Interatomic Potentials for SiO_2

M. J. Sanders,[b] M. Leslie,[a] and C. R. A. Catlow[b]

[a] *Daresbury Laboratory, Daresbury, Warrington, Cheshire, U.K.*
[b] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.*

Interatomic potentials, which include bond-bending terms, allow us to model accurately the properties of α-quartz and the structures of other polymorphs of SiO_2.

There is considerable incentive for developing reliable interatomic potential models for silicates. With such models, well established computer modelling techniques[1] would allow detailed predictions to be made of the structural, cohesive, and defect properties of silicate minerals and the way their properties change with temperature and pressure. In an earlier study,[2] we showed that for pyroxenoids it was possible to develop a classical Born model, pair potential description, which successfully predicted the structural properties of several members of this class of mineral. These models have since been elaborated and applied, again with success, to structure prediction of olivines and garnets[3,4] It is clear, however, that simple two-body central-force models have serious limitations. They do not yield accurate structures for framework structured minerals; and it has been shown[5] for quartz, that such models cannot consistently describe elastic, dielectric, and dynamical data. This work presents an important extension of potential models for silicates to include bond-bending terms. We show that, by including these terms, it is possible to reproduce quantitatively all the main properties of quartz and of other polymorphs of SiO_2. The success of the work opens up the possibility of making detailed predictions of the properties of other framework structured minerals *e.g.* feldspars and zeolites.

In our model for SiO_2 the classical Born model potentials with parameterised pair potentials have been supplemented by specific bond-bending terms. Terms of this nature have been included in a previous analysis;[6] but only force constants were derived whereas an explicit potential model is needed for use in computer modelling studies. We consider the inclusion of bond-bending terms for O–Si–O bonds. For all such bonds, therefore, we include in our model a quadratic energy term E_B of the type: $E_B = K_B(\theta - \theta_0)^2$, where $(\theta - \theta_0)$ is the deviation of the bond angle from an 'ideal' value which we take for the O–Si–O bond as the tetrahedral angle (109.47°); K_B is the harmonic force constant for the bond-bending component of the potential. Details of the calculation of first and second derivatives that are needed for calculation of the lattice properties are given in reference 7. The terms describe the rigidity that is conferred upon the SiO_2 tetrahedra by the component of sp^3 hybridized, covalent bonding around the silicon atom. The model nevertheless still uses formal ionic charges which appear to be the most convenient way of correctly describing the cohesive properties of the crystal. In this context, we should note that as argued by Catlow and Stoneham,[8] the use of formal ionic charges in a potential model does not require that the electron distribution in the solid should correspond accurately to this description. Moreover, partial charges can be readily used in our models, provided they can be unambiguously assigned (which we consider will present considerable difficulties[8]) and provided these can be made to be consistent with the cohesive properties of the compound. Unlike the earlier lattice dynamical study[6] our model also incorporates a description of atomic polarisability for the oxygen atoms using the shell model.[1] We should note that the shell rather than the core positions are used to calculate the bond-bending energy.

The variable parameters of our model (including K_B, the shell model parameters, and the parameters in the two body short range potential for the Si–O interaction) were determined by a standard empirical fitting procedure,[1] that is, the variables were adjusted *via* a least squares fitting method until the measured elastic and dielectric properties of quartz were reproduced as accurately as possible. Structural parameters were included in the fitting procedure; these add several independent pieces of data to the data base. The resulting potential is reported in Table 1, while in Table 2 we compare the observed crystal properties with those calculated. In fitting the parameters to the structure of alpha quartz the coordinates of the oxygen shell were fitted as parameters, but in the subsequent calculations were allowed to vary in order to obtain the minimum energy configuration.

Table 1. Potential parameters and oxygen core/shell displacements.[a]

Parameter	Si–O Potential	O–O Potential
A/eV	1283.9073	22764.000
B/Å	0.3205	0.149
C/(eV/Å^6)	10.6616	27.88
Oxygen core charge/|e|	+0.8482	
Oxygen core shell/|e|	−2.8482	
Core/shell spring constant/(eV/Å^2)	74.9204	
X Shell displacement/Å[b]	+0.0997	
Y Shell displacement/Å[b]	−0.0302	
Z Shell displacement/Å[b]	−0.0666	
Bond-bending constant/(eV/radians^2)	2.097	

[a] Buckingham form of the short range potential used: $V_{ij}(r) = A \exp(-r_{ij}/B) - C/r_{ij}^6$. [b] X, Y, and Z components of displacements of oxygen shells, relative to cores.

