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Realistic models of amorphous silica: A comparative study of different potentials

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The creation of realistic models of amorphous silica has been studied using the Monte Carlo based method of Wooten, Winer, and Weaire, where the bond-topology is optimized with respect to an interatomic potential model. The commonly used Keating potentials are compared and their strengths and weaknesses are assessed. The mean oxygen bond-angle obtained using these potentials turned out to be too small. A modification of the potential parameters is shown to correct this feature and thus produce better results when used with the Wooten-Winer-Weaire method.

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Amorphous SiO₂ (*a*-SiO₂) consists of Si(O_{1/2})₄ tetrahedra that are bridged together by oxygen atoms. In the amorphous state these tetrahedra are connected to each other in a disordered fashion. Unlike in the case of crystals the exact atomic structure of amorphous silica, and amorphous solids in general, cannot be measured directly. In this situation computational approach can serve as a powerful tool in creating realistic models for amorphous silica, which then need to be validated by calculating various physical properties and by comparing them with experimental results.

There are various computer simulation models which can be used to construct *a*-SiO₂. Amorphous structures can be generated by heating and cooling the system by using the molecular dynamics (MD) method.¹ Coordination defects present in systems created by MD can be avoided completely by using the Monte Carlo approach of Wooten, Winer, and Weaire (WWW).² In the WWW method the structure of the material represented by a continuous random network is evolved by bond-switch Monte Carlo moves. The WWW method was originally developed for silicon, but with small modifications it can be used also for silica, which, however, has been discussed in the literature only scarcely. For example the Si/SiO₂ interface has been studied by Tu and Tersoff³ and the growth of SiO_x has been studied by Burlakov *et al.*⁴ using an extended WWW algorithm.

In this work the atomistic structure of *a*-SiO₂ is studied using the WWW approach, but with the emphasis on devel-

oping the interaction potential model. Our method contains several optimization steps that speed up the simulations.⁵ Two different potentials are used to describe the elastic energy of the bond topology, the original Keating potential⁶ and its simplified form (here called the simplified Keating potential).⁷ The latter potential has been used recently in studies of different stoichiometries of SiO_x.^{3,4,8}

The original form of the Keating potential expresses the energy of the crystal as a function of the nearest neighbor positions. The two-body and three-body parts describe the effects of bond stretching and bond bending, respectively:

$$V_K = \sum_{i \in \text{bonds}} \frac{1}{2} k_i^b [b_i^2 - b_{i0}^2]^2 + \sum_{ij \in \text{angles}} \frac{1}{2} k_{ij}^\theta [b_i b_j \cos \theta_{ij} - b_{i0} b_{j0} \cos \theta_{ij0}]^2, \quad (1)$$

where b_{i0} is the equilibrium distance of bond i , and θ_{ij0} is the equilibrium angle between bonds i and j . The parameters for silica are listed in Table I, in which four parametrizations named KA,⁹ KB,¹⁰ KC,¹¹ and KD (Ref. 12) of the Keating potential are presented. In KC and KD the values of the parameters are only defined relative to each other and in this work we will use the values $\alpha=4.1$ and $\beta=3.6$.

TABLE I. Parameters for V_K . In this work $\alpha=4.1$ and $\beta=3.6$.

	KA (Ref. 9)	KB (Ref. 10)	KC (Ref. 11)	KD (Ref. 12)
$b_{\text{Si-Si}}(\text{\AA})$	—	2.35	2.35	—
$b_{\text{Si-O}}(\text{\AA})$	1.619	1.60	1.69	1.62
$k_{\text{Si-Si}}^b (\text{eV/\AA}^4)$	—	0.4111	α	—
$k_{\text{Si-O}}^b (\text{eV/\AA}^4)$	3.5718	6.8023	α	β
$\cos \theta_{\text{Si}}$	-1/3	-1/3	-1/3	-1/3
$\cos \theta_{\text{O}}$	-0.900	-0.809	-0.8387	-0.8387
$k_{\text{Si-Si-Si}}^\theta (\text{eV/\AA}^4)$	—	0.0822	0.17α	—
$k_{\text{O-Si-O}}^\theta (\text{eV/\AA}^4)$	2.6193	2.5966	0.17α	0.08β
$k_{\text{Si-O-Si}}^\theta (\text{eV/\AA}^4)$	0.9524	1.1154	0.0567α	0.0267β
$k_{\text{Si-Si-O}}^\theta$			$\sqrt{k_{\text{Si-Si-Si}}^\theta k_{\text{O-Si-O}}^\theta}$	

