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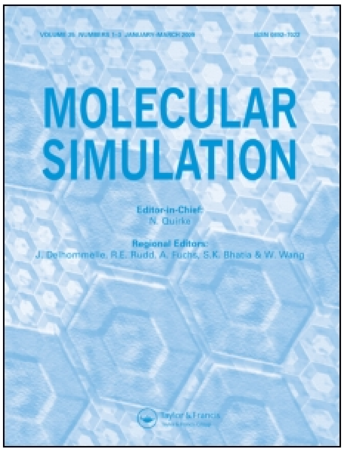

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Potentials for Molecular Dynamics Simulation of Silicate Glasses

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POTENTIALS FOR MOLECULAR DYNAMICS SIMULATION OF SILICATE GLASSES

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A new potential model has been developed for the simulation of amorphous silica based on the *ab initio* potential model of Pyper. This model promises to be of value in the simulation of silica at high pressures.

KEY WORDS: Silica, ab initio potential, high pressure.

INTRODUCTION

After the pioneering work of Woodcock, Angell, and Cheeseman [1] on the simulation of vitreous silica, there have been several molecular dynamics (MD) simulations on modelling the structure of glassy SiO_2, and alkalisilicate glasses. Most of these studies have used Born Mayer Higgins type potentials, and they have enjoyed a lot of success in predicting the radial distribution functions (RDFs), but usually give poor bond angle distributions (BADs).

We have reported recently on the development of a potential model which we have derived for this purpose [2]. Our model has been more realistic than the other potential models, since in deriving these potentials, we have tried both to predict the correct elastic and dielectric properties as well as the correct structure for crystalline silica, and at the same time modelling the right structure for vitreous silica.

We have used this potential model successfully to model the melting of β-cristobalite at constant pressure [3]. The same model predicts water-like melting behaviour of silicon dioxide in agreement with recent experiments.

In this paper we report on another potential model which was derived whilst refining the potential model reported in reference [2] to get a better structure for vitreous silica. We have based this potential model on the quantum mechanical potential model derived from oxygen–oxygen interactions by Pyper [4].

COMPUTATIONAL DETAILS

Details of the computational procedures are reported elsewhere [2], but briefly the long range coulomb part of the potential is calculated using Ewald's method [5], and employing full ionic charges on both the silicons and the oxygens. Both the direct lattice part and the reciprocal lattice part of the Ewald sum are computed. The Si–O short range interactions are modelled using a four range Buckingham potential i.e.

$$E_{ij} = A_{ij} \exp(-r_{ij} / p_{ij}),\ r_{ij} < r_I \qquad (1)$$

$$E_{ij} = A_1 (r_{ij})^5 + B_1 (r_{ij})^4 + C_1 (r_{ij})^3 + D_1 (r_{ij})^2 + E_1 r_{ij} + F_1,\ r_1 < r_{ij} < r_2 \qquad (2)$$

$$E_{ij} = P_1 (r_{ij})^3 + Q_1 (r_{ij})^2 + R_1 r_{ij} + S_1,\ r_2 < r_{ij} < r_3 \qquad (3)$$

$$E_{ij} = - C_{ij} /(r_{ij})^6\ r_3 < r_{ij} < r_c \qquad (4)$$

where r_{ij} is the distance between i and the nearest image of j, and r_c is the short range cutoff. The function is splined at r_1, r_2, and r_3 to have continuous energy, and first and second derivatives. The function has a minimum at r_2. The O–O short range interactions are modelled using the *ab initio* potential derived by Pyper [4]. This potential has eleven ranges, and in each range we fit it to a cubic spline, i.e.

$$E_{ij} = T_n (r_{ij})^3 + U_n (r_{ij})^2 + V_n r_{ij} + W_n,\ d_{n-1} < r_{ij} < d_n \qquad (5)$$

where T_n, U_n, V_n, and W_n are the parameters for range n.

