Empirical interatomic potential for silicon with improved elastic properties

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An alternative parametrization is given for a previous empirical interatomic potential for silicon. The new potential is designed to more accurately reproduce the elastic properties of silicon, which were poorly described in the earlier potential. The properties of liquid Si are also improved, but energies of surfaces are less accurate. Detailed tests of the new potential are described.

Recently, there has been intense interest in developing empirical interatomic potentials for covalent systems, particularly for silicon. Such potentials, which express the total energy of a system of atoms as an explicit function of the atomic positions, are so useful (if sufficiently accurate) that at least eight independent groups have proposed ten such potentials for silicon in the last four years.[1] Unfortunately, some of these potentials have not been tested or characterized sufficiently to draw any conclusions regarding their accuracy or usefulness.

In a recent paper,[2] I proposed a form for an empirical interatomic potential appropriate for covalent systems, and suggested a specific set of parameters for silicon. While the properties of silicon were well described overall, the potential gave a poor description of bond-bending forces. For many applications, such forces are rather important, and so it seems desirable to seek an alternative set of parameters which give a better description of the elastic properties of silicon.

Unfortunately, I have not been able to find a single set of potential parameters which describe the elastic properties of silicon accurately, while at the same time preserving the good description of surface reconstructions of the previous parametrization. However, by sacrificing some accuracy in the description of highly rebonded surface structures, a potential has been obtained which appears to be superior *for certain applications* to that reported earlier. This paper gives the parameters for the new potential, along with results of a variety of tests which highlight its strengths and weaknesses.

As discussed in Ref. 2, the energy is modeled as a sum of pairlike interactions, where, however, the coefficient of the attractive term in the pairlike potential (which plays the role of a bond order) depends on the local environment, giving a many-body potential. The form of the energy E, as a function of the atomic coordinates, is taken to be

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} ,$$

(1a)

$$V_{ij} = f_C(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})] ,$$

$$f_R(r) = A \exp(-\lambda_1 r) ,$$

$$f_A(r) = -B \exp(-\lambda_2 r) ,$$

(1b)

$$f_C(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left[\frac{\pi}{2}(r-R)/D\right], & R - D < r < R + D \\ 0, & r > R + D \end{cases}$$

(1c)

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n} ,$$

$$\zeta_{ij} = \sum_{k \ (\neq i,j)} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] ,$$

(1d)

$$g(\theta) = 1 + c^2/d^2 - c^2/[d^2 + (h - \cos\theta)^2] ,$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n} ,$$

$$\eta_{ij} = \sum_{k \ (\neq i,j)} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] .$$

(1e)

Here, i, j, and k label the atoms of the system, r_{ij} is the length of the ij bond, and θ_{ijk} is the bond angle between bonds ij and ik. The physical motivation and interpretation of the respective terms are discussed in Ref. 2.

As in the earlier work, the parameters in the potential are determined by fitting to a database consisting of cohesive energies of real and hypothetical bulk polytypes of silicon, along with the bulk modulus and bond length in the diamond structure. However, in addition the potential is now required to reproduce all three elastic constants of silicon to within about 20%.

The resulting parameters are summarized in Table I, along with the previously reported parameters. For convenience, the potential with the new parameters is referred to as Si(C), while the old parameters give Si(B). [Si(A) then denotes a still earlier potential,[3] which has many attractive features, but unfortunately does not give diamond as the ground state.[4]]

As discussed in Ref. 2, the parameters λ_3, α, R, and D were not systematically optimized. Preliminary tests indicate that omitting the term involving λ_3 (i.e., taking $\lambda_3 = 0$) does not greatly change the results obtained. Since this (along with $\alpha = 0$) greatly simplifies the potential, and especially the calculation of forces, anyone using this potential might wish to first try taking $\lambda_3 = 0$, instead of the value given in Table I.

TABLE I. Parameters for silicon, to be used in Eq. (1). New parameters are denoted Si(C), previous parameters of Ref. 2 are denoted Si(B). As discussed in text, values of R, D, α, and λ_3 were not systematically optimized.

