JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 19 15 NOVEMBER 2002

An *ab initio* parametrized interatomic force field for silica

P. Tangney[a] and S. Scandolo
Princeton Materials Institute and Department of Chemistry, Princeton University, Princeton, New Jersey 08540, and International School for Advanced Studies, via Beirut 2-4, 34013 Trieste, Italy, and INFM/Democritos, National Simulation Center, via Beirut 2-4, 34013 Trieste, Italy

(Received 7 June 2002; accepted 20 August 2002)

We present a classical interatomic force field for liquid SiO_2 which has been parametrized using the forces, stresses and energies extracted from *ab initio* calculations. We show how inclusion of more electronic effects in a phenomenological way and parametrization at the relevant conditions of pressure and temperature allow the creation of more accurate force fields. We compare the results of simulations with this force field both to experiment and to the results of *ab initio* molecular dynamics simulations and show how our procedure leads to comparisons which are greatly improved with respect to the most widely used force fields for silica. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1513312]

I. INTRODUCTION

Silica is ubiquitous in nature and is of enormous technological importance. It also serves as a prototype material for many other network-forming materials. For this reason its structural and dynamic properties have been extensively studied both experimentally and by means of simulation.[1] However, many questions remain about its microscopic bonding properties and their relationship to experimentally observed macroscopic properties. In addition to this, the thermodynamic behavior of silica under extreme conditions such as those found deep in the Earth's mantle is of interest to geophysicists. Experimental techniques have not yet evolved to the point where the properties of materials can be well constrained under such high temperatures and pressures. Atomistic simulation would seem to be a natural solution for studying silica and other minerals since, in principle at least, it allows full access to the microscopic mechanisms at work and it is not constrained to any given pressure or temperature range.

The development of accurate interatomic force fields is crucial for simulation to be of use. In this paper we describe the construction of a force field for silica and show how the use of information from *ab initio* electronic structure calculations is an important ingredient in the parametrization and testing of any empirical potentials.

We may divide atomistic approaches into two distinct categories: *ab initio* and empirical approaches.

Ab initio approaches[2,3] allow a very accurate description of the energy surface on which the ions move but with the serious drawback that the size of the system and the time scale of the simulation which is affordable are small (typically less than a few hundred atoms and less than a few picoseconds on a parallel supercomputer). For a number of dynamic and thermodynamic quantities this can be problematic as finite-size errors may be larger than is desirable. The problem is particularly severe in silica, both in the solid and in the liquid phases. Liquid silica is highly viscous and thus atomic diffusion is very slow, requiring long simulation times. A remarkable structural complexity characterizes the solid portion of the phase diagram, requiring large simulation cells. In both cases, sizes and timescales affordable with *ab initio* methods do not allow a reliable estimate of quantities such as viscosity and compressibility (in the liquid) and finite-temperature elastic constants, thermal conductivity and phase boundaries (in the solid), just to name a few.

In empirical approaches the interatomic potential is given as an explicit function of the atomic coordinates, the so-called force field. The representation of electronic effects in a simplified phenomenological way allows an increase in efficiency relative to *ab initio* methods of many orders of magnitude and this results in reduced finite-size effects and much greater precision in the calculation of thermodynamic and dynamic averages. However this is at the expense of considerable loss of accuracy in the description of the ions' potential energy surface.

The reliability of an empirical force field depends on two key elements. First, a force field must capture phenomenologically the electronic effects which are important for ionic motion. Such requirement can be met by tailoring its functional form so as to include the relevant phenomenology. However, even in the case of simple ionic systems, such as SiO_2 and MgO, this represents a challenge.[4,5] The long-range nature of interactions and the distortability of the oxide ions mean that forces are truly N-body in character and cannot be well approximated as a sum of two-body and three-body contributions.

Particularly if one wants to model disordered phases, it is important that the empirical model used is sufficiently general to include N-body interactions. Rowley *et al.*[5] have shown, in the case of solid MgO, how careful inclusion of all the physical processes at work allows one to accurately reproduce phonon spectra.

The second element that determines the reliability of a force field is the method by which the model is parametrized.

---

[a] Author to whom correspondence should be addressed. Electronic mail: tangney@sissa.it

Force fields may be parametrized either by fitting to experimental data, or by fitting to *ab initio* calculations, or both. A problem with many of the empirical force fields which have been used in the past is that they have been designed to reproduce a particular property (e.g., experimental geometries or *ab initio* energetics[6,7]) and then used in different physical situations to predict different properties. In order to be able to confidently transfer a potential from the physical situation in which it is parametrized to the situation in which it is to be used, one needs to be confident that the model is flexible enough in terms of its representation of the relevant electronic effects to extend between the two situations. For example, changes in pressure may lead to fundamental changes in electronic structure. Unless the empirical model used can represent these changes in a phenomenological way, a potential parametrized at a given pressure may lose accuracy when it is applied at a different pressure. Similarly, a potential which is parametrized to reproduce the properties of clusters[6,7] may suffer a loss of accuracy when it is applied to a bulk system. This may be due both to differences in the local electronic structure of atoms between clusters and bulk systems and, particularly in ionic systems, the contribution of long-range electrostatic interactions to the forces experienced by ions.[8] Recently it was shown that the reliability of an empirical force field can be increased dramatically by restricting both the fitting procedure and the domain of application of the force field itself to a well-defined physical situation.[9]

