Force Fields for Silicas and Aluminophosphates Based on *Ab Initio* Calculations

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(Received 11 December 1989)

We address the problem of finding interatomic force fields for silicas from *ab initio* calculations on small clusters. It is shown that the force field cannot be determined from cluster data alone; incorporation of bulk-system information into the force field remains essential. Bearing this in mind, we derive a force field based on both microscopic (*ab initio*) and macroscopic (experimental) data. This force field combines accuracy with transferability to other polymorphs. The possibility of parametrizing other elements is also demonstrated.

PACS numbers: 71.45.Nt, 71.10.+x, 78.30.Hv, 91.60.−x

Theoretical modeling of complex solids such as large silica polymorphs, which include zeolites, uses the classical force-field approach because accurate *ab initio* quantum-chemical calculations on solids with large unit cells or amorphous compounds are not yet feasible.[1] Within this approach the interatomic interactions are described by simple two- or three-body potentials. Historically, these potentials were determined empirically, i.e., chosen so as to given the best description of a set of experimental quantities.[2] Recently, Lasaga and Gibbs[3,4] and Tsuneyuki *et al.*[5] have derived potentials for silica based on *ab initio* calculations on small clusters. While the latter approach is more attractive from a theoretical point of view, these force fields give a less accurate description of α quartz than the empirical force field. In this Letter, we present a scheme for the development of bulk force fields, starting from *ab initio* calculations on small clusters which are representative of the infinite system. It will be shown that cluster calculations provide a solid basis for the development of a bulk force field, ensuring that nearest-neighbor interactions are properly described. However, the fact that the interatomic potentials range beyond nearest-neighbor distances makes it essential to incorporate information on the infinite system (e.g., α quartz) into the force-field derivation.

H_4SiO_4 is the simplest cluster that contains the SiO_4 building unit of the silicas. We have calculated the potential-energy surface of this cluster for a distortion mode in which the Si-O bond is stretched symmetrically (T_d mode) and for one where the oxygen atoms bend towards one another pairwise (D_{2h} mode). In both cases we started from the optimized geometry of the cluster ($d_{\mathrm{SiO}} = 1.63$ Å, $d_{\mathrm{OH}} = 0.95$ Å, $\Theta_{\mathrm{OSiO}} = 109.47°$, and $\Theta_{\mathrm{SiOH}} = 119.52°$). For the T_d mode self-consistent field (SCF) calculations were performed for Si-O distances between 1.35 and 2.00 Å at 0.05-Å intervals. The O-Si-O angle varied between 70° and 150° (5° intervals) in the D_{2h} mode. For these calculations we used the GAMESS code.[6] The core electrons were treated with the pseudopotential approach of Barthelat, Durand, and Serafini,[7] while the remaining electrons were described using the valence part of the 6-31-G basis,[8] augmented with d-polarization functions on silicon ($\alpha = 0.45$) and oxygen ($\alpha = 0.8$). The potential energy for the T_d mode is quite similar to that obtained by Tsuneyuki *et al.*[5] The energy differences within this part of the potential-energy surface are roughly 10 eV.

The proposed interatomic potentials of the force field are of the form

$$\Phi_{ij} = q_i q_j / r_{ij} + A_{ij} \exp(-b_{ij} r_{ij}) - c_{ij} / r_{ij}^6 , \qquad (1)$$

where Φ_{ij} is the interaction energy of atoms i and j, which consists of a Coulomb term and a covalent (short-range) contribution, cast into the usual Buckingham form. The Coulomb forces are described by a single free parameter, the effective silicon charge. The condition of charge neutrality then fixes $q_{\mathrm{O}} = -\frac{1}{2} q_{\mathrm{Si}}$. We allow for only two different short-range interactions: Si-O to describe the silica bond and the O-O nonbonded interaction, which modifies the Coulomb repulsion and ensures the tetrahedral arrangement of oxygen atoms around the silicon atom. For the description of the cluster potential-energy surface, we have to take the hydrogen atoms into account as well. We can restrict ourselves to an electrostatic interaction ($q_{\mathrm{H}} = \frac{1}{4} q_{\mathrm{Si}}$), since the O-H bond length is kept constant.

