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First-Principles Interatomic Potential of Silica Applied to Molecular Dynamics

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A new method to provide interatomic pair potentials from *ab initio* Hartree-Fock self-consistent-field calculations is proposed; potentials are calculated for model clusters of silica (SiO_2). They are tested in the molecular-dynamics simulation of crystalline states, in which four known polymorphs of silica are shown to be dynamically stable.

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Design and prediction of properties of materials is one of the most challenging problems in computational physics. Recent developments in many-body calculations for condensed-matter physics give promise to the reliable description of electronic states. If one looks into crystal structures, first of all, one has to establish a well-defined, first-principles method to provide interatomic interactions by which one can reproduce and even predict the stability of crystal structures for given materials. Although there is a rather long history for trials to determine interatomic potentials,[1-7] they have been primarily empirical: A potential with adjustable parameters is derived from experimental results for structures, elasticity, etc. In this context an opposite procedure would be desirable. Here we propose that we can provide interatomic potentials extracted from *ab initio* cluster calculations, which are fed into bulk calculations to predict, rather than be adjusted to, crystal structures. In the cluster calculation we employ the Hartree-Fock self-consistent-field method, which is one of the established many-body methods and is known to give very precise structures of molecules. More important, study of unknown polymorphs or materials becomes feasible only with nonempirical approaches.

Since the interatomic potentials depend, in principle, on the full atomic configuration, they are decomposed into two-atom potentials, three-atom potentials, etc. It is, then, an interesting question to ask to what extent physical properties can be described by "optimized" two-atom (pairwise) potentials. Here we envisage that the optimized potentials are those which are best fitted to *ab initio* cluster calculations including many-body effects. The ability of these potentials to reproduce the stability of polymorphs of crystals may then be tested by molecular-dynamics (MD) simulation.

In this view we report in this Letter a nonempirical approach to determine the interatomic potential for silica (SiO_2). Despite its simple chemical unit, silica is known to assume various crystal structures (polymorphs) whose densities vary in as wide a range as 2.3 (α-cristobalite) to 4.3 g/cm^3 (stishovite). As evident from this variation, silica is not a close-packed system, so that a sensitive test of the interatomic potential may be made. We also note that empirical total-energy calculations, which are often employed in the discussion of the stability of crystal structures, optimize the system by varying some parameter that preserves the symmetry of the crystal. This procedure, however, can be quite inadequate, since in some cases the crystal disintegrates upon removing symmetry restrictions. Thus we study dynamical stability by the MD simulation as a more reliable test. For silica, there is a pioneering work by Woodcock *et al.* with an empirical pair potential. We have also tested the potential employed by them, and the MD result shows that the initial α-quartz and α-cristobalite structures transform, respectively, into higher-symmetry states, that the bulk modulus of quartz is significantly larger than the experimental result, and that the Si-O distance is not reproduced unless a constant-volume (a nonthermal equilibrium) condition is used. Thus, although there have been a number of empirical and nonempirical approaches for silica,[8,9] it is shown here for the first time that we can reproduce with common pair potentials virtually all the known[10] polymorphs of silica (α-quartz, α-crystobalite, coesite, and stishovite) and their elastic properties.

We start from the total-energy calculation of the tetrahedral $SiO_4{}^{4-}$ cluster, which occurs in crystalline silica as well as in its melt. We regard the cluster as embedded in a crystal, so that we add four point charges, e^+, as shown in the inset of Fig. 1, which guarantee the charge neutrality and also mimic the Madelung potential arising from the rest of the crystal. The distance between an oxygen atom and the point charge is set equal to the usual Si-O distance in silicates (1.65 Å). The Gaussian basis functions employed are $(12s8p)/[5s3p]$ (Ref. 11) with two d orbitals (with the exponent,

$\alpha=0.118, 0.424)$[12] for silicon and $(9s5p)/[3s2p]$ with p functions (with $\alpha=0.059$)[13] for negative-ion states of oxygen. We assume no electron orbitals around the point charges.