The goal of the present work is to construct an improved force field for silica at low pressure by attending to the two key considerations outlined above. To improve the ability of the potential to capture the important electronic effects we have taken account of the large polarizability of the oxygen ion. The parametrization is improved[10] by parametrizing this model using *ab initio* data (forces, stresses, and energies) on configurations generated at low pressures. We compare results using this potential with one of the most commonly used pair potentials for silica[6] and with the results of *ab initio* molecular dynamics simulations, and show that our strategy improves significantly the accuracy of current force fields for silica.

There have been a large number of potentials proposed for silica. Many of these, such as the three-body potential of Vashishta *et al.*[11] are intrinsically biased in favor of a tetrahedral crystal structure and therefore are poor subjects for comparison since we aspire to creating a potential which is suitable for disordered phases. Demiralp *et al.*[12] have proposed a many-body potential for silica which improves on the prediction of the crystal structures with respect to pair potentials. The many-body character of this potential is a charge equilibrium model which allows for local changes in the ionicity. Although it is very likely that the degree of ionicity changes with pressure, there is no evidence to suggest that this happens dynamically at a given pressure or temperature. The polarizability of the oxygen ion is well established however[13,14] and it may be that inclusion of charge-transfer mimics to a certain extent the effects of polarization. It is likely that inclusion of charge transfer is necessary for transferability between polymorphs with different silicon coordination. For example, for modelling the pressure induced transition from fourfold coordinated quartz to sixfold coordinated stishovite. A polarizable potential for silica has previously been proposed by Wilson *et al.*[13] and shown to be important for reproducing the infrared absorption spectrum of the amorphous solid. For this model the parameters were empirically chosen whereas here all parameters are found from *ab initio* data. Other differences between the force field of Ref. 13 and the one proposed here include differences in the nonelectrostatic pairwise interaction terms and different methods of evolving the dipole field.

Here we concentrate on comparison with one of the most commonly used potentials for silica and with the results of *ab initio* molecular dynamics simulations. The pair potentials of van Beest, Kramer, and van Santen, (BKS)[6] and Tsuneyuki *et al.* (TTAM)[7] have been extensively used in the past to model silica. We point out some limitations of the mathematical form of these potentials and show how our polarizable potential improves significantly the description of the various silica structures with respect to the BKS potential. We restrict our comparison to the BKS parametrization as this gives better crystal structures than TTAM and most of the problems with these potentials is attributable to their functional form which is identical.

II. FITTING EMPIRICAL POTENTIALS TO *AB INITIO* DATA

In this section we describe the empirical model that we have used for silica, the details of the *ab initio* calculations to which we have fit the parameters of the classical potential and the method used to generate these parameters from the *ab initio* calculations.

A. Modeling ionic systems

In atomistic simulations, the ionic limit is normally represented by a pair potential consisting of point charge electrostatic interactions, a short range exponential repulsion to approximate the overlap repulsion between rigid localized orbitals on nearby atoms and longer-range nonelectrostatic attractive terms. For silica the commonly used form is the following Born–Mayer form:[8]

$$U_{ij}=\frac{q_i q_j}{r_{ij}}+B_{ij}e^{-\alpha_{ij}r_{ij}}-\frac{C_{ij}}{r_{ij}^6}, \tag{1}$$

where U_{ij} is the interaction energy between ions i and j, $r_{ij}=|\mathbf{r_i}-\mathbf{r_j}|$ is the distance between ions i and j, q_i is the charge of ion i which plays the role of a parameter and B_{ij}, α_{ij}, and C_{ij} are constant parameters.

There have been a number of parametrizations of this potential form for silica in the past.[7,6,15] Most recently, van Beest, Kramer, and van Santen (BKS)[6] have fit the parameters to reproduce the energetics of small hydrogen-terminated silica clusters as well as the experimental structural parameters and elastic constants of quartz. The resulting potential has been extensively applied to study a large range of dynamic and thermodynamic properties of silica in many different phases and under many different thermodynamic conditions.[16]

The use of the BKS potential as a realistic representation of silica assumes that (i) the electronic structure of silica is well described as a system of small rigid spherically symmetric ions which are undistorted by their environment; (ii) there is no significant difference in the electronic structure of the Si and O ions across the different phases, pressures and temperatures; (iii) the electronic structure of ions in bulk silica is well described by that in small clusters.

