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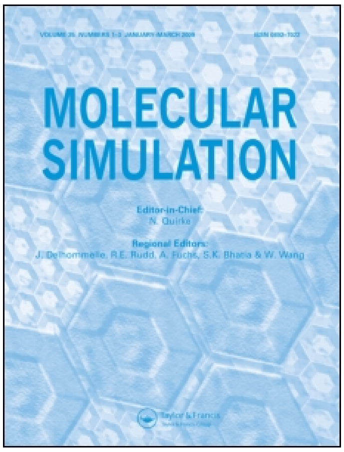

Molecular Simulation

Publication details, including instructions for authors and subscription information:
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Molecular Dynamics Simulation of Alkali Silicates Based on the Quantum Mechanical Potential Surfaces

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To cite this Article Habasaki, Junko and Okada, Isao(1992) 'Molecular Dynamics Simulation of Alkali Silicates Based on the Quantum Mechanical Potential Surfaces', Molecular Simulation, 9: 5, 319 — 326
To link to this Article: DOI: 10.1080/08927029208049124
URL: http://dx.doi.org/10.1080/08927029208049124

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Molecular Simulation, 1992, Vol. 9(5), pp. 319–326
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MOLECULAR DYNAMICS SIMULATION OF ALKALI SILICATES BASED ON THE QUANTUM MECHANICAL POTENTIAL SURFACES

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(Received April 1992, accepted August 1992)

Two potential parameter sets for alkali silicates were derived on the basis of *ab-initio* MO calculations. One is a model containing completely ionic alkali (model I), and another is that derived from cluster calculations (model II). These sets were tested against the crystal, glass, and liquid of metasilicates. The model II can reproduce these structures well under constant pressure conditions, and is found to be better than model I as a whole.

KEY WORDS: MD simulation, alkali metasilicates, nonempirical potential parameters, crystal structure.

INTRODUCTION

Modelling techniques using molecular dynamics simulation have a potential to contribute to the design and improvement of materials and the methods can be used to predict properties of materials. Recent progress of the modelling methods in mineralogy has been reviewed by Catlow and Price [1]. Although alkali silicates are typical glass-forming materials and a study of the structures and properties is important not only for an industrial use but also for a fundamental understanding of minerals and glasses, an adequate potential model for predicting the unknown properties has not yet been established. Modelling by *ab-initio* quantum mechanical potential surfaces has been used for calculations in mineral physics by several authors. The simple pair additive potential derived from the quantum mechanical calculation was shown to be effective enough to reproduce the polymorphs of silica by Tsuneyuki *et al.* [2]. The effective parameters used to reproduce the several Mg silicates were also derived by them using the potential energy surfaces of both SiO_4^{4-} and MgO_2^{2-} clusters at the same time. Since they assume that the SiO_2 chemical unit is neutral, the method is applicable only when the condition $q_{Mg} = -q_O$ is a good approximation; q_α is the charge number of α.

In the present work the method was extended to derive parameters for some alkali metasilicates having different stoichiometry from that of Mg silicates.

Two sets of potential models for alkali (M = Li, Na and K) silicates were tested in the present work. One is a model containing completely ionic alkali, whose parameters in the repulsive part were derived from $M^+ - M^+$ interaction. Another is that derived from cluster $(e^+\text{–O–M–O–}e^+)^{-1}$ calculation. In both cases the parameters for the repulsive parts of Si and O were taken from literature [2].

METHOD AND RESULTS

Potential functions of Gilbert-Ida type with an r^{-6} term were chosen, since the potential type is simple and is additive not only for pairs but also for the kind of atomic species.

$$\Phi_{ij} = q_i q_j e^2/r + f_0(b_i + b_j) \exp\{(a_i + a_j - r)/(b_i + b_j)\} - c_i c_j/r^6, \qquad (1)$$

where q is the charge number and e the elementary charge; a, b and c are the parameters characteristic of each atom, f_0 is a normalization constant (1 kcal Å^{-1} mol^{-1} = 4.184 kJ Å^{-1} mol^{-1}) and r is the distance between the centres of the atoms.

Model I. A Potential Model with Completely Ionic Alkali

The total energies of M^+–M^+ supermolecules with several distances (0.6–3.0 Å for Li, 1.2–3.5 Å for Na and 1.6–3.5 Å for K) were calculated by an *ab-initio* Hartree Fock self-consistent-field method. Gaussian type basis sets were used for Li, Na and K; the constructions are [721/31], [631111/6111] and [43321/421], respectively [3, 4].