TABLE II. V_{SK} parameters.

	SKA (Ref. 3)	SKB (Ref. 4)	SKC
$b_{Si-Si}(\text{\AA})$	2.35	2.35	2.35
$b_{Si-O}(\text{\AA})$	1.6	1.6	1.61
$k_{Si-Si}^b(\text{eV/\AA}^2)$	9.08	9.08	9.08
$k_{Si-O}^b(\text{eV/\AA}^2)$	27.0	27.0	27.0
$\cos \theta_{Si}$	-1/3	-1/3	-1/3
$\cos \theta_O$	-1.0	-0.766	-1.0
$k_{Si-Si-Si}^\theta(\text{eV})$	3.58	3.58	3.58
$k_{Si-O-Si}^\theta(\text{eV})$	0.75	0.75	2.00
$k_{O-Si-O}^\theta(\text{eV})$	4.32	4.32	4.32
$k_{Si-Si-O}^\theta$		$\sqrt{k_{Si-Si-Si}^\theta k_{O-Si-O}^\theta}$	

The simplified Keating potential has a slightly different form:

$$V_{SK} = \sum_{i \in \text{bonds}} \frac{1}{2} k_i^b [b_i - b_{i0}]^2 + \sum_{ij \in \text{angles}} \frac{1}{2} k_{ij}^\theta [\cos \theta_{ij} - \cos \theta_{ij0}]^2, \quad (2)$$

where b_{i0} is the equilibrium distance of the bond and θ_{ij0} is the equilibrium angle between bond i and j . The parameters in Eq. (2) for silica are given in Table II, for which the original fitting was done to vibrational properties of quartz by Kleinman *et al.*⁷ In Refs. 3 and 4 the WWW studies of silica were done using parameter values of Kleinman *et al.*,⁷ except that the oxygen bond angle term was different. The difference lies in the value of k_θ which is zero in Kleinman's work but has the same non-zero value in both of the WWW studies. The difference between the parameterizations of Refs. 3 and 4 is the value of θ_0 , being either 180° (potential SKA) or 144° (potential SKB). In this work the parameters for the oxygen bond-angle term have been modified to better fit the experimental bond-angle distribution (potential SKC).

In addition to the Keating potential a repulsive potential is added to prevent nonbonded atoms from overlapping during the simulation. This potential acts between atoms that are neither nearest neighbors nor second nearest neighbors with respect to the bond topology. This prevents the overlap of two nonbonded atoms during the minimization scheme. In this work a simple form was chosen to describe the repulsive potential:

$$V_r = \begin{cases} \frac{1}{2} \sum_{i,j} k^r [r_{ij}^2 - r_r^2]^2, & r_{ij} < r_r \\ 0, & r_{ij} \geq r_r, \end{cases} \quad (3)$$

where the summation goes over atoms i and j , which are neither nearest neighbors nor second nearest neighbors with respect to the bond topology. The radius of the interaction has to be chosen such that it does not affect the energetics of allowed amorphous silica structures. The distance between oxygen atoms which are second nearest neighbors with re-