Clearly, these assumptions have a limited range of validity. It has been shown that even in the simplest oxides the oxygen ion is highly deformable[5] and polarizable[13] and that this can have a significant effect on the dynamic properties. In addition, one may expect gradual changes in electronic structure with pressure which result in changes in the relative stabilities of the various polymorphs and, at 8 GPa, in changes in silicon coordination from 4 to 6. Moreover, the long range electrostatic response of a bulk system is only marginally present in a small cluster.

Here we show how more realistic potentials may be constructed for ionic systems if one goes beyond the approximations inherent in previous approaches. Major differences between this approach and other standard approaches include: (a) Following Wilson and Madden,[13,17] we use a more flexible form for the potential which incorporates the effects of dipole polarization of the oxygen ions including the effective dipoles induced by the short-range forces between ions. (b) Since the force field is to be designed for use in bulk silica, the *ab initio* calculations from which the force field is parametrized are performed on a relatively large unit cell under periodic boundary conditions to minimize the finite size and surface effects which may be present in cluster calculations. (c) We apply the potential to silica at low pressures and so fit the parameters to *ab initio* calculations at low pressures.

Although the inclusion in the potential form of some of the many-body interactions improves the transferability, it should be recognized that no classical model can fully take account of the chemical changes which are possible under different thermodynamic conditions. For this reason we suggest that this potential only be used at very low pressures and that under more extreme conditions, new parametrizations should be performed.

B. The force field

Much work has been done to improve upon the simple Born–Mayer form of the potential for ionic systems. For MgO, which is one of the simplest oxides, there has been a detailed analysis of the many-body contributions to the interionic forces.[5] It has been shown that the dominant many-body effects are due to the polarizability and the compressibility/distortability of the oxygen ions. Here we concentrate on the electrostatic effects which are the most important for determining structure.

We use a potential of Morse–Stretch form to describe the pairwise interactions between ions

$$U_{ij}=\frac{q_i q_j}{r_{ij}}+D_{ij}\left[e^{\gamma_{ij}[1-(r_{ij}/r_{ij}^0)]}-2e^{(\gamma_{ij}/2)[1-(r_{ij}/r_{ij}^0)]}\right], \tag{2}$$

where the interaction between an atom of type i and an atom of type j is defined by the parameters q_i, q_j, D_{ij}, γ_{ij}, r_{ij}^0 and the distance between them r_{ij}. This form was chosen over the Born–Mayer form as it proved to be more transferable between different phases. The exponential part of this potential was truncated at a radius of 18 a.u. The pair potentials of Eqs. (1) and (2) both diverge for small bond lengths, and this may often be a problem at high temperatures and pressures. However, one of the benefits of our parametrization procedure (to be discussed in Sec. II C) is that it provides us with parameters for which this problem is extremely rare, at least at the thermodynamic conditions discussed in this paper. Nevertheless, as a failsafe procedure, one may replace this potential with a quadratic form for distances $r < r_c$, where r_c is just greater than the position of the maximum in the potential, provided that the two potentials are matched in value and derivative at r_c.

In addition to this pair potential we have included the effects of dipole polarization of the oxygen ions. A single parameter α, corresponding to the dipole polarizability, is assigned to the oxygen ion.

Following Madden *et al.*[5] we have allowed for the induction of dipole moments both by electrostatic forces and the short-range repulsive forces between anion and cation, where the short-range contribution to the dipole moments is given by

$$\mathbf{p}_i^{\mathrm{SR}}=\alpha\sum_{j\neq i}\frac{q_j\mathbf{r}_{ij}}{r_{ij}^3}f_{ij}(r_{ij}), \tag{3}$$

where

$$f_{ij}(r_{ij})=c\sum_{k=0}^{4}\frac{(br_{ij})^k}{k!}e^{-br_{ij}} \tag{4}$$

and $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$ and b and c are parameters of the model.

The dipole moment on each ion must then be computed and the charge–dipole and dipole–dipole interactions calculated using an Ewald summation scheme. The standard method of evolving the dipole field is to use a fictitious Lagrangian approach in which the dipoles are evolved in a manner analogous to the Car–Parrinello method for electronic structure calculations.[17,18] However, recent work[19] has pointed out that this method does not allow the fictitious degrees of freedom to take their minimum energy values on average as had previously been thought. It is not known how relevant this problem is in the case of polarization but to avoid any possible biasing of the dynamics we have chosen a different approach in this work.