Subtraction of energy of two M^+ ions isolated at infinite distance from total energy gives the interaction energy in each case. The interaction energies were fitted to equation (1). An r^{-6} term was omitted for alkali–oxygen interactions in this model.

The charge number of M was set as +1. As the charge number of Si, the value obtained for SiO_2 by Tsuneyuki *et al.* (referred to as TNM hereafter) [2] was adopted, that is $q_{Si} = +2.40$. Consequently, according to the charge neutrality, $q_O = -1.467$ for M_2SiO_3 composition.

The parameters a, b and c, of Si and O of TNM were used without change, because the cluster surrounded by point charges seems to be a good model not only for silica but also for silicates. The values thus obtained are given in Table 1.

Molecular dynamics simulations were performed for crystals of lithium and sodium metasilicates at constant pressure (0.1 MPa) and at constant temperature (300 K) starting from experimentally obtained configurations. Structural properties such as atomic coordinates of the last 2000 steps were averaged after a run of 2000–4000 steps. The step time was 21.0–4.0 fs. A steady state was attained within 2000 steps in most cases with respect to the fluctuation of the energy and density.

Model II A Potential Model Derived from Cluster Calculation

The total energies of the cluster $(e^+ - O - Li - O - e^+)^{-1}$ were calculated using

Table 1 Parameters of the potentials for completely ionic alkali model (I)

Ion	q	a/Å	b/Å	c/Å^3 kcal$^{1/2}$ mol$^{-1/2}$
Li	1.0	0.8941	0.0740	0.0
Na	1.0	1.2395	0.0893	0.0
K	1.0	1.8118	0.1377	0.0
Si	2.40*	0.8688*	0.03285*	23.18*
O	−1.467	2.0474*	0.17566*	70.37*

*Taken from [2].

Table 2 Parameters of the potentials derived from the cluster in model (II)

Ion	q	a/Å	b/Å	$c/Å^3\,kcal^{1/2}\,mol^{-1/2}$
Si	2.40*	0.8688*	0.03285*	23.18*
O	−1.38	2.0474	0.17566*	70.37*
Li	0.87	1.0155	0.07321	10.87**
Si	2.40*	0.8688*	0.03285*	23.18*
O	−1.387	2.0474*	0.17566*	70.37*
Na	0.88	1.0805	0.08461	0.0
Si	2.40*	0.8688*	0.03285*	23.18*
O	−1.367	2.0474*	0.17566*	70.37*
K	0.85	1.4081	0.10070	0.0

*Taken from [2].
**For the term $c_{Li}c_O$.

the *ab-initio* Hartree Fock self-consistent-field method. The (9s5p)/[3s2p] basis set with a diffuse function for oxygen (with $\alpha = 0.059$) was used. The surfaces at 12 Li − O distances from 1.2 to 3.0 Å for stretching of both M − O were calculated with a constant $e^+ - O$ distance (1.6 Å).

Then, the total potential of the cluster was expressed in terms of sum of the Gilbert-Ida type functions, Equation (1), in which the values of a, b and c for the O atoms were taken from those presented in TNM. Several sets of a_{Li}, b_{Li}, and c_{Li} fitting the total potential surface were obtained for several given values of q'_{Li} (q': charge number in the cluster) from +0.7 to +1.0e. q'_O was fixed to keep the charge neutrality of the cluster.

MD simulations of lithium metasilicate (Li_2SiO_3) crystal at constant pressure (0.1 MPa) were performed to select the best one among these sets of parameters that can reproduce the density and the structure [5], [6]; in the MD, q_O was fixed according to the charge neutrality of the crystal and not of the cluster.

A set of q_{Li}, a_{Li}, b_{Li} and c_{Li} predicting for the density the experimental value within $\pm 0.10\,g\,cm^{-3}$ was finally chosen, which could also reproduce the structure. The values are given in Table 2. The best set fitting the potential surface of the cluster did not yield the best density or the best structure of the crystal.

MD simulations for liquid and glass at several temperatures were performed for 6000–8000 steps and 10000–20000 steps ($\Delta t = 4fs$) respectively, starting from the configurations obtained by the earlier work using an empirical potential model [9]. The structures are consistent with the results by X-ray diffraction analysis [10].

A similar procedure was performed for the sodium salt; the potentials of the cluster $(e^+ - O - Na - O - e^+)^{-1}$ were calculated at 10 Na = O distances from 1.4 to 3.5 Å. In the pair potentials the c_{Na} term was omitted.

The *ab-initio* MO calculations for the corresponding cluster were performed for 10 K − O distances from 1.7 to 4.0 Å. For the deliquescent potassium salt, detailed crystal structure was unknown. Therefore, the parameters for the salt were selected to reproduce the density of the melt under 0.1 MPa, the c_K term being also omitted.

