{ij}}{2} (r_{ij} - r_{0ij})^2, \quad (2)$$

where k_{ij} is the spring constant and r_{0ij} is the equilibrium distance between particles. Unlike interactions provided by Eq. (1), this potential is applied only to covalent bonded pairs ($S-O_c$, $Si-O_c$, $B-O_t$ and $B-O_n$) listed separately. In addition, a three-body potential energy term was applied to maintain a feasible valent angle for $Si-O_c-Si$, $B-O_c-B$ and $Si-O_c-B$ bonds:

$$U_{ijk} = \frac{k_{tb}}{2} (\cos \theta_{ijk} - \cos \theta_0)^2, \quad (3)$$

where k_{tb} is the spring constant of the three-body potential, 100.0 eV, θ_{ijk} is the angle between ij and ik bonds, θ_0 is the equilibrium angle, 148.3° (taken from [15] for $Si-O-Si$ angle); i , j and k are the indexes of O_c atom and its covalent-bonded neighbors, correspondingly.

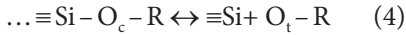
The values of A_{ij} , ρ_{ij} and C_{ij} were taken from papers [1, 11, 12, 15, 19]. Simulations were performed with different combination of these parameters. The more suitable for the glass structure description set of the parameters is summarized in Table 1 with corresponding references. The parameters of the valent bond potential (2) are given in Table 2. The atomic charges were suggested to be found as 4δ , 3δ , a , -2δ and $-\delta-a$ for Si, B, Me, O_c and O_n , correspondingly. The values of δ and a are set to 0.4e and 1.0e. Our MD program allows deleting

Table 1

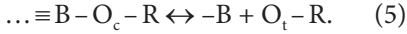
The Buckingham pair potential parameters used in this study

pair	A, eV	ρ , Å	C, eVÅ ⁶	Reference
Si – O _t /O _c	13702.905	0.193817	54.681	[19]
B – O _t /O _c	206941.81	0.124	35.0018	[19]
Me – O _t /O _c	4383.7555	0.243838	30.700	[5]
O _t /O _c – O _t /O _c	352.56	0.35	0	[1]
Si – B	337.584	0.29	0	[1]
Si – Me	861.744	0.29	0	[1]
Si – Si	836.16	0.29	0	[1]
B – B	121.056	0.29	0	[1]
Me – Me	9500.0	0.23	0	[12]

(adding) valent bonds from (to) the corresponding list to mimic processes of bonds dissociation and glass forming:



and



If the bonds automatically break (form) then the interatomic distance is higher (lower) than a maximal bond distance parameter (r_m). The values of this parameter are given in Table 2. The further dissocia-

tion with participation of Si⁺ or B⁺ species is not allowed. The charges of Si⁺ and B⁺ species are chosen to keep electroneutrality during reactions (4) and (5).

Table 2

Valent bonds parameters (including the maximal bond distance, r_m) used in this study

pair	k , eV	r_0 , Å	r_m , Å
Si – O _t	10 ⁻⁴	1.625	—
Si – O _c	10 ⁻⁴	1.650	2.0
B – O _t	10 ⁻⁵	1.400	—
B – O _c	10 ⁻⁵	1.430	1.9

Results and Discussion

The obtained structure of the system is presented in Fig. 1. One can see that the simulated glass consists of branchy chains of Si – O/B – O bonds which can form various combinations and loops. In principle, there are two possible boron coordinations in borate glasses, triangular and tetrahedral [24]. In our case almost all boron in the glass is four-coordinated, Fig. 1.

Radial distribution functions (RDFs) are presented in Fig. 2. All RDF-curves consist of one sharp and several broad maximums. This is typical of liquids or amorphous systems and indicates the

presence of the short-range and the absence of the long-range orders. There are no series of well-resolved maxima, specific for crystalline solids. The first maximum of RDF-curve corresponds to the most probable distance in the near-neighbor coordination. According to Fig 2(a), the distance between Me and O_t is less than that between Me and O_c. It can be explained by more negative charge of O_t species (Simulation Details section) and, therefore, stronger Coulomb interaction. RDFs almost do not depend on temperature, the differences are observed only for the RDFs

with the sharpest maxima, for example, Si–O. For these RDFs the value of the first maximum decreases with temperature increasing and the peak becomes broader, Fig. 2(b). This process occurs, most likely, due to the thermal motion. The first maximum for B–O_t/O_c and Si–O_t/O_c pairs locates at distance of 1.375–1.425 and 1.575–1.675 Å, correspondingly, which

is close to B–O и Si–O interatomic distances in borosilicate glasses [15].