The potential energy surface is then obtained by our changing the Si-O distances or O-Si-O angles with three different modes. One potential energy surface is depicted in Fig. 1, in which we stretch all the Si-O bonds keeping the T_d symmetry of the cluster. We have also obtained the results for the C_{3v} mode, in which only one Si-O distance is changed, and the D_{2d} mode, in which O-Si-O angles are varied with constant Si-O distance.

It has turned out that these three potential energy surfaces can be fitted well by a sum of pairwise interatomic potentials. We have employed the function form,

$$U_{ij}(r)=U_{ij}^{\mathrm{Coulomb}}(r)+f_0(b_i+b_j)\exp[(a_i+a_j-r)/(b_i+b_j)]-c_ic_j/r^6, \tag{1}$$

which consists of Coulomb interaction with some corrections discussed below, Born-Mayer-type repulsion, and dispersive interaction. Here r is the distance between atoms and a_i (b_i) is the effective radius (softness parameter) of the ith atom with the standard force $f_0=1$ kcal Å^{-1} mol^{-1}. We also include Coulomb interactions with the point charges.

A caution must be made in the evaluation of the Coulomb interaction in the cluster, because the effective charge in the bulk, Q_i, is different from that in a $\mathrm{SiO_4}^{4-}$ cluster, $\tilde{Q}_i$: In terms of the fractional charge, Δn, transferred from a Si atom to an O atom per Si—O bond, we have $Q_{\mathrm{O}}=-2\Delta ne$ and $Q_{\mathrm{Si}}=4\Delta ne$, while we have $\tilde{Q}_{\mathrm{O}}=-(1+\Delta n)e$ and $\tilde{Q}_{\mathrm{Si}}=4\Delta ne$. We express the Coulomb interaction in the cluster as a sum of long-range and short-range parts as

$$\begin{gathered} U_{ij}^{\mathrm{Coulomb}}=\tilde{Q}_i\tilde{Q}_j[1-g_{ij}(r)]/r+Q_iQ_jg_{ij}(r)/r, \\ g_{\mathrm{SiO}}(r)=(1+\zeta r)\exp(-2\zeta r), \quad g_{\mathrm{OO}}(r)=[1+11(\zeta r)/8+3(\zeta r)^2/4+(\zeta r)^3/6]\exp(-2\zeta r). \end{gathered} \tag{2}$$

The correction, $g_{ij}(r)$, in the long-range part (the first term) involving $\tilde{Q}$ reflects the distribution of the excess charge of oxygen, for which we assume a hydrogenlike orbital with a radius $1/\zeta$ here. The radius is of the order of the ionic radius of O, so that we employ $1/\zeta=1.4$ Å following Pauling.[14] Since the remaining short-range part is expected to be insensitive to the environment, we use the bulk Q_i there. Once the parameters a_i, b_i, and c_i are optimized from the cluster calculation, we switch $\tilde{Q}$ back into Q (i.e., $U_{ij}^{\mathrm{Coulomb}}=Q_iQ_j/r$) in the bulk simulation. Thus the final pair potentials have the same functional form as suggested by Gilbert and Ida.[15]

From the cluster calculation, the charge obtained by the Mulliken analysis, which is $\tilde{Q}_{\mathrm{O}}\sim-1.7e$ (i.e., $\Delta n\sim0.7$) for the equilibrium bond length, is shown to be a function of the Si-O distance (Fig. 1). The feature that the atomic charge varies with the bond length clearly indicates a many-body character of interatomic forces in the covalent system. The physical mechanism will be discussed in more detail elsewhere. To concentrate on the pair-potential approach, however, we have used constant Q_i ($\tilde{Q}_i$). Since small-cluster results are insufficient to determine the long-range Coulomb interaction, and because the absolute value of the Mulliken charge itself depends on the choice of basis function, we have not included Δn in the fitting procedure. Instead we tried several fixed values of Δn around the Mulliken charge. Among the trial values studied here, the fitted parameters with $\Delta n=0.6$ reproduce the best crystal parameters. Since the fitting procedure for a_i, b_i, and c_i is nonlinear, more than one set of parameters are obtained. We have chosen the one (Table I) which optimizes the structure and compressibility of α-quartz[16] in a static simulation by the program WMIN.[17]