The choice of modes allows separate fitting of the various interactions. The D_{2h} mode determines the O-O interaction; once this interaction is parametrized, the T_d mode can be used to fit the Si-O interaction. With a particular choice for q, the latter interaction can be fitted unambiguously. A subtlety arises for the O-O parameters. In previous attempts,[4,5] these parameters were all determined on the basis of cluster information alone. If this is done, a very good description of the potential-energy surface of the cluster is found, but the set of pa-

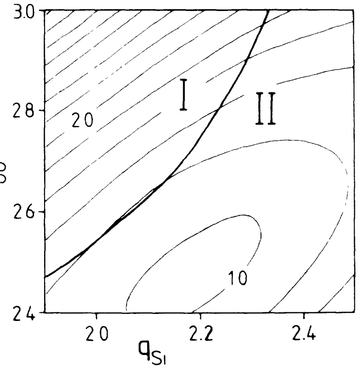

FIG. 1. Two-dimensional phase diagram of quartz in "bulk" parameter space ($c_{OO}=0$). The contour plots represent the χ^2 values of the fit to the *ab initio* data. The minimum corresponds to an average difference of 0.01 eV between force-field prediction and SCF energy. The thick line denotes the α-β phase boundary obtained when the force fields are applied to quartz (I denotes α; II is β).

rameters is to some extent redundant: Reasonable fits to the cluster data can be found for a whole range of parameter combinations, but the predictions for α quartz vary dramatically. If one derives a force field solely on the basis of cluster information, its accuracy when applied to bulk silica is unpredictable. To illustrate this, we vary both the effective silicon charge ($1.9 < q_{Si} < 2.5$) and the repulsion exponent of the O-O interaction ($2.4 < b_{OO} < 3.0$ Å^{-1}), keeping $c_{OO}=0$. These parameters will be referred to as "bulk" parameters. For each choice of q_{Si} and b_{OO}, we fit the remaining parameters to the *ab initio* data (A_{OO}, A_{SiO}, b_{SiO}, and c_{SiO}, referred to as "cluster" parameters). The D_{2h} mode is thus described by a single free parameter. Still, the description of the *ab initio* energy surface is accurate to within 0.1 eV; the average error does not exceed 0.02 eV.

With all force fields derived in this way, we have performed unrestrained lattice minimizations[9] of α quartz. It has been found that the energy-minimized structure does not always have the α-quartz symmetry. For α quartz the fractional coordinates of the silicon atoms are ($uu\frac{1}{3}$), ($u00$), and ($0u\frac{2}{3}$), with $u=0.4697$ (experimentally). For β quartz, the high-temperature phase of α quartz, they lock to the symmetric position $u=\frac{1}{2}$.[10] Figure 1 shows both the χ^2 values of the best fits of cluster parameters to the *ab initio* data and the symmetry of quartz after energy minimization with these force fields. Surprisingly, the best description of the cluster data (lowest χ^2) is given by a set of parameters that yield the wrong low-temperature symmetry of quartz. Along with the symmetry change, the values of elastic constants change dramatically.

Figure 2 shows the ratio of computed to experimental values for the unit-cell dimensions and the diagonal elements of the elastic tensor for one-dimensional scans of bulk parameters q_{Si} and b_{OO}. At the α-β phase boundary there is a discontinuity for the elastic constants C_{11} and C_{33}. Along with it (not shown in the graph) C_{14} vanishes as required by the new symmetry conditions. This observation makes clear that it is essential for the development of a high-quality force field to include data on an infinite system (albeit experimental or theoretical) in the fitting procedure.