The three body interactions between the O–Si–O, and the Si–O–Si triads are modelled using a potential of the form:

$$E_{ijk} = 1/4\ A_{ijk} (B_{ijk})^2 \exp(-r_{ij} /\rho_1) \exp(-r_{ik} /\rho_2) \qquad (6)$$

where

$$A_{ijk} = K_{ijk} /2(\theta_0 - \pi)^2 \qquad (7)$$

$$B_{ijk} = (\theta_0 - \pi)^2 - (\theta - \pi)^2, \qquad (8)$$

K_{ijk} is the three body spring constant and θ_0 is the equilibrium bond angle, i.e. 109° 28′ in the case of O–Si–O interactions, and 144° in the case of the Si–O–Si interactions, and θ is the calculated bond angle.

In order to be able to integrate the equations of motion using a large timestep we have had to use a large three body cutoff of 3.2 Å and a splined three body potential. Therefore we have used equation (6) as our three body potential only if both r_{ij} and r_{ik} are less than 2.9 Å; otherwise if either r_{ij} or r_{ik} is greater than 2.9Å and less than 3.2 Å then the relevant exponential term containing R_{ij} or r_{ik} is replaced by a fifth order polynomial in r_{ij}^2 or r_{ik}^2. If we define x as:

$$x = y^2 - z^2 \qquad (9)$$

where y can be either r_{ij} or r_{ik} and z is the spline point in the three body potential, then the polynomial in r_{ij} or r_{ik} will have the following form:

$$P(x) = G_1 + H_1 x + I_1 x^2 + J_1 x^3 + K_1 x^4 + L_1 x^5 \tag{10}$$

The parameters for the short range Si–O interactions, and the three body potentials are listed in Table 1. The three body interactions for each silicon are limited to four nearest neighbours, and the three body interactions around each oxygen are limited to two nearest neighbours. The parameters for the O–O potential are collected in Table 2.

The simulation is started with 192 particles (64 Si^{4+}, 128 O^{2-}) with the β-cristobalite crystal structure in a cubic calculation box with periodic boundary conditions. Vitreous silica was prepared by melting the system at 10000 K and then cooling successively to 5000 K, 2500 K, 1200 K, and 293 K for seven and a half picoseconds, giving a total annealing time of thirty seven and a half picoseconds. Newton's equations of motion are integrated using Beeman's [6] algorithm and a timestep of 3.0 femtoseconds. The velocities were rescaled during the first 1000 timesteps at each temperature to equilibrate the system.

RESULTS AND DISCUSSION

As stated above the parameters for the potential model are fitted to the structure, and

Table 1 Si–O and Three Body Potential Parameters

Parameter	*Si–O potential*	*unit*
A_{ij}	744.5	eV
ρ_{ij}	0.36469	Å
C_{ij}	0.0	eV(Å)^6
A_1	−18.6721257	eV/(Å)^5
B_1	192.9160662	eV/(Å)^4
C_1	−796.1441777	eV/(Å)^3
D_1	1654.2484939	eV/(Å)^2
E_1	−1753.8937200	eV/Å
F_1	773.0999316	eV
P_1	0.0	eV/(Å)^3
Q_1	0.0	eV/(Å)^2
R_1	0.0	eV/Å
S_1	0.0	eV
r_1	1.5	Å
r_2	2.5	Å
r_3	3.5	Å
r_c	7.6	Å
k_{ijk}(O–Si–O)	34487.0	eV/rad^2
k_{ijk}(Si–O–Si)	19971.0	eV/rad^2
ρ_1	0.36469	Å
ρ_2	0.36469	Å
z	2.9	Å
$G_1 \times 10^4$	3.8848919	eV
$H_1 \times 10^3$	−9.5340652	eV/Å
$\mathrm{I}_1 \times 10^2$	13.1886589	eV/(Å)^2
J_1	−28.2465714	eV/(Å)^3
K_1	1011.609681	eV/(Å)^4
L_1	−9761.880606	eV/(Å)^5

