

Dissociative valence force field potential for silicon

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A procedure for obtaining potentials for covalent solids where many-body terms are important is presented. The potential is based on a variation of the chemically intuitive valence force field formalism. We have incorporated, in a systematic manner, the proper energetics for the dissociation of the solid. For silicon, the model accurately predicts the experimental phonon dispersion relations, cohesive energy, room-temperature Debye-Waller factor, and stabilization energy of the {100} symmetric dimer reconstruction.

Computer simulations of atomic and molecular motions have offered scientists a microscopic view of chemical and physical processes. The limiting feature, however, is often our knowledge of the interaction potentials or forces among the atoms. For large ensembles of species, where many interactions are evaluated during the course of a classical simulation, the most commonly used potential is one that is pairwise additive. Although tremendous insight has been gained from simulations using these potentials, the vast majority of systems require potentials which are not pairwise additive. For example, a diamond lattice structure like silicon, where there is directional bonding, cannot be reasonably treated by single-minimum radial pair potentials. In such systems there is a need for short-ranged many-body potentials which are quickly and easily evaluated.

One chemically intuitive formulation for conceptualizing directional covalent bonding is the valence force field (VFF) approach where the interactions are expressed as bond stretches, bond bends, and interactions between bends and stretches.¹ The limitation of this prescription is that, in general, these expansions are only valid for small atomic displacements of the atoms from equilibrium values. In many cases we are interested in modeling processes, e.g., molecular beam epitaxial crystal growth, where the energetics of configurations far from equilibrium are required.

We present in this Brief Report a new formulation of the intuitive VFF approach of chemical forces which incorporate in a relatively straightforward way the proper dissociation energetics. We start with Keating's VFF formalism which expands the distortion energy in scalar functions λ_{ij} of the dot products of the vectors connecting nearest-neighbor atoms.² We then rewrite his original expansion so that only two parameters are needed to fit the phonon dispersion relations of silicon. The key of our model is to parametrize the λ_{ij} , not as dot products, but rather as functions of interatomic distances such that the proper energetics, e.g., cohesive energies, are described. A constraint is applied to maintain the same force constants for the new λ_{ij} as for the Keating ones; thus the fit to the dispersion curves is maintained.

Keating's approach has been treated in detail previously.² Briefly, it was shown that the energy of a crystal can

be written as a function of the scalar products of the vectors connecting nuclear positions. Keating defined these functions for a diamond lattice as

$$\lambda_{klmn} = (\mathbf{x}_{kl} \cdot \mathbf{x}_{mn} - \mathbf{X}_{kl} \cdot \mathbf{X}_{mn})/2a, \quad (1)$$

where a is defined as $R_e/\sqrt{3}$, R_e is the scalar nearest-neighbor distance in the undeformed lattice, $\mathbf{x}_{kl}$ is the vector connecting atoms k and l , and $\mathbf{X}_{kl}$ is the vector connecting the positions of atoms k and l in the undeformed lattice. Furthermore, since these λ 's are small near equilibrium, it was assumed that they could be used as a basis for a series expansion for the distortion energy for small displacements. Using the assumption of nearest-neighbor interactions, Keating expressed the energy per unit cell Φ as

$$\begin{aligned} 2\Phi = & k_1 \sum_4 \lambda_{ii}^2 + k_2 \sum_{12} \lambda_{ij}^2 + k_3 \sum_{24} \lambda_{ij} \lambda_{ik} \\ & + k_4 \sum_8 \lambda_{ij} \lambda_{kl} + k_5 \sum_{24} \lambda_{ii} \lambda_{jk} + k_6 \sum_{24} \lambda_{ii} \lambda_{ij} \\ & + k_7 \sum_{12} \lambda_{ii} \lambda_{jj} + O(\lambda^3), \end{aligned} \quad (2)$$

where the vectors connect nearest neighbors and the numbers under the summation sign refer to the number of terms in the summation. The approximation originally made for silicon was to truncate the expansion after the first two terms. This two-term truncation did not describe well the phonon dispersion relations, especially for the transverse acoustic modes [Fig. 1(a)]. Furthermore, Eq. (2) as written implies that there are seven force constants (k_1 - k_7), when there are only five independent nearest-neighbor force constants for the diamond structure.¹

By rearranging the terms in the expansion so that five independent force constants are apparent, we can extract the dominant two terms. The expansion is now

$$\begin{aligned} 2\Phi = & a_1 \sum_{12} (\lambda_{ii} + \lambda_{jj})^2 + a_2 \sum_{24} (\lambda_{ii} + \lambda_{ik})^2 \\ & + a_3 \sum_{24} (\lambda_{ij} + \lambda_{ik})^2 + a_4 \sum_{24} (\lambda_{ii} + \lambda_{jk})^2 \\ & + a_5 \sum_8 (\lambda_{ij} + \lambda_{kl})^2, \end{aligned} \quad (3)$$

where the five independent force constants are a_1 - a_5 .