The dipoles on each ion are found self-consistently at each time step by iterating to self-consistency the equation

$$\mathbf{p}_i^n=\alpha\mathbf{E}(\mathbf{r}_i;\{\mathbf{p}_j^{n-1}\}_{j=1,N},\{\mathbf{r}_j\}_{j=1,N})+\mathbf{p}_i^{\mathrm{SR}}, \tag{5}$$

where the dipole moment on ion i, $\mathbf{p}_i$ depends on the electric field $\mathbf{E}(\mathbf{r}_i)$ at position $\mathbf{r}_i$ which in turn depends on the positions and the dipole moments of all the other ions. At each time step the iteration is begun using initial electric field strengths $\{\mathbf{E}^0(\mathbf{r}_j)\}_{j=1,N}$ which have been extrapolated from their values at the previous three time steps. The fact that the polarization scheme can never be perfectly converged leads to a drift in the conservation of energy in a molecular dynamics simulation, however, for the simulations of liquid silica at 3100 K reported below the rate of drift of energy was less than a total of 5 K over a 100 ps run. We have used a time step to integrate the equations of motion of 0.723 femtoseconds and for 576 atoms the CPU time required for each calculation of all contributions to the energy, forces and stress was less than 8.0 seconds on a single 300 Mhz SGI origin MIPS R12000 processor. This time is significantly reduced at lower temperatures and for systems of higher symmetry where fewer iterations are required to converge the dipole field. It may also be reduced in a variety of ways by allowing for a larger drift in the conserved quantity which for these calculations was much smaller than is tolerable. For example, for 576 atoms of quartz at 300 K it was possible to increase the time step to 1.446 fs and decrease the CPU time per step to approximately 5.4 seconds for a drift in the conserved quantity of less than 0.4 K per picosecond.

C. Potential parametrization

The parameters of the empirical force field were found as follows. In order to sample the largest number of uncorrelated configurations we choose to fix the conditions of the fitting procedure at 3000 K and zero pressure. At these conditions silica is in the liquid phase. This ensures that a large number of configurations with different bond geometry and topology are included in the fit. Nonetheless, since the average Si coordination at zero pressure is always close to four, differences in electronic structure between configurations are expected to be smaller than those that would be obtained by including high-pressure configurations (e.g., with sixfold coordinated Si). Therefore, the quality of the fit and, as a consequence, the reliability of the force field at similar conditions (low pressure), are expected to be improved.

Beginning with a suitable starting potential (in this case we use the BKS potential), a molecular dynamics trajectory is generated for the system of interest. From this trajectory a number of atomic configurations (typically 10–15) are chosen which are well separated from one another in time such that correlation between configurations is minimized. *Ab initio* calculations of total energies, forces, and stress are performed on these configurations. The calculations employed density functional theory (DFT)[20] using the plane wave pseudopotential method[21] with a gradient corrected exchange and correlation functional.[22] The differences in the forces for calculations using different approximate exchange and correlation energy functionals (e.g., local density approximation and generalized gradient approximation) are generally slightly smaller, but of the same order as the differences in the forces between the *ab initio* calculation and the best-fit empirical potential. All calculations were performed on periodically repeated unit cells containing 24 SiO_2 units. We used norm-conserving pseudopotentials[23] with s and p nonlocality for Si and s nonlocality for O. The cutoff radii for all channels of the pseudopotentials were $1.10a_B$ for O and $2.04a_B$ for Si. An energy cutoff in the expansion of the wave functions of 130 Rydberg was necessary in order to converge the calculation of the stress.

From these calculations, the potential is parametrized by minimizing the function

$$\Gamma(\{\eta_i\}) = w_f \Delta F + w_s \Delta S + w_e \Delta E \tag{6}$$

with respect to the parameters $\{\eta_i\}$ where

$$\Delta F = \frac{\sqrt{\Sigma_{k=1}^{n_c} \Sigma_{I=1}^{N} \Sigma_{\alpha} |F_{\mathrm{cl},I}^{\alpha}(\{\eta_i\}) - F_{ai,I}^{\alpha}|^2}}{\sqrt{\Sigma_{k=1}^{n_c} \Sigma_{I=1}^{N} \Sigma_{\alpha} (F_{ai,I}^{\alpha})^2}},$$

$$\Delta S = \frac{\sqrt{\Sigma_{k=1}^{n_c} \Sigma_{\alpha,\beta} |S_{\mathrm{cl}}^{\alpha\beta}(\{\eta_i\}) - S_{ai}^{\alpha\beta}|^2}}{3B\sqrt{n_c}},$$

$$\Delta E = \frac{\sqrt{\Sigma_{k,l}^{n_c} ((U_k^{\mathrm{cl}} - U_l^{\mathrm{cl}}) - (U_k^{ai} - U_l^{ai}))^2}}{\sqrt{\Sigma_{k,l}^{n_c} (U_k^{ai} - U_l^{ai})^2}}.$$

Here $F_{\mathrm{cl},I}^{\alpha}$ is the αth component of the force on atom I as calculated with the classical potential, $F_{ai,I}^{\alpha}$ is the force component as calculated *ab initio*, $S_{\mathrm{cl}}^{\alpha\beta}$ is the stress tensor component as calculated with the classical potential and $S_{ai}^{\alpha\beta}$ is the stress tensor component as calculated *ab initio*, B is the bulk modulus,[24] (U_k^{cl} and U_k^{ai} are the potential energy of configuration k as calculated classically and *ab initio*, respectively, n_c are the number of atomic configurations for which *ab initio* calculations have been performed. Once a parameter set has been found, a new molecular dynamics trajectory is generated from which a new set of configurations are extracted. *Ab initio* calculations are performed on these configurations and a new parameter set obtained from these calculations. This process is repeated until the difference in the values of $\Gamma(\{\eta_i\})$ from successive minimizations converges to a small enough value.

