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Borosilicate glass potentials for radiation damage simulations

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ABSTRACT

Three borosilicate glass (SiO_2–B_2O_3) fixed charge potentials from the literature are compared (Delaye and Ghaleb, 1996; Kieu et al., 2011; Rushton, 2006) and their suitability for use in simulations of radiation damage is assessed.

For a range of densities, we generate glass structures by quenching at 5×10^{12} K/s using constant volume Molecular Dynamics. In each case, the bond lengths, mean bond angles, bulk modulus, melting point and displacement energy thresholds are calculated, and where possible compared to experimental data. Whereas the bond lengths and mean bond angles are reasonably well predicted, we find that the potentials predict melting temperatures, bulk moduli and densities that are higher than experimental data.

The displacement energy thresholds are generally lower than those for ionic crystalline materials, but show a wider spread of values. However, the barriers for atomic rearrangements, after atoms have been displaced in the equilibrium structures, are very high. This indicates, that the radiation damage produced in the ballistic phase of a collision cascade, is likely to persist for extended time scales. This is in contrast to crystals, where interstitials and vacancies can diffuse rapidly between successive radiation events.

1. Introduction

High-Level nuclear Wastes (HLW) from spent nuclear power station fuels and decommissioned nuclear weapons must be safely removed from the environment. One leading method of achieving this, is long term storage by immobilisation in glass waste forms prior to permanent disposal in a geologically stable repository [4,5]. A primary concern with this method, is that over long time-scales, the radioactive material could leach out of the glass and contaminate the environment. It is for this reason we must understand how glass responds to radiation damage over long time scales. In the early stages of waste encapsulation the material is heated due to β-decay, however, in this work it is the damage caused by α-decay that will be the main focus of the study.

Experiments on physical samples are limited to relatively short times (10 years), compared to geological time scales. Experiments are also carried out at higher dose rates, such as by using ion beams to simulate the collision cascade process. As a result, atomistic simulation methods can play an important role in the understanding of how these glasses behave after a radiation event. Although Molecular Dynamics (MD) simulations can only access very short times ($\sim$ 1 ns), kinetic Monte Carlo (kMC) simulation techniques can be used to access longer time scales.

In order to simulate the radiation event, it is necessary to have a good model of the amorphous glass structure. Amorphous materials are more difficult to handle computationally than crystals, since there is no equivalent concept of a vacancy or interstitial. In addition, although the structures have short range order, there are many different atomic configurations that are possible, so statistical averaging over different structures is very important. In addition, good inter-atomic potentials to describe these systems is essential.

In this work, we compare three inter-atomic potentials from the literature, and test their suitability for Molecular Dynamics (MD) simulations of radiation effects in borosilicate glass. We investigated two potentials from Delaye's group (Delaye1996 [1] and Kieu2011 [2]), and one potential from Rushton (Rushton2006 [3]). Only the potentials of Kieu were developed specifically for the simulation of large sets of compositions around the SiO_2–B_2O_3–Na_2O glass. The Delaye1996 potential was developed for simulating R7T7 glass, and the Rushton2006 potential was developed for Magnox glass.

The 'best' potential model for simulating borosilicate glass was then used to determine threshold displacement energies, and some typical energy barriers for atomic movement after such atomic displacements.

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2. Methodology

Computer simulations of borosilicate glass and sodium borosilicate glass were performed using MD. For borosilicate glass, the structures consisted of 70 mol% SiO_2 and 30 mol% B_2O_3. We refer to this glass as, BSi, in this paper.

For sodium borosilicate glass, we used the SBN12 blend which is described in Ref. [2]. This glass consists of 59.66 mol% SiO_2, 28.14 mol% B_2O_3 and 12.20 mol% Na_2O. We refer to this glass as, NaBSi, in this paper.

A brief overview of each inter-atomic potential that we have investigated, is given in Sections 2.1–2.3 below. These potentials are suitable for near equilibrium conditions and must be joined to a screened Coulomb potential for close particle separation. Our splining method is described in Section 2.4, and the method for generating glass structures is described in Section 2.5.

2.1. Delaye1996

The Delaye1996 potential [1] is used to model BSi glass. This potential contains both 2 and 3 body terms. The 2-body interaction is modelled by the Born–Mayer–Huggins potential. The potential energy, $\Phi(r_{ij})$, of two ions separated by r_{ij} is given by Eq. (1) below:

$$\Phi(r_{ij}) = A_{ij}\exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) + \frac{1}{4\pi\epsilon_0}\frac{z_i z_j}{r_{ij}} \tag{1}$$

where A_{ij}, and ρ_{ij} are parameters of the model and can be found in the original paper [1]. z_i and z_j are the ion charges. This potential uses full formal charges for each ion.

A Stillinger–Weber [6] 3-body term is applied to the O–Si–O and Si–O–Si bond angles. We choose not to put any restriction on the O–B–O bond angle as was done by Connelly [7]. The adjustable parameters are listed in the original paper [1] in Table 4.