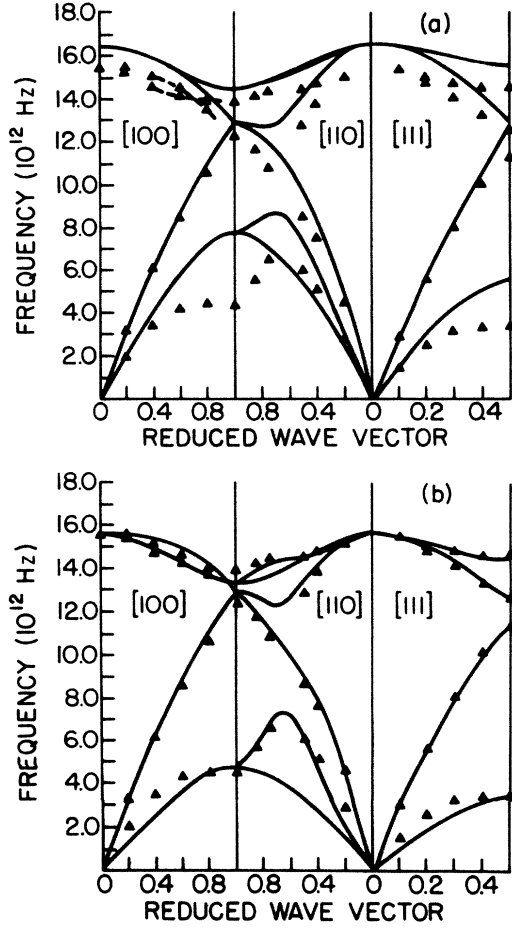


FIG. 1. Vibrational dispersion relations for the high-symmetry directions in bulk silicon. (a) Keating's original model with k_1 and k_2 of Eq. (2) fit to the bulk compressibilities (from Ref. 2). The filled triangles are the experimental data of Ref. 3. The dotted lines show the experimental crossing of the optic modes in the [100] direction. (b) Vibrational dispersion relations for a_1 and a_2 in Eq. (3) fit to the values of the frequencies at the zone boundaries.

Whereas the original two-parameter fit does not reproduce well the phonon dispersion relations, the first two terms of Eq. (2) *do* incorporate the essential interactions for describing the phonon dispersion relations of silicon [Fig. 1(b)]. Equation (3) can now be rewritten for a single atom rather than a unit cell with strictly two-body (2B) and three-body (3B) terms as

$$V_{2B} = \frac{3}{2}(a_1 + a_2) \sum_4 \lambda_{ii}^2, \quad (4)$$

and

$$V_{3B} = \sum_6 [a_2 \lambda_{ij} (\lambda_{ij} + \lambda_{ii} + \lambda_{jj}) + a_1 \lambda_{ii} \lambda_{jj}], \quad (5)$$

where again the summation is over nearest neighbors.

While Eqs. (4) and (5) are valid representations for the strain energy of a diamond lattice near equilibrium, they are not suitable for dynamics calculations where other geometrical configurations are required. We thus *redefine* the λ_{ij} terms so that the proper dissociation energetics are described. Since the phonon dispersion relations have

already been fit by the choice of a_1 and a_2 , the new λ_{ij} must have the same second derivatives, with respect to position at equilibrium, as the Keating λ_{ij} . The two-body potential is made dissociative by rewriting Eq. (4) as

$$V_{2B} = 3(a_1 + a_2)(\lambda_{ii}^2 - D_1^2/4a^2) + A \exp(-BR_i^2), \quad (6)$$

where λ_{ii} in the λ_{ii}^2 terms is given by

$$\lambda_{ii} = \begin{cases} \frac{D_1}{2a} \left[1 - \exp \left(\frac{\gamma(R_i^2 - 3a^2)}{R_i^2 - R_{\max}^2} \right) \right], & R_i < R_{\max}, \\ \frac{D_1}{2a}, & R_i \geq R_{\max}, \end{cases} \quad (7a)$$

$$\lambda_{ii} = \begin{cases} \frac{D_1}{2a}, & R_i \geq R_{\max}, \end{cases} \quad (7b)$$

and R_i is the scalar distance between the two atoms, $\gamma = (R_{\max}^2 - 3a^2)/D_1$, $R_{\max}$ is the potential cutoff, and D_1 is a parameter fit to the energetics. A value of zero for the pair energy at infinite separation is attained in Eq. (6) by subtracting the constant $3(a_1 + a_2)(D_1^2/4a^2)$ from Eq. (4). Also, the last term in Eq. (6) was added to increase the short-range repulsion. Neither correction changes the strain energy expansion about equilibrium and, hence, the predicted dispersion relations. The added constant term, however, accounts for part of the cohesive and sublimation energies.