We note that in the literature[4,5] authors have often developed a series of force fields, each with different charges, ultimately selecting the one with the highest predictive power. Although it is not explicitly mentioned in the above articles, one might say that the charge is fitted to (experimental) bulk quantities. While these authors justify their external adjustment of effective charge by pointing to the long-range character of the Coulomb force, we find that adjustment of short-range parameters to bulk properties is also inevitable. Our calculations indicate that this problem is not eliminated by considering

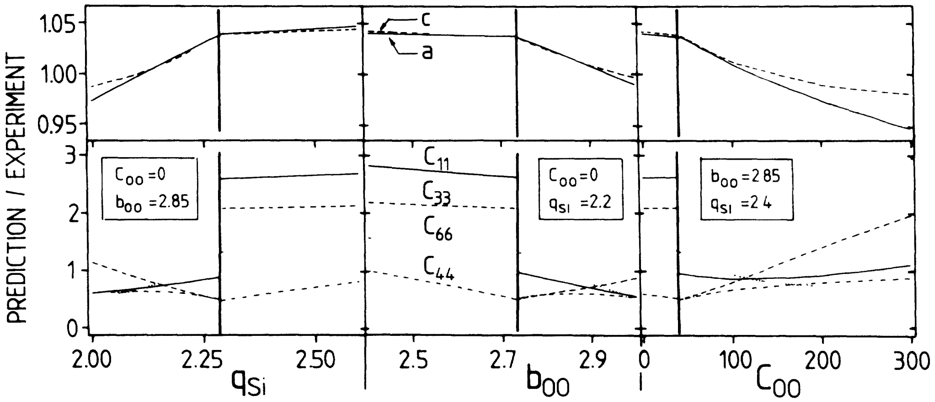

FIG. 2. Force-field predictions for all the cell dimensions (upper curves) and elastic constants (lower curves), scaled to the experimental values for α quartz vs bulk parameters q_{Si}, b_{OO}, and c_{OO}. The thick lines indicate the α-β transition; the latter phase is characterized by extremely high values of C_{11} and C_{33}. Note that the curves for q_{Si} and b_{OO} are almost perfect mirror images of each other.

TABLE I. Force-field parameters.

	Short-range parameters			Atomic
i-j	A_{ij} (eV)	b_{ij} (Å^{-1})	c_{ij} (eV Å^6)	charges
O-O	1388.7730	2.76000	175.0000	$q_O = -1.2$
Si-O	18003.7572	4.87318	133.5381	$q_{Si} = 2.4$
Al-O	16008.5345	4.79667	130.5659	$q_{Al} = 1.4$
P-O	9034.2080	5.19098	19.8793	$q_P = 3.4$

larger clusters like $H_6Si_2O_7$; the effect of the short-range interactions over intertetrahedral distances is only properly accounted for if bulk information is used.

By iterating between fitting of the cluster parameters to the *ab initio* data and optimizing the values of bulk parameters by comparison of the predictions of elastic constants and unit-cell dimensions for quartz with experiment,[11,12] we have derived a mixed *ab initio* empirical force field, the parameters of which are given in Table I. It proved to be essential to include a nonzero c_{OO} term. As is evident from Fig. 2, the effect of increasing q_{Si} is quite similar to a decrease in b_{OO}. While the respective roles of these parameters are to some extent interchangeable, the effect of varying c_{OO} is different, which justifies the inclusion of a r^{-6} term to improve the quality of the force field.

The results of a lattice energy minimization of quartz with our force-field parameters are given in Table II, where they are compared both with experiment and with results obtained with Tsuneyuki's *ab initio* force field as well as with two empirical force fields. Both the lattice parameters and the elastic constants are described better by our force field than by all other force fields. The potentials also have an increased accuracy when applied to the other SiO_2 polymorphs: α cristobalite, coesite, stishovite, and the molecular sieve silicalite. Comparison with experiment and with results obtained with the Tsuneyuki potentials reveals that our force field is more accurate by a factor of 2. This proves that incorporation of α-quartz data into the fitting procedure enhances the predictive power for all extended structures and not for α quartz alone.

Apart from giving a very accurate description of many physical properties of quartz, the present approach to force-field development has another major advantage. It can easily be extended to include other chemical elements that form tetrahedral network oxides, in particular, $AlPO_4$ compounds. Al-O and P-O interaction parameters have been determined from a series of SCF calculations on $Al(OH)_4{}^-$ and $P(OH)_4{}^+$ clusters distorted along the T_4 mode. In these calculations we have used a basis set of the same quality as for the $Si(OH)_4$ cluster. As our aim is to find transferable potentials, we adopt the same O-O potentials as for SiO_4. This immediately fixes the sum of charges of phosphorus and aluminum; the only degree of freedom left is the charge separation between Al and P. In view of the applicability of the potentials to zeolites, we have set the charge ***difference*** equal to the difference of formal charges.