Due to the inclusion of the 3-body terms, this potential is the most computationally intensive. The three body term also induces an extremely large penalty when the bond angles move away from their equilibrium values.

2.2. Kieu2011

The original paper by Kieu et al. [2], describes potentials for modelling both borosilicate (BSi) and sodium borosilicate (NaBSi) glass.

This potential contains only 2-body terms. A Buckingham pair potential (given by Eq. (2) below), is used to model these interactions.

$$\Phi(r_{ij}) = A_{ij}\exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) + \frac{1}{4\pi\epsilon_0}\frac{z_i z_j}{r_{ij}} - \frac{C_{ij}}{r_{ij}^6} \tag{2}$$

The adjustable parameters A_{ij}, ρ_{ij} and C_{ij} for each ion interaction are listed in the original paper [2]. The boron–oxygen interaction is a special case, where the parameter, A_{ij}, depends upon the composition of the glass. The ion charges (z_i and z_j), also depend upon the glass composition. This composition is characterised by the two molar ratios, $R = [Na_2O]/[B_2O_3]$ and $K = [SiO_2]/[B_2O_3]$.

Since the parameter values and charges depend upon the composition of the glass, we denote the potential used for BSi glass as Kieu2011_v1, and potential used for NaBSi glass as Kieu2011_v2.

2.2.1. Kieu2011_v1

For borosilicate glass (BSi), $R = 0$ and $K = 2.33$, and therefore, the charges obtained are close to the values used in the Guillot–Sator potential model [8]: $z_{Si} = 1.89, z_O = 0.945$ and $z_B = 1.4175$. We used these charges in the Kieu2011_v1 potential.

For the boron–oxygen interaction, $A_{ij} = 180390.53$ eV, $\rho_{ij} = 0.124$ Å and $C_{ij} = 35.0019$ eV Å^6.

2.2.2. Kieu2011_v2

For the sodium borosilicate glass that we studied (NaBSi), $R = 0.4335$ and $K = 2.12$. This is described as the SBN12 blend in the original paper. The ion charges were: $z_{Si} = 1.869128$, $z_O = -0.965872, z_B = 1.528756$ and $z_{Na} = 0.451628$. The parameter, A_{ij}, for the boron–oxygen bond, is 205751.1464 eV. The remaining parameters (ρ_{ij} and C_{ij}) are the same as before.

2.3. Rushton2006

The Rushton2006 potential [3,9] is used for modelling BSi glass, and also contains only 2-body potentials. In this case, a Lennard-Jones pair potential plus the Coulomb term (Eq. 3) is used to model the atomic interactions.

$$\Phi(r_{ij}) = \frac{\sqrt{A_i A_j}}{r_{ij}^{12}} - \frac{\sqrt{B_i B_j}}{r_{ij}^6} + \frac{1}{4\pi\epsilon_0}\frac{z_i z_j}{r_{ij}} \tag{3}$$

The parameters A and B for each ion are given in the original paper. z_i and z_j are the full formal charges for each ion.

2.4. Application to collision cascades

Some of these potentials tend to $-\infty$ at short range due to the electrostatic coulomb term ($z_i z_j / r_{ij}$) and the Buckingham term ($-C_{ij}/r_{ij}^6$). Therefore, the potential energy reaches a maximum value at short range, which can be as low as 150 eV (for a Si–O bond). Hence, during a radiation damage cascade, it becomes possible for some atoms to unnaturally fuse together. The short range interactions between atomic nuclei are more accurately modelled by the ZBL potential [10]. We therefore join these potentials to the ZBL potential at short range with a spline function given by Eq. (4).

$$F(r) = \exp\left(a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4 + a_5 r^5\right) \tag{4}$$

The constants a_0 – a_5 are set such that the potential energy and its first and second derivatives are continuous.

2.5. Modelling of glass formation

The glass structures are amorphous and have no long range order, therefore, we cannot simply generate a structure as we would for a crystal lattice. The procedure for generating a glass structure is to perform an MD simulation of a quench from a molten state.

Atoms are placed at random positions inside a cubic box, ensuring no two atoms are closer than 1 Å. Such a configuration has a large potential energy, and therefore a high initial temperature when simulated with MD, typically exceeding 10,000 K. At every time-step the temperature is controlled by rescaling the velocities of all the atoms. If the temperature exceeds the desired value by 7%, then the velocities are rescaled to the desired temperature. We equilibrate at 6000 K for 10 ps then quench at 5×10^{12} K/s to 50 K. The final minimisation to 0 K is obtained via conjugate gradient minimisation. A schematic of this process is shown in Fig. 1.

3. Results

3.1. Density

For each inter-atomic potential we performed a set of quenches using constant volume MD. We vary the volume to obtain sets of quenched glass structures at a range of different densities. Fig. 2 shows the plots of the average potential energy per atom as a