As the system initially does not have crystalline lattice and a corresponding look of RDF-curves, it is necessary to find another criterion of transition between liquid and solid states. Such a criterion can be, for example, mean square displacement (MSD), which characterizes

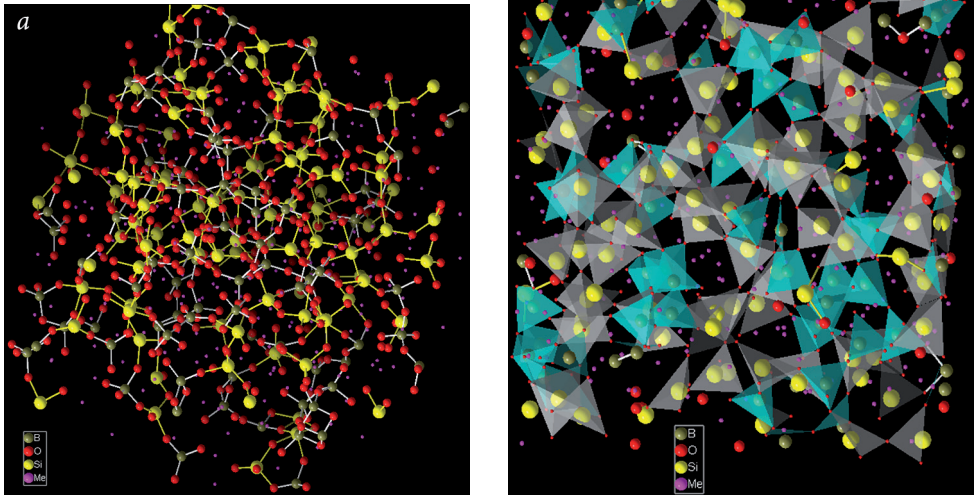


Fig. 1. The structure of the simulated system after 30'000 timesteps at 298 K in (a) stick-and-ball and (b) polyhedral representation. Blue polyhedra correspond to boron central atom, gray — to silicon

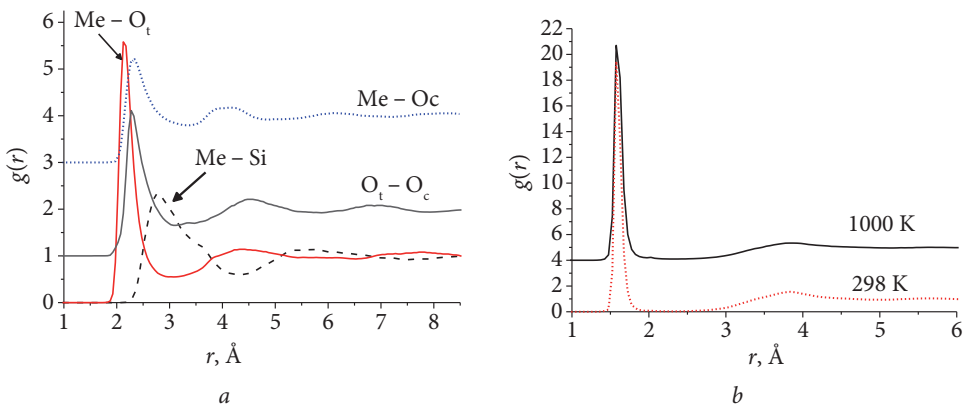


Fig. 2. Some radial distribution functions, $g(r)$ of the simulated glass: (a) for 298 K; (b) for pair Si – O_t at 298 and 1000 K

a mobility of ions. In the simulated borosilicate glass, MSDs of most ions tend to reach a plateau with some oscillation at temperature of 298 K, except one for Me ions increased linearly, Fig. 3(a). The time derivative of MSD grows with temperature increasing, Fig. 3(b). This means that all species start to diffuse and the system behavior becomes liquid-like. Analogous effects can be seen on trajectories of the ion motion. At temperature of 298 K most ions vibrate around one point (although with big enough amplitude), Fig. 4(a). An exception is the Me ion, its trajectory consists of a series of hops between positions

with long enough oscillation time. With temperature increasing, Me ion spends less time in one position, more often hops and covers greater distance, Fig. 4(b). Its movement character becomes more and more liquid-like.