The sets of parameters thus obtained for the sodium and potassium salts were also listed in Table 2.

The atomic configurations obtained by both model I and II are listed in Table 3 with the experimental values for the lithium and sodium salts. The predicted atomic configurations for the potassium salt are also given in Table 3; it is assumed here

Table 3 Atomic coordinates

(a)

Atom	Coordinate	Close packing	Li_2SiO_3 This work		Experimental	
			Model I	Model II	[5]	[6]
Li	x	0.167	0.1704	0.1722	0.160	0.170
	y	0.333	0.3399	0.3387	0.320	0.330
	z	0.0	−0.0179	−0.0240	0.0	0.0
Si	x	0.0	0.0000	0.0004	0.0	0.0
	y	0.167	0.1610	0.1653	0.164	0.167
	z	0.500	0.4976	0.4986	0.537	0.496
O(1)	x	0.167	0.1387	0.1389	0.141	0.147
	y	0.333	0.3041	0.3062	0.321	0.310
	z	0.375	0.4143	0.4156	0.450	0.406
O(2)	x	0.0	0.0001	−0.0002	0.0	0.0
	y	0.167	0.1055	0.1056	0.100	0.108
	z	0.875	0.8344	0.8432	0.860	0.845

(b)

Atom	Coordinate	Close packing	Na_2SiO_3 This work		Experimental	
			Model I	Model II	[7]	[8]
Na	x	0.167	0.1641	0.1692	0.166	0.166
	y	0.333	0.3367	0.3421	0.339	0.339
	z	0.0	−0.0264	−0.0279	0.0	0.0
Si	x	0.0	0.0012	0.0001	0.0	0.0
	y	0.167	0.1468	0.1534	0.157	0.166
	z	0.500	0.5143	0.5072	0.537	0.563
O(1)	x	0.167	0.1242	0.1279	0.129	0.130
	y	0.333	0.2844	0.2900	0.287	0.286
	z	0.375	0.4629	0.4431	0.481	0.506
O(2)	x	0.0	0.0023	0.0003	0.0	0.0
	y	0.167	0.0690	0.0813	0.084	0.077
	z	0.875	0.8270	0.8321	0.872	0.895

(c)

Atom	Coordinate	Close packing	K_2SiO_3 This work	
			Model I	Model II
K	x	0.167	0.1552	0.1617
	y	0.333	0.3299	0.3317
	z	0.0	−0.0101	−0.0111
Si	x	0.0	−0.0036	0.0089
	y	0.167	0.1268	0.1442
	z	0.500	0.4895	0.4870
O(1)	x	0.167	0.1036	0.1122
	y	0.333	0.2490	0.2738
	z	0.375	0.4900	0.4895
O(2)	x	0.0	0.0023	0.0149
	y	0.167	0.0690	−0.0001
	z	0.875	0.8270	0.7346

that the crystal does not take an oblique lattice. For this salt, the initial configuration in the same crystal form as in lithium and sodium salts was used. Some other parameters for crystal structure of the metasilicates are given in Table 4.

Table 4 Structural parameters of the alkali silicate crystals

(a)

	Li_2SiO_3				Na_2SiO_3		
	[5]	[6]	I	II	[8]	I	II
a_0/Å	9.36	9.38	9.57	9.55	10.43	10.67	10.42
b_0/Å	5.395	5.40	5.47	5.44	6.02	6.18	6.00
c_0/Å	4.675	4.68	4.73	4.68	4.81	4.98	4.88
Density/ g cm^{-3}	2.52	2.52	2.40	2.45	2.68	2.46	2.65
Distance/Å							
Si–O	1.55–1.65	1.64–1.66			1.57 or 1.67		
Average	1.60	1.65	1.60	1.61	1.62	1.60	1.62
Li–O	2.02–2.14	1.92–2.18		Na–O	2.27–2.45	2.3–2.40	2.18–2.48
Average	2.08	2.01	2.02	2.00	2.36	2.35	2.33

(b)

	K_2SiO_3 (estimated)		$K_2Si^{VI}Si_3^{IV}O_9$ [11]
	I	II	
a_0/Å	12.18	11.37	
b_0/Å	7.03	6.49	
c_0/Å	5.52	5.33	
Density/ g cm^{-3}	2.17	2.60	
Distance/Å			
Si–O	1.61	1.62	1.592–1.659
K–O	2.92	2.70	2.791–3.297

Table 5 Calculated density (g cm^{-3})

	Liquid (1673 K)	Glass (300 K)	Crystal (300 K)
Li_2SiO_3	2.19 (2.06) [13]	2.35 (2.32) [14]	2.45 (2.52) [5, 6]
Na_2SiO_3	2.28 (2.19) [13] (2.16) [16]	2.54 (2.57*) [16]	2.65 (2.68) [7, 8]
K_2SiO_3	2.06 (2.11*) [13]	2.46 (2.48) [15]	2.60
$Li_2Si_3O_7$	2.30 (2.15) [13]		

The values in parentheses are the experimental values.
*Extrapolated values.

