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A new potential for radiation studies of borosilicate glass

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ABSTRACT

Borosilicate glass containing 70 mol% SiO_2 and 30 mol% B_2O_3 is investigated theoretically using fixed charge potentials. An existing potential parameterisation for borosilicate glass is found to give good agreement for the bond angle and bond length distributions compared to experimental values but the optimal density is 30% higher than experiment. Therefore the potential parameters are refitted to give an optimal density of 2.1 g/cm^3, in line with experiment. To determine the optimal density, a series of random initial structures are quenched at a rate of 5×10^{12} K/s using constant volume molecular dynamics. An average of 10 such quenches is carried out for each fixed volume. For each quenched structure, the bond angles, bond lengths, mechanical properties and melting points are determined. The new parameterisation is found to give the density, bond angles, bond lengths and Young's modulus comparable with experimental data, however, the melting points and Poisson's ratio are higher than the reported experimental values. The displacement energy thresholds are computed to be similar to those determined with the earlier parameterisation, which is lower than those for ionic crystalline materials.

1. Introduction

Borosilicate glass is an important material with numerous applications. Particular importance in the nuclear context is its use in the confinement and storage of radioactive waste. Borosilicate glasses have been the most widely used material for the immobilisation of both HLW (High-Level Wastes) and LLW (Low-Level Wastes) [1,2]. In addition to their good chemical durability, mechanical integrity and thermal stability, borosilicate glasses are flexible with waste loadings and possess the capability of incorporating most of the waste elements. The process of incorporating HLW into borosilicate glasses is known as waste vitrification.

If HLW is incorporated into a glass, radiation damage can occur. The radioactive material has to be stored for many years, so computer simulation can be used to help predict the outcome. One way to model the radiation damage process is using classical molecular dynamics (MD). In order to study the effect of radiation on the glasses by MD it is necessary to have a model for the interaction potentials between the atoms in the system. Previous studies [3–5] have proposed interatomic potentials that model some aspects of borosilicate glass but other aspects are not modelled sufficiently well, in particular the density. In the potential proposed in Ref. [3] a three-body term is included, which helps produce the correct structure but is far too strong for use in cascade studies. The predicted density using this model is ≈ 1.8 g/cm^3. With the potential from Ref. [4], the density corresponding to the minimum energy structure is found to be 2.7 g/cm^3, which is almost 30% greater than the experimental value of around 2.1 g/cm^3. However other aspects of the model are in good agreement with experiment. After quenching, the model from Ref. [5] produced glasses with a density of 3.67 g/cm^3 [7].

The objective of this work is therefore to modify the parameters of the potential energy used in Ref. [4] in order to develop a model that generates glass structures with a density closer to the experimentally observed value of 2.1 g/cm^3. We optimise the parameters using both the GULP [6] code for small systems and our own MD code for large systems, by quenching a randomly distributed set of atoms in a simulation box with periodic boundary conditions following the procedure described in Ref. [7].

2. Interaction potentials

The interatomic potential describes the interaction between pairs of atoms or the interaction of an atom with a group of atoms. All atoms repel one another if the distance between the centres $r = |\mathbf{r_i} - \mathbf{r_j}|$ becomes sufficiently small, as the inner electrons start to overlap. However, at larger distances the atoms can attract or repel one another, depending on the atomic charges. The potential must have an attractive and repulsive component if binding is to

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occur. There are many classes of potentials. We use the Buckingham potential to describe the interaction for large values of r and the Ziegler–Biersack–Littmark (ZBL) potential [8] for small values of r when the atomic cores overlap. The Buckingham potential is a pairwise additive function with no three-body terms of the form:

$$V_{ij}(r) = A_{ij}\exp\left(-\frac{r}{\rho_{ij}}\right) + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r} - \frac{C_{ij}}{r^6}, \quad (1)$$

where A_{ij}, ρ_{ij} and C_{ij} are parameters of the model, as given in Table 1. The second Coulomb term is the interaction between ions with charges q_i and q_j on atoms i and j, respectively. The charges are assumed to be fixed and ϵ_0 is the electrical permittivity of free space. This operates in the region $r > \alpha_2$.