Fig. 5 demonstrates the number of Si and B species as a function of time. The changes in these quantities are provided by dissociation of $B-O_c$ and $Si-O_c$ bonds according to equations (4) and (5). Since dissociation in the suggested model occurs upon reaching the determined distance (Table 2), the observed fluctuations of the particles numbers are related with

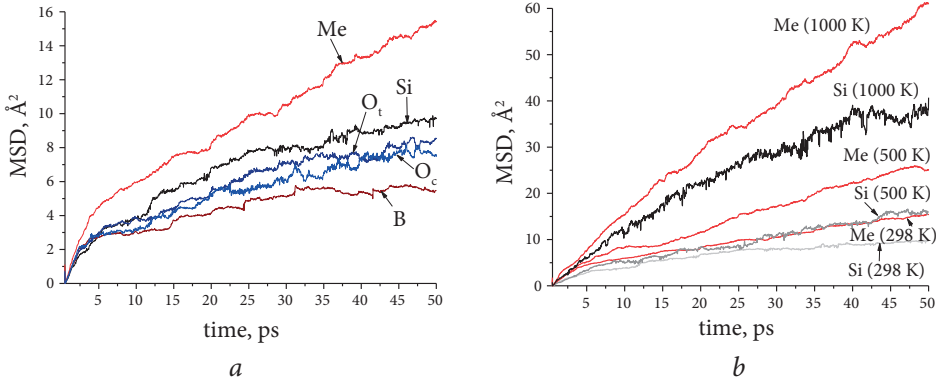


Fig. 3. The mean square displacement (MSD) of the simulated borosilicate glass: (a) for different ions at 298 K; (b) for Me and Si ions at different temperatures

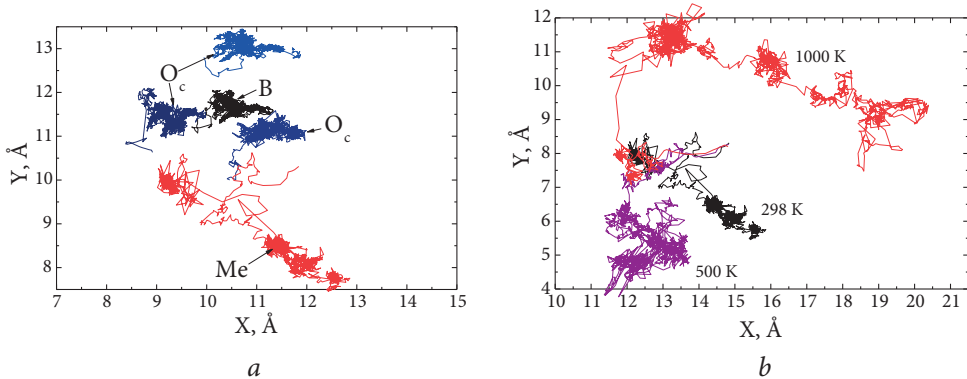


Fig. 4. Trajectories of motion in the simulated borosilicate glass for: (a) different ions at 298 K; (b) the same Me ion at different temperatures

changing in the B/Si–O_c distances. According to Fig. 5, the suggested pair potentials provide stronger B–O_c bonding, then Si–O_c one, as the amplitude of the Si number oscillation is bigger. Also, Fig. 5 demonstrates that the amplitudes of these oscillations increase with temperature. This is a result of thermal motion which promotes overcoming of forces of interatomic attraction, as noted above in the discussion of the radial distribution functions. The bonds breaking and formation realized by methodology of non-constant force field allow glass structure to be “dynamical,” i.e. to destroy ones atomic groups and to cre-

ate others. A variety of formed molecular groups can see in Fig. 1.

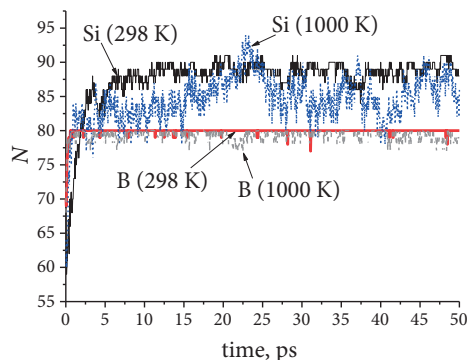


Fig. 5. The number of Si and B species as a function of simulation time

Conclusions

In the paper reference classic pair potentials have been tested for molecular dynamic simulation of borosilicate glasses. The suggested combination of the potentials and ionic charges describes interatomic distances in borosilicate glasses reasonably well. Oxygen atoms were divided into bridging and non-bridging by the

value of electrical charge. The transition between these states is possible due to bond formation/dissociation. These phenomena are implemented by non-constant force field molecular dynamics. It has been shown that the degree of the bond dissociation increases with temperature growth.

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