Therefore each molecular dynamics trajectory generated during the parametrization process is generated for liquid silica at 3000 K and zero pressure. In order to create a new set of configurations the previously created liquid is heated to a higher temperature (~5000 K) where diffusion is more rapid and allowed to equilibrate for about 20 picoseconds. Then the liquid is gradually cooled over a similar time frame and allowed to equilibrate at approximately 3000 K for a further 20 ps. The configurations on which *ab initio* calculations are performed are extracted from the continuations of these equilibration trajectories and successive configurations are typically separated in time by about 1 ps. The quantities w_f, w_s, and w_e were chosen to reflect the amount of available data for each quantity, i.e., $w_f > w_s > w_e$. It was found

TABLE I. Force field parameters (atomic units).

q_{O}	q_{Si}	α	b	c
−1.382 57	2.765 14	8.893 78	2.029 89	−1.504 35
$D_{\mathrm{O-O}}$		$D_{\mathrm{Si-O}}$		$D_{\mathrm{Si-Si}}$
2.4748×10^{-4}		1.9033×10^{-3}		$-2.084\,60 \times 10^{-3}$
$\gamma_{\mathrm{O-O}}$		$\gamma_{\mathrm{Si-O}}$		$\gamma_{\mathrm{Si-Si}}$
12.070 92		11.152 30		10.455 17
$r^0_{\mathrm{O-O}}$		$r^0_{\mathrm{Si-O}}$		$r^0_{\mathrm{Si-Si}}$
7.170 05		4.637 10		5.750 38

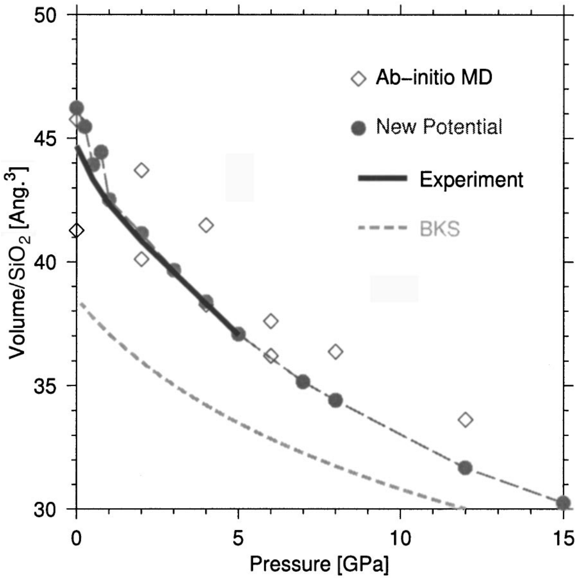

FIG. 1. Equation of state of liquid silica for the new potential compared to experiment (Ref. 26), *ab initio* simulations (Ref. 27) and classical simulations using the BKS potential (Ref. 31). Time and size constraints and the very high viscosity of liquid silica at low pressures mean that the *ab initio* system cannot diffuse enough to give meaningful averages of thermodynamic properties. Different initial configurations account for the different *ab initio* volumes at the same pressure.