We should note here that we attempted to fit a conventional central-force shell model to the crystal data given in Table 2. The calculated properties for the best fit for this type of model are given in this table. The agreement with experiment is notably inferior to that shown with the bond-bending potential; the calculated phonon dispersion curves, discussed below, are also unsatisfactory. Moreover, we find that the parameters for the repulsive interaction are essentially the same as those obtained when the bond-bending terms are included. It appears, therefore, that the bond-bending terms may simply be added to existing central force potential models.

In order to perform a comprehensive test of the validity and transferability of our model we have investigated: (i) phonon dispersion curves of alpha quartz, (ii) the structural properties of alpha quartz under high applied pressures, (iii) the structural and cohesive properties of other polymorphs of SiO_2 (α-Cristobalite, Coesite, and α-Tridymite).

Regarding test (i), calculated and experimental phonon dispersion curves show excellent agreement in contrast to the poor results obtained when the bond-bending term was not included. Details will be given in a separate publication. The remainder of our discussion concerns the structural criteria (ii) and (iii). The structure of alpha quartz has been studied as a function of applied pressures ranging from 0 to 28.2 kbar.†[9]

Table 2. Observed and calculated crystal properties of α-quartz.

	Experimental[a]	3 Body SiO_2 potential	2 Body SiO_2 potential
Elastic constants (10^{11} dyn cm^{-2})[b]			
C_{11}	8.683	8.815	6.204
C_{33}	10.598	10.605	7.466
C_{44}	5.826	5.296	3.301
C_{66}	3.987	4.269	2.737
C_{14}	−1.8064	−1.666	−1.012
C_{13}	1.193	1.151	1.629
Static dielectric constants			
E_{11}	4.520	4.452	5.513
E_{33}	4.640	4.812	6.086
High frequency dielectric constants			
	1.549	2.04	2.069

[a] Ref. 13. [b] 1 dyn = 10^{-5} N.

Table 3. Observed and calculated change of Si–O–Si angle with pressure

Pressure (kbar)	Experimental Si–O–Si angle (°)	Calculated Si–O–Si angle (°)
0.0	144.1	143.9
10.6	141.5	141.2
21.1	139.4	139.1
28.2	138.7	137.9

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† 1 bar = 10^5 Pa.

The most pronounced structural change is in the Si–O–Si bond angle. The extent to which our potential is capable of reproducing this change provides a good test of the model. We therefore carried out our energy minimisation studies of SiO_2 using the observed cell dimension for pressures of 10.6, 21.1 and 28.2 kbar. The change in structure with pressure is reproduced well by our calculations as shown in Table 3, where calculated and experimental bond angles are compared.

The most demanding test of our model is, however, provided by the extent to which it can predict the structures of the other polymorphs of SiO_2. Full energy minimisation studies, varying both unit cell dimensions and atomic co-ordinates were performed for α-Cristobalite,[10] Coesite,[11] and α-Tridymite,[12] These phases which are thermodynamically stable only at higher temperatures can nevertheless be studied as metastable structures at low temperature. In all cases we compare our calculations with room temperature data. Coesite and α-Tridymite provide an especially good test for our model owing to the considerable variability in bond angles and bond lengths. In every case, the energy minimisation studies reproduce well the observed structures. For α-Cristobalite the calculated cell dimensions are within 1% of the observed values for the *a* and *b* axes and within 1.5% for the *c* axis; the maximum displacement of any atom from the observed position in the unit cell is under 0.10 Å. Similar small discrepencies are observed for Coesite and α-Tridymite. In both cases the cell dimensions are within 1% of the observed values and the maximum atom displacement is 0.10 Å.

Thus the potential model for quartz summarised in Table 1 performs well in reproducing the known properties of polymorphs of SiO_2. The tests we have applied are demanding and the success of our study encourages application of the model to the study of other framework structured silicates. Refinements of the model will be investigated; these will include the investigation of partial charges. The work described in this paper suggests that it is possible to model silicates by a relatively simple form of interaction potential, and one which can be incorporated into computer modelling codes.

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