By changing the values of the parameters used in Ref. [4] and in particular the values of the parameter ρ_{ij} that determines the effective diameters of the atoms, we obtain a model that more accurately describes the density of borosilicate glass. To decrease the density, we increased the parameters ρ_{ij} applying the mixing rule [9]:

$$\rho_{ij} = \frac{1}{2}(\rho_{ii} + \rho_{jj}). \quad (2)$$

For values of $r < \alpha_1$ the standard ZBL potential is used [8]. We use an exponential spline function to connect between the Buckingham potential and the ZBL potential to give a smooth curve for the potential function and its derivatives. The spline function is defined in the region $\alpha_1 \leqslant r \leqslant \alpha_2$:

$$S_{ij}(r) = \exp(c_0 + c_1 r + c_2 r^2 + c_3 r^3 + c_4 r^4 + c_5 r^5) \quad (3)$$

where c_0, c_1, c_2, c_3, c_4 and c_5 are constants. The values of these are given in Table 2, while the values of spline parameters α_1 and α_2 are shown in Table 1.

3. Results

3.1. Optimised potential parameters

To determine the optimum parameters given in Tables 1 and 2, we use two software packages, GULP [6] and an MD package developed by Loughborough University, LBOMD [10]. GULP is used first to do some quick estimates on small systems before using LBOMD on large systems for more detailed investigations. For each interatomic potential, we performed a set of quenches using constant volume MD in GULP for a range of different volumes to obtain sets of quenched glass structures at different densities.

The minimum of the curve gives the optimum density for the chosen set of potential parameters. We see from Fig. 1 that the borosilicate glass with $\rho_{Si-Si} = 0.41$ Å, $\rho_{B-B} = 0.49$ Å and $\rho_{B-Si} = 0.45$ Å has a minimum energy at the experimental density of 2.1 g/cm^3. We also find that the borosilicate glass with $\rho_{Si-Si} = 0.41$ Å, $\rho_{B-B} = 0.47$ Å and $\rho_{B-Si} = 0.44$ Å had a minimum value at the density of 2.2 g/cm^3. Thus as expected, the optimum density decreases as the effective radii of the atoms increase. To obtain the curve in Fig. 1 a system contain 2520 atoms is quenched using MD after first checking smaller systems (252 atoms) in GULP.

3.2. Structural properties

Quenching borosilicate glass with $\rho_{Si-Si} = 0.41$ Å, $\rho_{B-B} = 0.49$ Å and $\rho_{B-Si} = 0.45$ Å gives a glass density of 2.1 g/cm^3. The corresponding bond angle distributions of the borosilicate glass are shown in Figs. 2–5. The bond lengths are also in agreement with experimental data with the average B–O bond length being 1.37 Å, and the average for Si–O being 1.63 Å.

The tetrahedral environment for Si atoms affects the shape of the O–Si–O angular distribution. In Fig. 2 the O–Si–O distribution has a maximum at about 109.4° corresponding to the intra-tetrahedral O–Si–O angle (experimentally this angle is around 109.5° (Ref. [4])). The distribution for the Si–O–Si angle (Fig. 3) shows a broader spread, with a maximum position consistent with the experimental result of 155.9°.

The local environment of boron is more complicated. The value of the B–O distance depends on the local boron coordination number. The O–B–O angular distribution in borosilicate glass (Fig. 4) indicates a peak with a maximum position consistent with the experimental results 119.7° in Ref. [4]. The distribution of the B–O–B bond angle has an average at 155.6° (Fig. 5).

3.3. Elastic moduli

The calculated mechanical properties of borosilicate glass are indicated in Table 3. The elastic moduli are calculated by GULP from the minimum energy configurations and the results shown in Table 3 are compared to the experimental values given in Ref. [4]. The values are higher than those found in experiment but show a reduction as the density of the optimal structure decreases.

Table 1
Parameters for the Buckingham potential. Note that the values of ρ_{ij} given above are the optimal values used largely throughout except where indicated, since in some places some of these are varied.

	A (eV)	C (eV · Å^6)	q_1 (e)	q_2 (e)	ρ_{ij} (Å)	α_1 (Å)	α_2 (Å)
B–B	121.1	0.0	1.4175	1.4175	0.49	0.35	0.65
Si–Si	834	0.0	1.89	1.89	0.41	0.4	0.75
B–Si	337.7	0.0	1.89	1.4175	0.45	0.4	0.75
Si–O	45296.72	46.1395	1.89	−0.945	0.161	0.65	1.2
O–O	9027	85.0321	−0.945	−0.945	0.265	0.19	1.6

Table 2
Spline parameters in Eq. (3) used to connect the pair potential to the ZBL potential. The c_n's are in units of Å^{-n}.

	c_0	c_1	c_2	c_3	c_4	c_5
B–B	3.169	44.43	−220.96	446.7	415.9	147.5
Si–Si	11.206	−23.43	65.54	-136.68	148.84	61.61
B–Si	−0.22283	79.59	−327.65	592.76	−505.26	165.86
Si–O	5.49	21.413	−89.7	138.08	−96.49	24.79
O–O	9.983	−18.06	27.28	−20.53	6.82	−0.79

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