	Si(B)	Si(C)
A (eV)	3.2647×10^3	1.8308×10^3
B (eV)	9.5373×10^1	4.7118×10^2
λ_1 (Å^{-1})	3.2394	2.4799
λ_2 (Å^{-1})	1.3258	1.7322
α	0.0	0.0
β	3.3675×10^{-1}	1.0999×10^{-6}
n	2.2956×10^1	7.8734×10^{-1}
c	4.8381	1.0039×10^5
d	2.0417	1.6218×10^1
h	0.0000	-5.9826×10^{-1}
λ_3 (Å^{-1})	1.3258	1.7322
R (Å)	3.0	2.85
D (Å)	0.2	0.15

Figure 1 summarizes the resulting energies and bond-lengths of various high-symmetry polytypes of Si(C), and compares them with results of experiment and of quantum-mechanical calculations[5] within the local-density approximation (LDA). The potential gives an excellent fit over the entire range of coordination.

Figure 1 compares structures with different atomic coordination. To test whether the energy difference between structures with the same coordination but different bond angles is well described, the properties of silicon in the $BC8$ structure are calculated. The $BC8$ structure, like diamond, has all atoms fourfold coordinated, and is
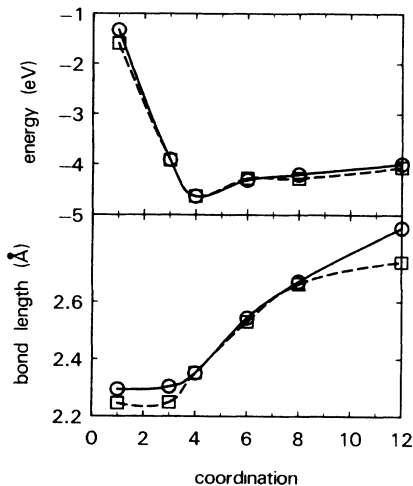

FIG. 1. Cohesive energy per atom, and bond length, plotted vs atomic coordination number, for several real and hypothetical polytypes of silicon: Si$_2$ dimer molecule, graphitic, diamond, simple cubic, bcc, and fcc. Squares are experimental values for observed phases, and calculations of Yin and Cohen (Ref. 5) for hypothetical phases. Circles are results of the present model. Lines are spline fits to guide the eye.

TABLE II. Calculated elastic constants (in Mbar) and phonon frequencies (in THz) of Si(C), compared with experiment.

Property	Theory	Experiment
c_{11}	1.5	1.7
c_{12}	0.8	0.6
c_{44}	0.7	0.8
LTO(Γ)	16	16
TO(X)	16	14
LOA(X)	12	12
TA(X)	9	5

of interest both as a pressure-induced metastable phase, and as a simple prototype for a tetrahedral amorphous structure. The structure is completely specified by two parameters, e.g., the lattice constant a and the internal parameter x. For this potential, $a = 6.64$ Å and $x = 0.1008$. The corresponding experimental numbers are 6.64 Å and 0.1003 ± 0.0008, so the description of the structure here is excellent. The energy of silicon in the $BC8$ structure is found to be 0.25 eV/atom above that in the diamond structure, about 0.1 eV/atom more than the value found[6] in LDA calculations.

Table II summarizes the elastic properties of Si(C). The elastic constants agree rather well with the experimental values, since this was an explicit criterion in the fitting procedure. In contrast, Si(B) gave a value of c_{44} almost an order of magnitude smaller than experiment.[2] The phonon energies are also well described here, except for the striking discrepancy for the transverse-acoustic mode [TA(X)], which is a familiar feature of short-ranged models and has been extensively discussed.[7]

Energies of point defects are crucial in determining the mechanism and rate of diffusion in solids, and have therefore been extensively studied in silicon. Results for point defects are summarized in Table III, along with results of LDA calculations[8,9] for comparison.

TABLE III. Calculated defect energies in Si(C), in eV, and results of previous LDA calculations. Here vac, int, and exch denote vacancy, interstitial, and the saddle point for exchange identified by Pandey (Ref. 9).

Defect	Theory	LDA[a]
vac	3.7	3–4
split vac	3.5	
int(T)	3.8	5–6
int(H)	4.7	4–5
int(X)	4.5	4[b]
int(B)	5.9	4–5
int(S)	4.7	
exch	5.7	4[c]

[a]Reference 8.
[b]Only one calculation available.

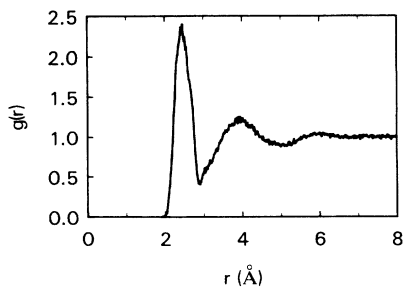FIG. 2. Radial distribution function $g(r)$ of liquid Si(C) at 3000 K.