Like the Si-O parameters, the Al-O and P-O parameters prove to be cluster parameters that can be determined unambiguously from the potential-energy surface of the clusters. The potential parameters are given in Table I. Application to berlinite,[13] the $AlPO_4$ analog of α quartz, and three of its polymorphs with well-determined structures [ALPO-5, ALPO-11, and VPI-5 (Ref. 14)] provides good insight into the possibility of extending a force field along the present route.

Table III gives the average ratio between force-field results and experiment, along with the mean deviation.

TABLE II. Comparison of force fields for α quartz. The numbers in parentheses are the quotient of calculated and observed values. Lengths are in Å. d_{SiO_1}-d_{SiO_2} is the difference in Si-O distance within a tetrahedron. The elastic constants (C_{ij}) are in 10^{11} dyn/cm^2.

		Ab initio		Empirical force fields[c]	
Observable	Expt.[a]	This work	Tsuneyuki[b]	Shell model	Rigid ion
a axis	4.913	4.941 (1.01)	5.018 (1.02)	4.837 (0.98)	5.312 (1.08)
c axis	5.405	5.449 (1.01)	5.548 (1.03)	5.347 (0.99)	5.895 (1.09)
u	0.4697	0.4648	0.4602	0.4638	0.5000
d_{SiO_1}-d_{SiO_2}	0.009	0.008	0.012	0.012	0.000
∠Si-O-Si	143.7	148.1	146.8	147.3	166.1
C_{11}	8.68	9.05 (1.04)	7.17 (0.83)	9.47 (1.09)	19.19 (2.21)
C_{33}	10.58	10.70 (1.01)	9.09 (0.86)	11.60 (1.08)	19.84 (1.88)
C_{44}	5.82	5.02 (0.86)	4.03 (0.69)	5.00 (0.85)	4.20 (0.72)
C_{66}	3.99	4.12 (1.03)	3.15 (0.79)	3.81 (0.95)	3.94 (0.99)
C_{12}	0.70	0.81 (1.16)	0.87 (1.24)	1.83 (2.61)	11.30 (16.1)
C_{13}	1.91	1.52 (0.80)	1.17 (0.61)	1.96 (1.02)	14.04 (7.20)
C_{14}	−1.80	−1.76 (0.98)	−1.43 (0.79)	−1.45 (0.80)	0.00 (0.00)

[a] References 11 and 12.

[b] Reference 5.

[c] Reference 1.

TABLE III. Reliability of force-field predictions, as obtained from comparison of prediction with experiment for five SiO_2 polymorphs and the four $AlPO_4$ polymorphs mentioned in the text. The numbers denote the average ratio between calculation and experiment and the spread therein.

Type of observable	SiO_2 polymorphs	$AlPO_4$ polymorphs
Unit-cell dimensions	1.00 ± 0.02	1.02 ± 0.02
Elastic moduli	1.10 ± 0.18	1.09 ± 0.21

Discrepancies between theory and experiment, in both structure and elastic properties, are similar for the $AlPO_4$ and SiO_2 systems. This is most encouraging, as the number of force-field parameters has increased and we have not taken any new bulk information into account. We note in passing that the large number of free parameters has so far hindered the development of an empirical force field for AlPO.

In conclusion, accurate force fields can be developed to model the properties of solids, starting from *ab initio* calculations on small clusters. This yields a proper microscopic basis for the nearest-neighbor interaction and ensures that the force field is applicable to different polymorphs. As the range of the interatomic forces goes beyond nearest neighbors, it is inevitable to complement microscopic information with macroscopic information. A combination of these two sources, which is new in force-field development, has been shown to produce a force field of unsurpassed accuracy, with a high degree of portability to polymorphs and extentability to other systems. While we have focused on silicas and aluminophosphates, we expect our approach to be of equal importance for force fields for other systems, e.g., (amorphous) carbon or silicon.

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