Table 2 O–O Potential Parameters

Parameter	*O–O potential*	*unit*
T_1	0.0	eV/(Å)^3
U_1	0.0	eV/(Å)^2
V_1	−3.2587296	eV/Å
W_1	5.9986039	eV
d_1	1.587	Å
T_2	7.6984470	eV/(Å)^3
U_2	−36.6523064	eV/(Å)^2
V_2	54.9084806	eV/Å
W_2	−24.7718503	eV
d_2	1.850	Å
T_3	−6.4601242	eV/(Å)^3
U_3	41.9277638	eV/(Å)^2
V_3	−90.4646493	eV/Å
W_3	64.8749131	eV
d_3	1.983	Å
T_4	−17.8935296	eV/(Å)^3
U_4	109.9450925	eV/(Å)^2
V_4	−225.3430121	eV/Å
W_4	154.0295110	eV
d_4	2.116	Å
T_5	19.6580943	eV/(Å)^3
U_5	−128.4326157	eV/(Å)^2
V_5	279.0642185	eV/Å
W_5	−201.7457223	eV
d_5	2.248	Å
T_6	−12.1429657	eV/(Å)^3
U_6	86.0337328	eV/(Å)^2
V_6	−203.0561330	eV/Å
W_6	159.5231277	eV
d_6	2.381	Å
T_7	1.2506142	eV/(Å)^3
U_7	−9.6366082	eV/(Å)^2
V_7	24.7349491	eV/Å
W_7	−21.2670661	eV
d_7	2.645	Å
T_8	−0.3844123	eV/(Å)^3
U_8	3.3373273	eV/(Å)^2
V_8	−9.5811103	eV/Å
W_8	8.9882646	eV
d_8	2.910	Å
$T_9 \times 10^3$	1.5084927	eV/(Å)^3
$U_9 \times 10^2$	−3.1761603	eV/(Å)^2
V_9	0.2229383	eV/Å
W_9	−0.5216626	eV
d_9	7.000	Å
$T_{10} \times 10^5$	6.9381122	eV/(Å)^3
$U_{10} \times 10^3$	−1.5402609	eV/(Å)^2
$V_{10} \times 10^2$	1.1388911	eV/Å
$W_{10} \times 10^2$	−2.8047318	eV
d_{10}	7.500	Å
$T_{11} \times 10^5$	−13876224	eV/(Å)^3
$U_{11} \times 10^4$	3.3302938	eV/(Å)^2
$V_{11} \times 10^3$	−2.6607660	eV/Å
$W_{11} \times 10^3$	7.0768744	eV
d_{11}	7.600	Å

Table 3 Observed and Calculated Proterties of α – quartz

Property	*Experimental [8]*	*Calculated*
Elastic constants (10^{11} dyn cm^{-2})		
C_{11}	8.683	8.644
C_{33}	10.498	11.848
C_{44}	5.826	3.472
C_{66}	3.987	3.912
C_{14}	−1.806	−1.326
C_{13}	1.193	0.388
Static dielectric constants		
E_{11}	4.520	4.330
E_{33}	4.640	4.754

the elastic and the dielectric properties of α-quartz. The properties of α-quartz calculated using this potential model are compared to the experimental results in Table 3.

In Figure 1 we have plotted the radial distribution functions for vitreous silica simulated using the present potential model. In Figure 2 we have shown the bond angle distributions for vitreous silica using the present potential model. Although the structure obtained does not agree with the experimental structure of silica glass, the indications from our constant pressure simulations suggest that [7] the structure obtained is that of silica glass at high pressure. The simulated glass actually has a pressure of 95 kbar, and also a high percentage of high coordinated silicons and oxygens (see Table 4). The present potential is stable at very high pressures in contrast to our previous model [2] and should be of great value for high pressure studies of vitreous silica.