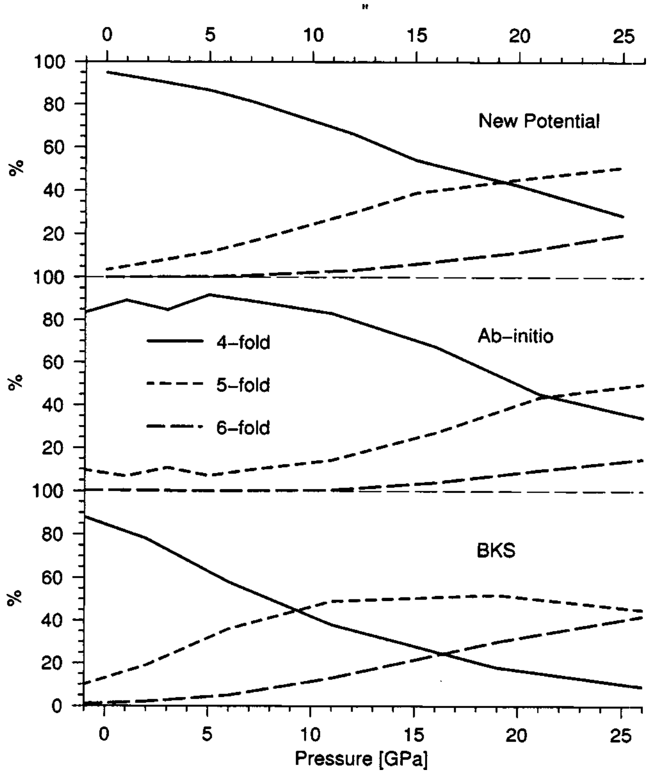

FIG. 2. Percentage of N-fold coordinated silicon atoms in liquid silica as a function of pressure for the new potential compared to *ab initio* simulations (Ref. 27) and the BKS potential (Ref. 31).

that the final fit was quite insensitive to the values chosen as long as w_e was relatively small due to the fact that only one energy may be extracted per configuration.

III. RESULTS

In order to obtain a benchmark for the parametrization of the new potential, we first tested the ability of the BKS potential to fit the *ab initio* data. The values of $\Delta F = 0.51$, $\Delta S = 0.057$, and $\Delta E = 0.82$ that we obtain for the BKS potential in the liquid at 3000 K and zero pressure point to a rather poor accuracy of this potential, at least at our working conditions for the fitting procedure. This is quite surprising if one considers that the ability of the BKS potential to reproduce some structural properties of the solid phases is good overall,[25] and confirms our suggestion that the simplest force fields should be used with great caution at physical conditions that differ from those where they have been parametrized or from those where they are known to provide accurate results. It is possible to substantially reduce these errors by minimizing Γ with respect to the parameters of the Born–Mayer potential, i.e., by constructing the "optimal" Born–Mayer potential for the liquid at 3000 K and zero pressure. However a large number of such minimizations were attempted and although it was possible to reduce ΔF and ΔS to values of about 0.3 and 0.015, respectively, the resulting potentials gave unrealistic values for the structural parameters and densities of the low pressure solid polymorphs. For example, the equilibrium density of quartz at 300 K varied for such potentials between values as low as 0.3 $\mathrm{g\,cm^{-3}}$ and as high as 4.5 $\mathrm{g\,cm^{-3}}$. A minority of these potentials worked reasonably well for quartz but they did not necessarily work well for the other polymorphs and choosing these potentials out of the many created would represent an empirical procedure. Here we would like to create a potential *ab initio*. We have created and tested only one parameter set for the polarizable potential and we report the results of those tests here. It is clear that the rigid ion model is too simple to allow for an accurate description of silica at low pressure and for a temperature range encompassing both solid and liquid phases, and it seems that more ingredients are required in the potential model in order to improve its ability to reproduce the *ab initio* forces.

The results of the fit of the polarizable model described in the preceding section were very encouraging. The values of ΔF, ΔS, and ΔE for the final parameter set were 0.16, 0.014, and 0.18, respectively, indicating a dramatic improvement over BKS, but also over the best (optimal) potential with the Born–Mayer form. The parameters are listed in Table I. The fact that inclusion of polarization both improves the ability of the potential to fit the *ab initio* forces and allows one to forego the empiricism of selecting a potential that reproduces experiment out of more than one created, strongly suggests that polarization is a crucial ingredient in the bonding of silica.

In order to check the reliability of our improved potential we compare its thermodynamic and structural properties with experiments[26] on the equation of state of liquid silica, and with available *ab initio* data[27] on the microscopic structure of the liquid. The equation of state of liquid silica at 3100 K is compared with experiment and with other atomistic simulations in Fig. 1. Volumes were obtained as averages along constant-pressure[28] molecular dynamics runs of at

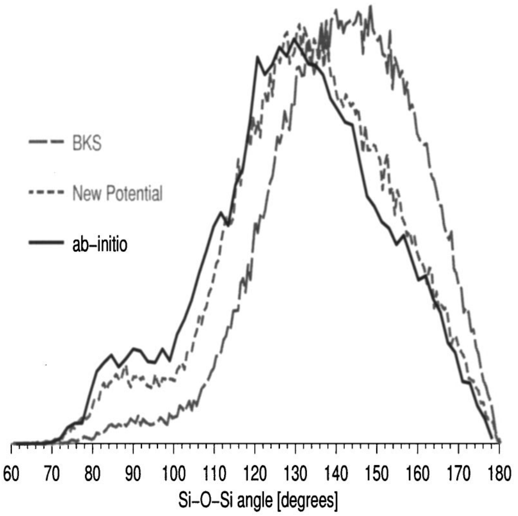

FIG. 3. Oxygen centered angle distribution in liquid silica for the new potential compared to *ab initio* simulations (Ref. 27) and simulations with the BKS potential.