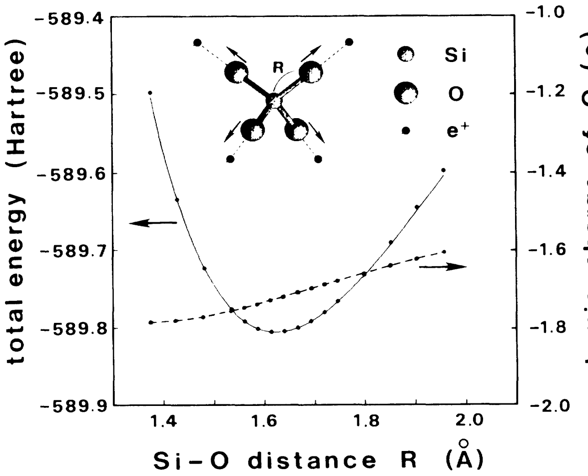

FIG. 1. Total energy and the Mulliken charge on an oxygen atom for T_d deformation of a $\mathrm{SiO_4}^{4-}$-$4e^+$ cluster shown in the inset. The solid circles are the cluster calculation, full curve is the fitted potential, and the broken curve is a guide to the eye.

Now we turn to the MD study. We have performed the dynamical stability test for four polymorphs of silica mentioned above. It has been experimentally shown that these polymorphs, which correspond to different pressure-temperature regimes, can also exist at normal pressure and temperature as metastable states. In the present simulation, the number of atoms in the system is

TABLE I. Potential parameters determined in this study.

	Q/e	a (Å)	b (Å)	c (kcal$^{1/2}$ Å^3 mol$^{-1/2}$)
O	−1.200	2.0474	0.17566	70.37
Si	+2.400	0.8688	0.03285	23.18

TABLE II. Structural parameters obtained here as compared with experimental results for various polymorphs of silica.

	α-quartz		α-cristobalite		Coesite		Stishovite	
	Obs.[a]	This work	Obs.[b]	This work	Obs.[c]	This work	Obs.[d]	This work
a (Å)	4.916	5.02	4.978	4.99	7.1356	7.23	4.180	4.27
b (Å)	4.916	5.02	4.978	4.99	12.3692	12.74	4.180	4.27
c (Å)	5.405	5.54	6.948	6.66	7.1736	7.43	2.666	2.75
α,β,γ	$\gamma=120°$	120°			$\beta=120.34°$	120.8°		
Si-O(1) (Å)	1.605	1.63	1.601	1.56			1.809	1.84
Si-O(2) (Å)	1.614	1.64	1.608	1.69			1.757	1.81
Si-O-Si	143.7°	147°	146.8°	142°				
Density (g/cm^3)	2.646	2.48	2.318	2.41	2.921	2.72	4.283	3.98
Bulk modulus (Mbar)	0.38(3)	0.337	$\cdots$	0.172	0.96(3)	1.08	3.35	3.11
Energy (kcal/mol)		−1235.1		−1231.2		−1236.9		−1234.1

[a] Reference 16.

[b] Reference 19.

[c] Reference 20.

[d] Reference 21.

324 (containing 36 unit cells), 216(18), 192(4), and 270(45) for α-quartz, α-cristobalite, coesite, and stishovite, respectively. We impose periodic boundary conditions in all directions. The Ewald sum method is used for evaluating the long-ranged Coulomb interaction. Starting from the ideal crystal configuration and random velocities, we let each atom move in Newtonian dynamics until equilibrium is achieved.[7,18] The pressure and temperature are kept equal to the normal value by scaling the size of the cell and the kinetic energy. The MD result with the pair potential obtained above shows that the four polymorphs are dynamically stable despite large differences in their topology and density. The structural parameters are summarized in Table II together with the atomic configuration in Fig. 2. The molar energy of the polymorphs are also listed in Table II. The energy difference between α-quartz and stishovite is smaller than the experimental result by about 10 kcal/mol.[22]

