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Molecular dynamics of vitreous silica — Variations in potentials and simulation regimes

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ABSTRACT

Two potential sets, and three thermodynamic regimes were utilised in MD simulations to prepare the corresponding structures of vitreous silica. Standard structure descriptors as RDF's, angle distributions, and primitive ring distributions showed subtle differences among glasses. Structural defects as overcoordinations and dangling bonds revealed higher sensitivity to both used potential sets and TD conditions. Overcoordination is largely driven by the density while the amount of dangling bonds is given by the type of the potential. Connectivity that balances under- and over-coordination is determined rather by TD conditions than type of potential used. Ring distribution as well as radial distribution function of rings shows robustness to alternating conditions of simulation.

1. Introduction

Experimental knowledge of glass structure is still insufficient despite huge progress in the last decades. The key problem is i) available techniques are mostly constrained to description of nearest or second nearest (with a decreasing precision) neighbours, and ii) there is(are) no universal descriptor(s) enabling uniquely and unambiguously describe the structure. Direct information about glass structure is offered by NMR (Nuclear Magnetic Resonance), IRS (Infra Red Spectroscopy), RS (Raman Spectroscopy), EXAFS (Extended X-Ray Absorption Fine Structure), ND (Neutron Diffraction), XRD (X-Ray Diffraction), and some other techniques while indirect knowledge about structure is supplied by various atomic-based models. The second crux is rather the theoretical one. Translational periodicity of crystal solid has opened rich realm of consequences of material properties coming out from this symmetry. The enormous number of data needed to describe the position of every atom shrunk to knowledge of the positions of atoms in the elemental cell and three translational vectors. Similar structural homomorphism is lacking for non-crystalline solids. Therefore a few "standard structural descriptors" are used; among them radial distribution function, RDF, or more detailed partial pair distribution function, PP RDF, are mostly used. Nevertheless, RDFs are one-dimensional projection of the spatial distribution of atoms and therefore cannot adequately catch structural anisotropy of non-crystalline solid. On the other hand RDF is the most common experimental result; it yields coordination numbers and bond lengths — information of uppermost significance for chemistry. For silica glasses Q^n-units, tetrahedron formed by central silicon with four vertices determined by oxygen atoms, with *n* giving the number of bridging oxygen, BO, are natural structural units. Its distribution (e.g. RS, NMR) or connectivity (NMR) is experimentally attainable and provides complemental information. Nevertheless, in glass community it is believed that glass essence is coded in medium range order (MRO) [1]. Rings or loops (various terminologies and definitions are used) are candidates of proper descriptors of MRO. They provide not geometrical but topological picture of glass structure. Primitive rings [2] or minimal ring [3], introduced as a loop that cannot decomposed into two shorter loops or as a loop with no "short cut" are mostly used. Other definitions can be found, e.g. strong rings, very strong rings [4], and basic rings [5].

Molecular dynamics (MD), atomistic simulation method, mimics the behaviour of atomic motion under given thermodynamic restrictions. Preparation of glass in MD starts at very high temperature to enable perfect mixing of atoms (ions) and to reach thermodynamic equilibrium. Gradual decrease of temperature (step by step or continuous) causes solidification of the studied system with a structure close to the experimental glass. Using classical physics approach, interatomic (mostly two- and sometimes more-particle) potentials enter into Newton's equations of motions as given (e.g. from ab-initio calculations and/or from fitting of experimental data). Treatment of thousands of particles is expected to be able to eliminate periodic boundary conditions conventionally imposed upon MD calculations [6]. Time window, on the other hand, accessible for performing the computational cooling is of a few orders shorter than in reality resulting in a high transformation temperature obtained for the simulated glass. Even though it is questionable if it is a real glass transition what is observed during simulation [7] the final computer product is a solid with its structure strongly reminding real glass. The direct comparison of simulated and real

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glass is even impaired by the fact that glass properties depend on cooling rate for both computer [8,9] and real glass [10]. Hence, glass prepared by MD should be tagged by the cooling regime used.

The aim of the paper is to explore two different empirical potentials utilised for MD simulations of vitreous silica and to study the influence of various thermodynamical conditions on both the standard structural quantities as RDF, angle distribution, and ring distribution and not commonly presented structural defects.

2. MD simulation

Vitreous silica was simulated by classical MD using two sets of pairwise potentials, BKS [11] and CHIK [12] (designation of both potentials comes from the first letters of author's family names), both having the same functional form

$$E_{ij} = A_{ij}\exp(-B_{ij}r) - \frac{C}{r^6} + \frac{z_i z_j e^2}{4\pi\varepsilon_0}\frac{1}{r} \tag{1}$$

parameters of which are summarized in Table 1.

The first two terms in Eq. (1) describe short-range interaction while the last one corresponds to the electrostatic long-range Coulomb potential. The Coulombic part was evaluated by summing over atoms up to 12 Å in the real space and beyond this border it was treated by Ewald's method [13] in dual space. All calculations were performed in the simulation cube comprising 7,200 atoms (2400 Si and 4800 O) with periodic boundaries. DL_Poly simulation code was utilised [14]. For each potential set the system was constrained to three different thermodynamical boundaries: one run was performed under a constant pressure (NpE ensemble) and two runs under constant volume (NVE ensembles). NVE ensembles were adjusted to i) the experimental density of vitreous silica (2.20 g cm^{-3}), and to ii) the density of quartz (2.65 g cm^{-3}) [15]. The system with the latter density was prepared with idea that, first, BKS potential was adjusted to quartz data and, second, the previous experience has shown a significantly smaller amount of structural defects in potassium silicate glass at quartz density [16]. Glasses prepared under the abovementioned conditions will be hereafter designated with e (experimental density), q (quartz density), and p (ambient pressure).