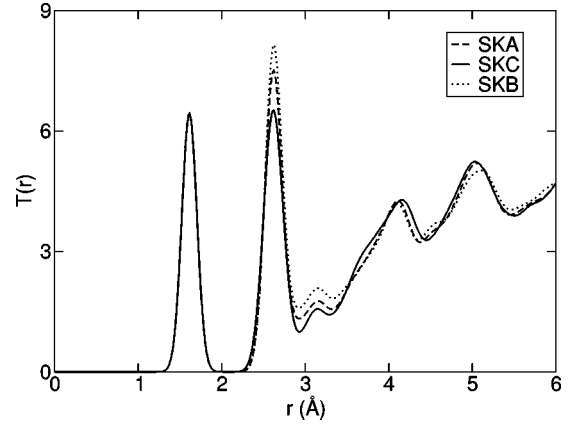


FIG. 1. Comparison of the radial distribution function $T(r)$ of the simplified Keating potentials. Curves have been convoluted with a Gaussian distribution with $\sigma=0.09$.

spect to the bond topology is 2.6 \AA , which was the value chosen for the distance r_r . In addition the spring constant k^r was set to 0.8 eV/\AA^4 .

The simulation system used to compare the potentials consists of $N=1536$ atoms arranged in an ideal betacristobalite structure at a density of $0.0662 \text{ atoms/\AA}^3$, which is a typical value for amorphous silica. The initial structure was mixed by doing $N/2$ random bond switches such that they all are accepted. This randomized structure was thereafter cooled down at constant volume from $k_B T=0.5 \text{ eV}$ to 0.05 eV by decreasing the temperature by 5% every $100 \times N$ th trial step. The radial distribution functions are given in the form of a weighted $T(r)$,^{13,14} which can be directly compared with experimental neutron-diffraction data.

In Fig. 1 we show our results for the three parametrizations of the simplified Keating potentials. Comparison of results obtained by using the KA and SKC potentials with experimental data is shown in Fig. 2. The other parametrizations of the original Keating potentials KB, KC, and KD give rise to similar but slightly worse results than KA and are as

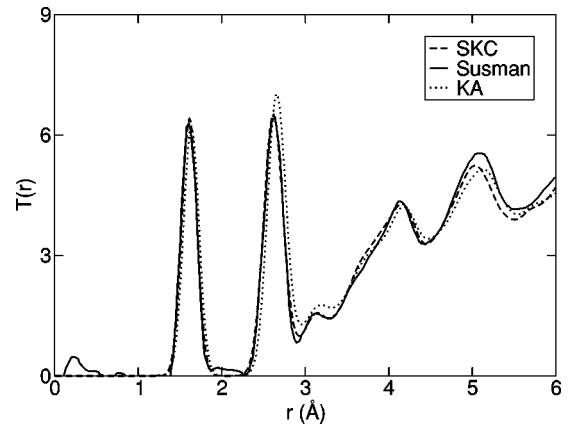


FIG. 2. Comparison of the radial distribution function $T(r)$ obtained by using the KA and SKC potentials with an experimental result (Refs. 13 and 14). The simulated curves have been convoluted with a Gaussian distribution with $\sigma=0.09 \text{ \AA}$ so that the first peak is reproduced correctly.

TABLE III. The mean value and the width of the θ_O (Si-O-Si bond angle) and θ_{Si} (O-Si-O bond angle) distribution and of the r_{SiO} distribution in Å as obtained using the different potentials.

	θ_O	σ_O	θ_{Si}	σ_{Si}	r_{SiO}	σ_{SiO}
Mauri a (Ref. 16)	151.4	11.3				
Mauri b (Ref. 16)	150.6	11.5				
Mozzi & Warren (Ref 15)	147.9	12.7				
KA	141.6	12.6	109.4	3.2	1.62	0.022
KB	139.0	11.9	109.4	3.0	1.60	0.012
KC	137.5	13.6	109.4	3.5	1.61	0.006
KD	137.4	14.1	109.4	4.1	1.62	0.004
SKA	140.2	14.8	109.4	3.1	1.60	0.010
SKB	133.1	14.2	109.4	2.7	1.60	0.008
SKC	148.1	11.7	109.4	4.4	1.60	0.013