least 50 ps following 20 ps of equilibration and with simulation cells containing 576 atoms. At lower pressures (<3 GPa) where diffusion is slower averages were obtained along runs of more than 100 ps. The temperature in the simulation was substantially larger than that of the experiment since at lower temperatures the time scale for substantial diffusion to occur is much greater than the time scales attainable with molecular dynamics. However, at zero pressure we have verified that thermal expansion of the liquid is small ($\sim 10^{-5}$ K^{-1}, consistent with experimental estimates[29]) and that taking account of it would in fact bring the zero pressure results into even better agreement with experiment. The overall agreement with experiment is rather good, and definitely better than any atomistic model proposed so far. The BKS model underestimates systematically the volume by $\sim$13%, a likely consequence of its inability to reproduce the *ab initio* stress (Fig. 2). Our improved potential compares with experiment even better than the *ab initio* results. This is not surprising, because although the *ab initio* results are, by definition, better than those of the empirical model for any given atomic configuration, the number of configurations, as well as the size and time scale of the simulation that was used to extract the equation of state for the empirical potential are much larger than those of the *ab initio* runs. It is also the case that *ab initio* simulations tend to either systematically overestimate (in the case of GGA) or systematically underestimate (in the case of LDA) the volume[30] and that, probably fortuitously, our potential predicts volumes that lie approximately midway between the two. Particularly at low pressures, the large viscosity of liquid silica means that even for our relatively large system size (576 atoms) obtaining a reliable statistical average of volume requires at least 50 picoseconds. For the *ab initio* system (72 atoms) a considerably longer run would be required.

We now focus on the microscopic structure of liquid silica. Since there is very little experimental data available for liquid silica we concentrate mainly on comparison with the results of *ab initio* molecular dynamics simulations. Figure 3 shows a comparison of the silicon–oxygen–silicon angle distributions in the liquid. It has been pointed out[13] that by counteracting the repulsion between silicon atoms, the inclusion of dipole effects can shift the oxygen centered angle distribution towards lower angles. This is clearly seen in this comparison between the results of the BKS simulations and the *ab initio* and polarizable potential simulations. The very close correspondence between the *ab initio* distribution and the polarizable potential distribution justifies both our description of the electrostatics in terms of dipoles and the inclusion of short-range induced dipoles which contribute very significantly to the dipole moment on each ion and which are therefore strongly linked to the distribution of angles. The peak at around 90 degrees in the polarizable and *ab initio* angle distributions is due to the presence of microscopic configurations consisting of rings containing two silicon and two oxygen atoms. These do not appear in the BKS distribution, indicating that they are energetically unfavourable with this potential.

Figure 3 shows the proportions of *N*-fold coordinated silicon atoms as a function of pressure compared to the results of Car–Parrinello simulations[27] and simulations using the BKS potential.[31] Our results are in much better qualitative agreement with the *ab initio* calculations than the classical BKS calculations despite the fact that simulations are performed at high pressures where the parameter set may become increasingly inaccurate. This implies that the inclusion of realistic physics into the potential improves its transferability as well as its accuracy. Our results indicate that the tetrahedral structure of the liquid is more stable at higher pressures than is predicted by the BKS potential. Since dif-

TABLE II. Quartz.

	Experiment (Ref. 32)	New potential	BKS
a [Å]	4.916	4.925	4.941
c [Å]	5.405	5.386	5.449
ρ [g/cm^{-3}]	2.646	2.665	2.598
Si–O–Si	143.7	144.5	148.1

TABLE III. Cristobalite.

	Experiment (Ref. 33)	New potential	BKS
a [Å]	4.957	4.936	4.920
c [Å]	6.890	6.847	6.602
ρ [g/cm^{-3}]	2.334	2.412	2.515
Si–O–Si	146.8	144.0	143.9

TABLE IV. Coesite.

	Experiment (Ref. 34)	New potential	BKS
a [Å]	7.136	7.165	7.138
b [Å]	7.174	7.162	7.271
c [Å]	12.369	12.377	12.493
β	120.34	120.31	120.76
ρ [g/cm^{-3}]	2.921	2.933	2.864
Si–O–Si	143.6	144.0	150.5

fusion is strongly linked to the presence of defects such as threefold and fivefold coordinated silicon atoms, the ability of a potential to reproduce the correct distributions of such defects is important if it is to properly describe the diffusion mechanism as a function of pressure.

As a final test of the reliability of the parameter set of our polarizable potential we examine its ability to describe quartz, cristobalite, and coesite which are the most important low pressure crystal structures. The various equilibrium crystal parameters at 300 K and zero pressure are given in Tables II, III, and IV. Although we have used no information about these polymorphs in our fitting procedure, the crystal parameters and the densities are much improved with respect to those predicted by the BKS potential, even for quartz for which BKS was designed. The fact that the Born–Mayer form cannot fit the *ab initio* forces very well and that for this potential form, a parameter set's ability to describe the silica structures seems to be, at best, only loosely related to the values of ΔF, ΔS, and ΔE would suggest that there is an ingredient missing in this potential which is fundamental to the bonding in silica. The striking improvement when polarization is included suggests that the structures are dominated by the electrostatic interactions and that polarization is an integral part of this.