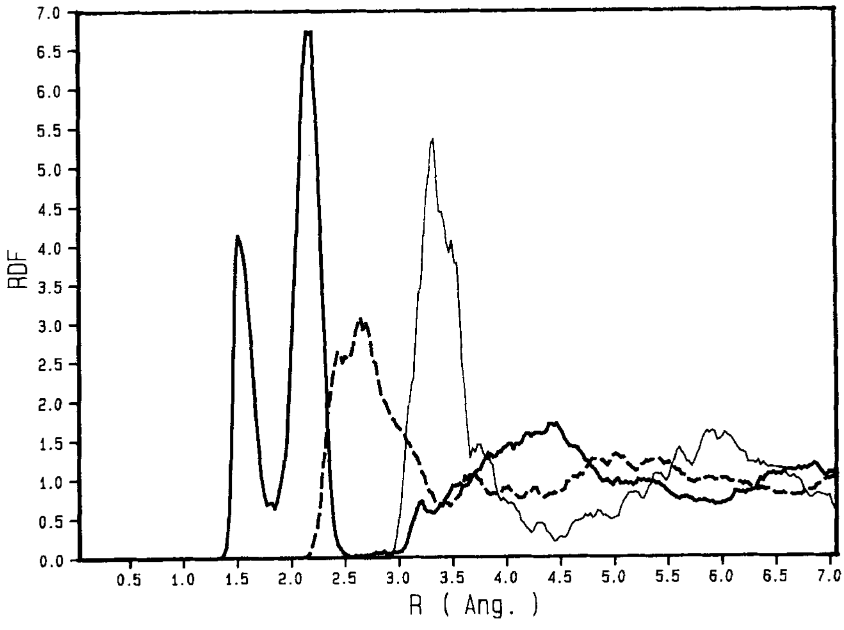

Figure 1 Si–O RDF (heavy solid line), O–O RDF (dashed line), Si–Si RDF (solid line).

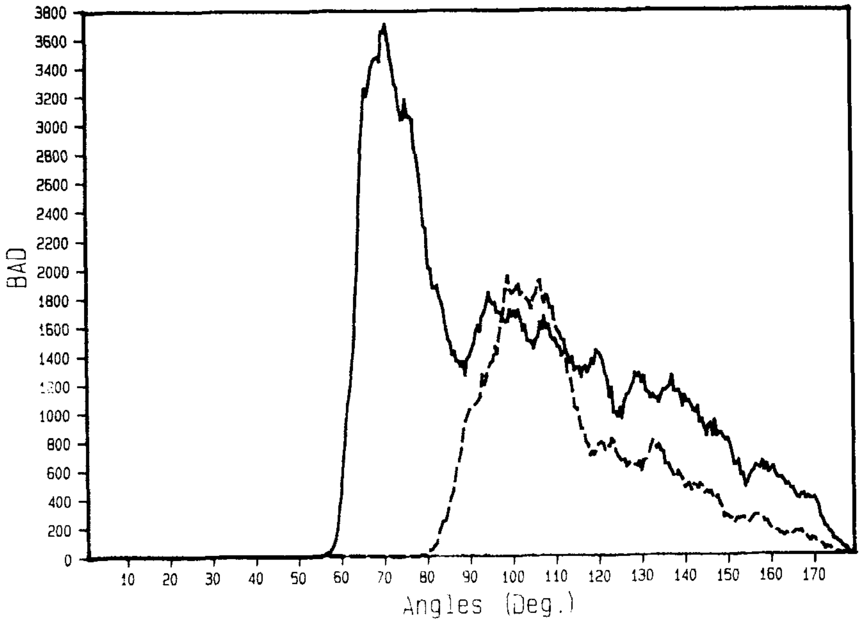

Figure 2 O-Si-O BAD (solid line), Si-O-Si BAD (dashed line).

Table 4 Coordination Numbers (as percent of total)

Coordination Number	
a-Silicon	
4	4.7
5	18.6
6	35.7
7	32.0
8	9.0
b-Oxygen	
2	22.8
3	43.3
4	33.9

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