such not plotted here. The second peak in $T(r)$ is the first O-O peak of two oxygen atoms that are connected to the same silicon atom. As one can see our reparametrized simplified Keating potential SKC yields the best result. This is because the stronger oxygen bond-bending term leads to a broader silicon angle and bond length distribution. The broader silicon angle distribution widens the second peak and thus the results get better. The differences in the curves are not large as the radial distribution function is not as sensitive to changes in the structure as some other characteristics are. For two systems to have a similar structure not only the peak positions have to be identical but also the areas under the peaks. From Fig. 2 it can be seen that the curve of SKC is very close to the experimental one which suggests that the short and medium ranged structure is quite realistically described. In Table III we present the results for the width and position of the bond-length distribution. The small width of the distributions is explained by the fact that the atoms in the WWW simulations are located in their 0-K position as a result of the minimizations.

Let us now move on to look at the bond-angle distribution in the network system, which for silica we can define two, namely, the angles O-Si-O and Si-O-Si. The distribution of the O-Si-O angle has a mean value of 109.47° and it is quite narrow. On the other hand the Si-O-Si angle-distribution is much wider with a mean value of 147° - 152° and with a standard deviation of approximately 11° - 13° .^{15,16} In Fig. 3 we show the bond-angle distribution functions obtained with the simplified Keating potentials. Similar to the earlier comparison between radial distribution functions and experimental results we present Fig. 4, where we have plotted bond-angle distributions for KA and SKC models together with experimental results. Once again only the results of the KA parametrization is plotted because KB, KC and KD parametrizations yield qualitatively similar results, but we present the mean value and the standard deviations for the different potentials in Table III. As can be seen from this table both the SKA and SKB parametrizations yield too small a mean value for the Si-O-Si bond angle; in particular the SKB result seems poor (also see Fig. 3). One can clearly see a peak at 125° - 130° which is caused by the high amount of three-

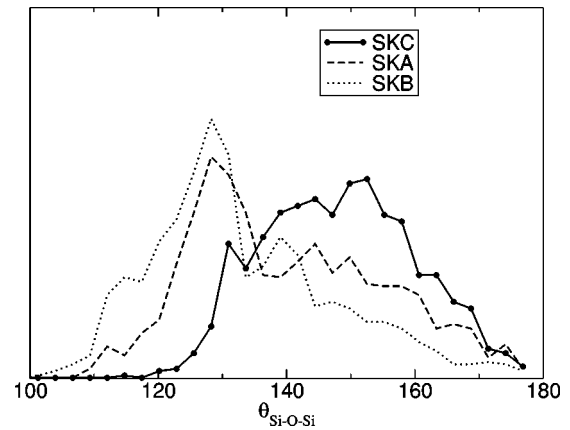


FIG. 3. Comparison of the distribution function of $\theta_{Si-O-Si}$ obtained with the simplified Keating potentials.

membered rings in the systems as well as other highly strained configuration which are especially common on the surfaces of pores.

In the case of the original Keating potential parametrizations the mean values of the distributions once again show values that are too low. However, as can be seen in Fig. 4 and Table III, the SKC parametrization yields a bond angle distribution and a mean value very close to those obtained experimentally. The reason for this is that the stronger bond-bending force constant favors higher oxygen-angle values while making the width of the silicon-angle and the bond-length distributions wider. The value of $k_{Si-O-Si}^\theta$ was chosen so that the distribution of the oxygen-angles is correct. This is the feature that all the other potentials fail to model correctly.