The densities of these salts according to model II including those in molten and glassy states are given in Table 5. The pair correlation functions for glassy and liquid lithium metasilicate by model II are quite similar to those obtained from MD simulation based on the empirical potential parameters in our previous work [9]. On the other hand, the Li-Li distance from model I is slightly longer owing to the completely ionic character of the model.

DISCUSSION

In model I, the charge transfer between M and O was neglected. Ionic radii thus determined are larger than those derived by the cluster calculation.

For the Li salt, the atomic configurations of the metasilicate crystals based on these two models were similar to each other. However the volumes in model I are larger than the experimental ones and the difference between model I and II becomes larger in going from Li salt to K salt. Thus, model II is better than model I.

In model II, the charge transfer between M and O is allowed. The charge on the oxygen in $(e^+-O-M-O-e^+)^{-1}$ cluster is $q'_O=(-q'_M-3)/2$, which differs from the charge in bulk M_2SiO_3, $q_O=(-2*q_M-q_{Si})/3$. We assumed that the repulsive parameters a, b, and c for the cluster are applicable for these crystals and that the difference in the parameters between cluster and bulk is mainly due to the different charges on the oxygen atoms ($q_M=q'_M$ and $q_O\neq q'_O$). The assumption seems to work well since the crystal structures and densities of the alkali silicates are well reproduced with these parameters.

The volume could be adjusted by choosing the set of q_M, a_M, b_M and c_M. This procedure brings some arbitrariness for selecting the parameters.

Net atomic charges and electron density distributions have been studied for some oxides and silicates by Sasaki *et al.* [11]. On the basis of accurate X-ray diffraction intensity data collected from spherical shaped single crystals, they have found that the charges of atoms are less ionic than the corresponding formal ones. For example, the charges of Li, O, Mg, Al, Si, Ca and Mn (in MnO, Mn_2SiO_4, $Mg_2Si_2O_6$, $LiAlSi_2O_6$ and $CaMgSi_2O_6$) are 0.7, −1.1 to −1.5, 1.4 to 1.8, 2.4, 2.2 to 2.6, 1.4 and 1.2 to 1.6 e, respectively. A similar method was applied to the system $K_2Si^{VI}Si_3{}^{IV}O_9$ and the charges on Si^{VI}, Si^{IV}, $O(1)_{br}$, $O(2)_{nbr}$ are found to be 3.3, 2.2, −1.4, and −1.4, respectively [12], where the superfix represents the coordination number and the suffixes br and nbr refer to bridging and nonbridging oxygens, respectively. The charges assumed in the present work seem to be reasonable as compared to these values, although the experimental values of the lattice energy are not available.

As shown in Table 4, the densities are found to be well reproduced by model II not only for the crystal but also for the liquid and the glass within several percents of errors. For the lithium and sodium salts, the calculated thermal expansivities seem to be smaller than the experimental ones. The charge distribution based on the very simple assumption may cause this discrepancy. Differences of effective charge distributions among crystal, liquid and glassy states were also neglected in the present work. The accurate measurements of the charge distribution in the crystals will be helpful to improve the potential parameters.

Beest *et al.* [17] have pointed out that the adjustment of short-range parameters to bulk properties is inevitable to improve the potential model of silica. This procedure will be also useful to improve the model.

However, it should be noted these parameter sets presented here can be applicable for systems with different $M_2O:SiO_2$ ratios and even with different kinds of M only by changing the charge on oxygen. An example of the obtained density of the melt with the different $Li_2O:SiO_2$ ratios is also given in Table 5.

ACKNOWLEDGEMENTS

A part of the calculations in this work were performed with HITAC M-680 and S-820 at the Institute for Molecular Science at Okazaki. The CPU time made available is gratefully acknowledged. The expenses of this work were defrayed partly by the Grant for the Encouragement of Young Scientists No. 03740311 from the Ministry of Education, Science and Culture, Japan. The MO calculations were performed with the Program GSCF3 written by N. Kosugi of Kyoto University. The original MD program for crystal was written by K. Kawamura of Hokkaido University. The authors would like to thank them for these programs.

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