FIG. 3. Radial distribution function $g(r)$ of amorphous Si(C) at 300 K.

The results in Table III are consistently within 1–2 eV of the LDA results, which is only a factor of 2 worse than the consistency among LDA results of different groups. Thus this potential is satisfactory even for the very difficult problem of describing point defects, which involve both severe rebonding and large strain.

Results for surfaces are less uniformly satisfactory for the new potential. The most striking problem is that adatoms on Si(111), which should lower the surface energy somewhat,[10] actually raise the surface energy by over 2 eV per adatom. This is similar to the problem which occurs in treating adatoms with the potential of Stillinger and Weber.[11] For the Si(100) surface, the energy gain associated with dimerization is found to be 1.4 eV with this potential. This is somewhat lower than the 2-eV gain expected from results of LDA calculations, although quite acceptable. The contraction of the dimer bond relative to the bulk bond length is well described.

Since the present potential is fitted only to static properties, it is important to test how well it works in describing excited configurations which are sampled in dynamical processes or at elevated temperatures. A convenient test is the simulation of liquid silicon, which was not well described by the previous potential.[2,12]

An accurate determination of the melting point is beyond the scope of the present study. In the short simulation times which are practical, it is hard to rule out the possibility of superheating of the crystal. However, limited studies suggest that the melting point for Si(C) may be 3000 ± 500 K, almost twice the experimental value. Since experimental measurements[13] of liquid Si are typically performed near the melting point, the simulation here is performed at 3000 K, using techniques described previously,[14] and a cell of 216 atoms.

The radial distribution function $g(r)$ is shown in Fig. 2, normalized so $g(\infty)=1$. The first peak falls at about 2.45 Å, with a maximum height of 2.4, and a full width at half maximum of about 0.52 Å; the second peak falls at 3.9 Å. The corresponding experimental numbers[13] are 2.50, 2.5, 0.6, and 3.8 Å, respectively. This level of detailed agreement is gratifying, given the very limited database to which the potential was fitted. However, one should bear in mind that the temperature in the simulation is much higher than in the experiment.
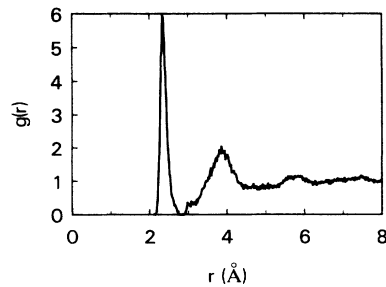
The density of the liquid at zero pressure is found to increase by about 4% upon melting (at a constant temperature of 3000 K), in good agreement with the 5% increase observed experimentally.

On the other hand, the first dip in $g(r)$ is much too deep, going down to about 0.5; the experimental $g(r)$ only dips to 0.85. It seems likely that the somewhat sharp cutoff of the potential between 2.7 and 3.0 Å is responsible for the sharp dip in $g(r)$ in this distance range. Also, the number of neighbors found by integrating up to the minimum of the first dip is about 4.6. The experimental coordination (obtained by an average of three methods) is larger, 6.4 neighbors. [However, no measure of the experimental uncertainty is given in Ref. 13. In view of the very weak dip in the experimental $g(r)$, the coordination in the liquid may not be a very meaningful quantity.]

When the liquid is quenched quickly, the resulting amorphous silicon (a-Si) has an average coordination of 4.25, rather than the value of 4.00 expected for a-Si. This coordination can be reduced by subsequent annealing (or, presumably, by slower quenching). Annealing goes more quickly when accompanied by a negative applied pressure, in analogy to the work of Kluge, Ray, and Rahman.[15]

The best sample obtained so far has an average coordination of 4.09, and a radial distribution function which is shown in Fig. 3. The energy is lowered significantly by this procedure, indicating that the initial high coordination is simply due to kinetic barriers to formation of the tetrahedral amorphous state from the liquid.

In conclusion, this new parametrization of an empirical potential for silicon has significant advantages for many applications. The elastic properties of the solid are considerably improved, as is the description of the structure of the liquid and amorphous states. Energies and bond lengths of polytypes are still well reproduced. However, energies of some surface geometries are considerably less accurate than for the previous parametrization of Ref. 2.

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