Next we will discuss the ring structure of amorphous silica. It is noted that when calculating the length of a ring in silica oxygen atoms are not included; only silicon atoms are taken into account. In real amorphous SiO_2 small rings are found to be inherent. This has been seen experimentally as two distinctive lines in the Raman spectra¹⁷ corresponding to three- and four-membered rings. The two-membered rings have a considerably higher energy and are as such very unlikely to occur. The elastic energy of two-, three-, and four-

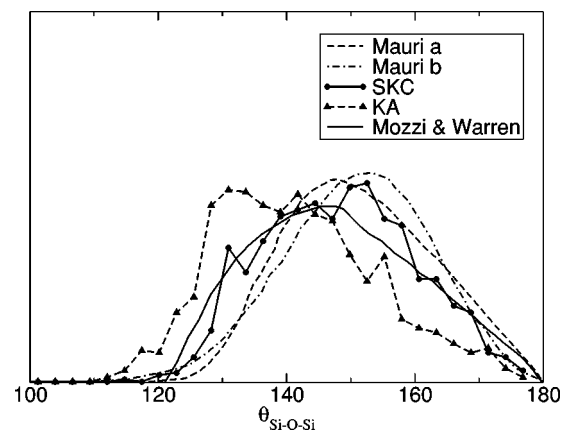


FIG. 4. Comparison of the distribution function of $\theta_{Si-O-Si}$ obtained with KA and SKC potentials with experimental data.

TABLE IV. The shortest-path ring statistics of the model potentials. The $6N_{\text{Si}}$ rings have been normalized with N_{Si} .

	3	4	5	6	7	8	9	10
KA	0.29	0.94	1.33	1.64	1.13	0.54	0.12	0.008
KB	0.41	0.89	1.35	1.53	1.16	0.55	0.11	0.008
KC	0.49	0.89	1.32	1.33	1.21	0.62	0.13	0.012
KD	0.46	0.83	1.35	1.48	1.22	0.54	0.13	0.008
SKA	0.45	0.88	1.22	1.48	1.23	0.59	0.15	0.006
SKB	0.65	0.88	1.23	1.41	1.08	0.56	0.16	0.038
SKC	0.17	0.86	1.62	1.65	1.14	0.50	0.06	0.004
Rino (Ref. 1)	0.06	0.52	1.4	2.11	1.18	0.40	0.06	0.01

membered rings have been calculated based on an *ab initio* method for small SiO_2 clusters.¹⁷

In order to investigate how well the potentials used in this study describe small rings, free clusters consisting of two-, three-, or four-membered rings were constructed. Potentials KB and SKC yielded the most realistic values for the three-membered rings. Of these two only the SKC model also yields an acceptable value for the two-membered ring. As for the other models SKB yields a very low value for the potential energy of a three-membered ring. Distributions of rings of different sizes in the simulated systems were calculated by starting from all bond angles of each silicon atom. Thus we have $6N_{\text{Si}}$ rings, where $N_{\text{Si}}=N/3$ is the number of silicon atoms. For a certain silicon angle created by two bonds the ring is defined to be the shortest path from one bond to the other. The ring distributions are given in Table IV, where they are also compared to a previous MD study¹ which used a more complex interatomic potential model. Results from potentials with smaller energies for the three-membered

rings yield a much larger proportion of these rings. This can be seen for both SKA and SKB models. Also the original Keating potentials (KA, KB, KC, and KD) yield a fairly large number of three-membered rings. On the other hand, the results of the SKC model are nearest to those obtained from the MD study. The higher number of six-membered rings these two models the (SKC model and Rino's MD model) have compared to the other models suggest that they have a more ordered structure.

In this work we have shown that none of the earlier Keating-type potential models for $\alpha\text{-SiO}_2$ gives a realistic description of the material. The largest difference between the experimental results and the simulations is in the distribution of the oxygen bond angle. We have also done a reparametrization of the simplified Keating potential where we make the oxygen bond-bending term stronger so that the oxygen angle distribution is reproduced correctly. It is also shown that this reparametrization reproduces the other structural properties we have looked at better than the previous ones, e.g., the radial distribution function and the bond-angle distribution.

The final conclusion is that using this potential model one is able to create amorphous silica models with the WWW method that have a realistic short and medium range structure. These models are thus suitable for further studies of the properties of this material.

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