All simulations started at 5000 K by mixing and equilibrating of the system during 25 ps. The cooling procedure consisted of 100° consecutive temperature steps; each step comprised at first the numeric control of the adjusted temperature (2500 time steps) followed by simulation obeying thermodynamic requirements (either constant volume or pressure) for the next 7500 time steps. The leap-frog algorithm was used for the numerical integration of Newton's equations of motion with an integration time step of 1 fs. Hence, the entire cooling procedure (down to 100 K) corresponds to the effective cooling rate of 10^{13} Ks^{-1}.

The snapshots of the simulated structures were analysed (150 structures at each temperature, i.e. 0.15 ps was the time interval between two snapshots and 7.5 ps structure evolution was recorded and analysed at each temperature) and the average quantities obtained from these snapshots are further presented. MD did not establish chemical bonds but they had to be determined indirectly by the distance criterion as follows: the bond between oxygen and silicon is established if $|\mathbf{r}_{Si} - \mathbf{r}_O| \le D$ ($D = 2.0$ Å) was used. If oxygen atom has one silicon atom within the sphere of radius D, it is considered as non-bridging (NBO), if two silicon atoms are within the sphere it is taken as bridging (BO), if more than two Si are inside the sphere, it is designated as overcoordinated (OO). At high temperatures free oxygen (FO) can be also identified as those with no Si within the sphere. Many of the bonds seem to be artificial and do not correspond to the real chemical bonds but they are rather a result of the temporary spatial packing. Therefore the following algorithm was used for the decomposition of 3-coordinated oxygen atoms. If OO is connected to at least one 5- or more- coordinated Si, the longest bond among those leading to the highest coordinated Si is removed. Remove of bond leading to the at least 5-coordinated Si (not to the 4- or less coordinated Si) is required so as the removal of the bond could not lead to the formation of the undercoordinated Si and therefore so as one type of structural defect would have not been replaced by another one. Below is the scheme, showing the result of the algorithm applied for OO with upperscripts $m \le l \le k$ displaying the corresponding coordination.

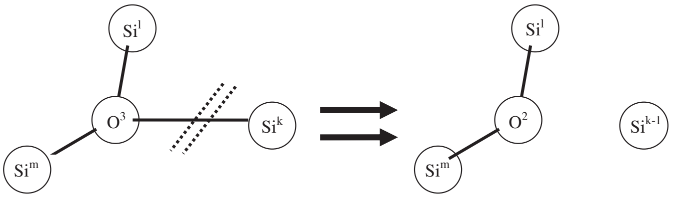

Table 1
Parameters of BKS and CHIK potential, see Eq. (1).

	BKS			CHIK		
	Si–Si	Si–O	O–O	Si–Si	Si–O	O–O
A	0	18,003.76	1388.77	3150.46	27,029.42	659.59
B	0	4.87	2.76	2.851	5.1586	2.59
C	0	133.54	175	626.75	148.1	26.84
z_{Si}	2.4			1.91		
z_O	−1.2			−0.955		

Of course, this algorithm eliminates not only the number of OO but proportionally decreases the number of overcoordinated Si.

Once bonds among atoms are established for simulated glass, distribution of Q-units, evaluation of structural defects, and primitive ring distributions were evaluated. To study spatial correlation of the rings, ring radial distribution function, RRDF, was introduced

$$RDFR(r) = \frac{1}{4\pi r^2 \rho}\frac{1}{N}\sum_{i,j}\delta(r-(r_i-r_j)) \tag{2}$$

where ρ is volume density of rings, N is the number of rings, and summation runs over positions of rings defined as

$$\mathbf{r} = \sum_{k=1}^{M}\mathbf{r}_k \tag{3}$$

where k runs over positions of (silicon) atoms forming the ring.

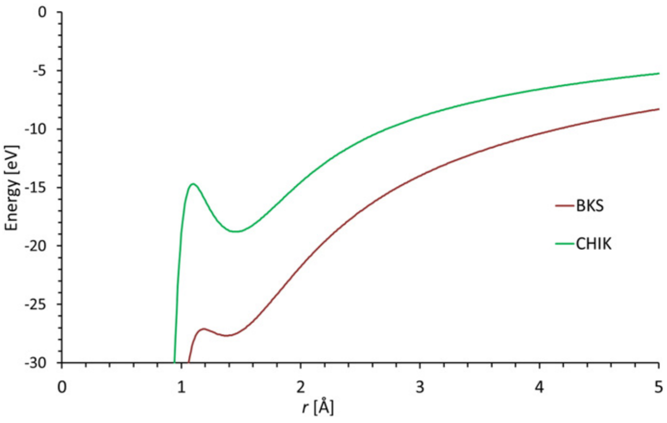

Fig. 1. Pair potential energy of Si–O for BKS (dark red) and CHIK (green) potential sets.