In conclusion, we have created a potential for silica from first principles which accurately predicts the structures of liquid silica and the low pressure crystalline silica structures. This potential has been created without any reliance on experimental data and is therefore truly *ab initio*. We have shown that the model used provides a good representation of the electrostatic effects in silica as evidenced by its ability to reproduce the experimental and *ab initio* structural properties and that this is due to the inclusion of dipole polarization, the dominant electronic screening mechanism in silica. We have also demonstrated how inclusion of the relevant electronic effects in an empirical potential, coupled with *ab initio* parametrization can be a powerful technique for modelling disordered systems where experimental data is scarce.

[1] R. J. Hemley, J. Badro, and D. M. Teter, in *Physics Meets Mineralogy: Condensed-Matter Physics in Geosciences*, edited by H. Aoki, Y. Syono, and R. J. Hemley (Cambridge University Press, New York, 2000), pp. 173–204.

[2] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[3] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[4] P. A. Madden and M. Wilson, Chem. Soc. Rev. **25**, 339 (1996); P. A. Madden and M. Wilson, J. Phys.: Condens. Matter **12**, A95 (2000).

[5] A. J. Rowley, P. Jemmer, M. Wilson, and P. A. Madden, J. Chem. Phys. **108**, 10209 (1998).

[6] B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990).

[7] S. Tsuneyuki, M. Tsukada, H. Aoki, and Y. Matsui, Phys. Rev. Lett. **61**, 869 (1988).

[8] N. H. March and M. P. Tosi, *Coulomb Liquids* (Academic, New York, 1984).

[9] A. Laio, S. Bernard, G. L. Chiarotti, S. Scandolo, and E. Tosatti, Science **287**, 1027 (2000); A. Laio, Ph.D thesis, SISSA, Trieste, 1999, available at http://www.sissa.it/cm/thesis/1999/laio.ps.gz

[10] F. Ercolessi and J. B. Adams, Europhys. Lett. **26**, 583 (1994).

[11] P. Vashishta, R. K. Kalia, J. P. Rino, and I. Ebbsjo, Phys. Rev. B **41**, 12197 (1990).

[12] E. Demiralp, T. Cagin, and W. A. Goddard III, Phys. Rev. Lett. **82**, 1708 (1999).

[13] M. Wilson, P. A. Madden, M. Hemmati, and C. A. Angell, Phys. Rev. Lett. **77**, 4023 (1996).

[14] A. Pasquarello and R. Car, Phys. Rev. Lett. **79**, 1766 (1997).

[15] L. V. Woodcock, C. A. Angell, and P. Cheeseman, J. Chem. Phys. **65**, 1565 (1976).

[16] See, for example, B. Coluzzi and P. Verrocchio, J. Chem. Phys. **116**, 3789 (2002); E. La Nave, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. **88**, 035501 (2002); J. Horbach and W. Kob, Phys. Rev. B **60**, 3169 (1999).

[17] M. Wilson and P. A. Madden, J. Phys.: Condens. Matter **5**, 6833 (1993).

[18] M. Sprik, J. Phys. Chem. **95**, 2283 (1991).

[19] P. Tangney and S. Scandolo, J. Chem. Phys. **116**, 14 (2002).

[20] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).

[21] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[22] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986); A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[23] N. Trouillier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[24] ΔS was calculated relative to a roughly estimated bulk modulus of $B = 30$ GPa.

[25] G. J. Kramer, N. P. Farragher, B. W. H. van Beest, and R. A. van Santen, Phys. Rev. B **43**, 5068 (1991).

[26] G. A. Gaetani, P. D. Asimow, and E. M. Stolper, Geochim. Cosmochim. Acta **62**, 2499 (1998).

[27] A. Trave, P. Tangney, S. Scandolo, A. Pasquarello, and R. Car (unpublished).

[28] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980).

[29] V. Swamy, S. K. Saxena, B. Sundman, and J. Zhang, J. Geophys. Res. **99**, 11787 (1994).

[30] D. R. Hamann, Phys. Rev. Lett. **76**, 660 (1996).

[31] J. L. Barrat, J. Badro, and P. Gillet, Mol. Simul. **20**, 17 (1997).

[32] L. Levien, C. T. Prewitt, and D. J. Weidner, Am. Mineral. **65**, 920 (1980).

[33] W. W. Schmahl, I. P. Swainson, M. T. Dove, and A. Graeme-Barber, Z. Kristall. **201**, 125 (1992).

[34] L. Levien, C. T. Prewitt, and D. J. Weidner, Am. Mineral. **66**, 324 (1981).