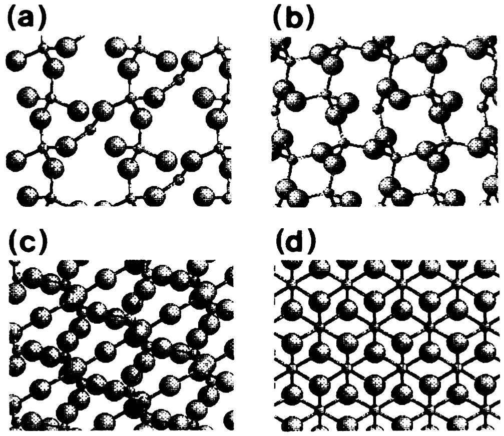

FIG. 2. Atomic configurations (averaged over time steps) obtained in the MD study for (a) α-quartz, (b) α-cristobalite, (c) coesite, and (d) stishovite. Note the elementary (a) eight-membered ring, (b) six-membered ring, (c) four-membered ring, and (d) SiO_6 coordination.

Since we have concentrated on considering force constants (curvature of the deformation potential) but not the binding energy itself, the potential does not necessarily give the correct absolute value for the total energy. Thus the present method, which is quite adequate for the study of structural stability, may be coupled to total-energy methods like band calculations to give a more accurate description of polymorphs including the thermodynamics of phase transitions.

We have also performed MD calculations under high pressure (up to 25 GPa for stishovite). We estimate the bulk modulus by fitting the pressure-volume result to a Birch-Murnaghan equation of state as is done in experimental analysis.[16,20,21] The obtained bulk moduli (Table II) are in good agreement with the experimental result even for stishovite, in which six oxygens surround each silicon, as well as for other polymorphs. Thermal expansion and phase transitions at higher temperatures will be discussed elsewhere.

Although both covalent and ionic characters should be present in silica, one would consider that tetrahedral units indicate dominant covalent bonding. The present result shows that (dynamical) stability of silica can nevertheless be reproduced by the pairwise potentials which are extracted from small clusters. Broadly speaking, the fact that different polymorphs are reproduced may be attributed to the strong bonds between silicon and the nearest oxygens. Still, it is rather remarkable that several polymorphs are reproduced with the same pair potentials, since the differences in the tilt angles between SiO_4 (or SiO_6) units are important in these polymorphs, which is precisely why an accurate determination of potentials is required. Effects of three-body interactions, which should be present in such properties as phonon dispersion or latent heat, is a future problem.

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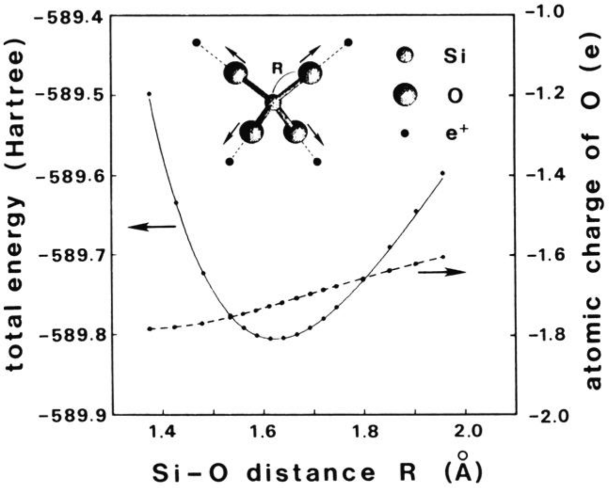

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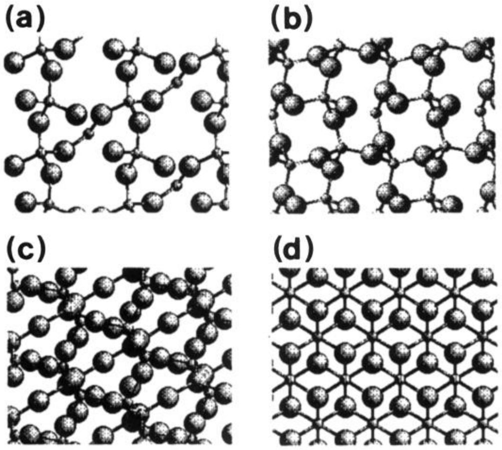

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