The chosen form of the three-body interactions is

$$V_{3B} = a_2 \lambda_{ij} (\lambda_{ij} + \lambda_{ii} + \lambda_{jj}) + a_1 (\lambda_{ii} \lambda_{jj} - D_2^2/4a^2), \quad (8)$$

where

$$\lambda_{ii} = \begin{cases} \frac{D_2}{2a} \left[1 - \exp \left(\frac{\gamma Q_{ii}}{Q_{ii} - Q_{\max}} \right) \right], & Q_{ii} < Q_{\max}, \\ \frac{D_2}{2a}, & Q_{ii} \geq Q_{\max}, \end{cases} \quad (9a)$$

$$\lambda_{ii} = \begin{cases} \frac{D_2}{2a}, & Q_{ii} \geq Q_{\max}, \end{cases} \quad (9b)$$

and

$$Q_{ii} = R_i^2 - 3a^2 + (R_i^2 - 3a^2)^4/Q_{\max}^3, \quad (10)$$

where $Q_{\max}$ is a cut-off parameter for λ_{ii} and γ here is $Q_{\max}/D_2$. Again, a value of zero for infinite atomic separation is attained in Eq. (8) by subtracting the constant $a_1 D_2^2/4a^2$ from the three-body interactions. Note that this term also contributes to the cohesive and sublimation energies.

A functional form for λ_{ij} is developed by first defining damping functions for the i and j bonds as follows:

$$D(R_i) = \begin{cases} \exp \left(\frac{(R_i^2 - 3a^2)^2}{R_i^4 - R_{\max}^4} \right), & R_i < R_{\max}, \\ 0, & R_i \geq R_{\max}. \end{cases} \quad (11a)$$

$$D(R_i) = \begin{cases} 0, & R_i \geq R_{\max}. \end{cases} \quad (11b)$$

The functional form proposed for λ_{ij} is

$$\lambda_{ij} = 3a(\mathbf{R}_i \cdot \mathbf{R}_j/R_i R_j + \frac{1}{3})D(R_i)D(R_j)/2. \quad (12)$$

The functional forms in Eqs. (6)–(12) combined with the parameters in Table I have been chosen to reproduce the phonon dispersion curves, the bulk cohesive and the surface sublimation energies, and to insure that the diamond lattice is the most stable structure at all densities as

TABLE I. Potential parameters for use in Eqs. (6)–(12).

a	1.357 Å	B	3.33 Å ⁻²
D_1	3.0034 Å ²	$Q_{\max}$	6.73 Å ²
D_2	1.2877 Å ²	a_1	0.399 eV/Å ²
$R_{\max}$	3.65 Å	a_2	0.157 eV/Å ²
A	97013 eV		

compared to face-centered cubic, body-centered cubic, and simple cubic lattices. Furthermore, Eqs. (11) and (12) do not predict a barrier for addition of a third atom to a pair of atoms if the angle of approach is 109.5°. Thus there should not be a large potential barrier for the addition of a single silicon atom to a silicon surface so as to produce close to a unit sticking coefficient, as is observed experimentally.⁴

Using the above potential, we have examined the symmetric dimer reconstruction of the Si{100} surface and found it to be more stable by 2.1 eV per dimer than the bulk terminated surface. This value is in excellent agreement with the experimental estimate of 2 eV per dimer.⁵ Preliminary results from molecular dynamics simulations show that the mean-square displacements of the atoms from equilibrium agree well with estimates derived from the room-temperature Debye-Waller factor assuming a completely harmonic lattice (Fig. 2).⁶ For the 300-K results, the only real discrepancy is in the first shell of neighbors, where the simulation result exhibits a first peak which is too sharp. Since the other peaks match very well, the difference is most likely due to anharmonicities in the potential with the overall fit being excellent. The 1200 K results show all of the neighbor peaks being sharper than predicted by a harmonic solid. This again shows the effects of anharmonicities becoming greater at higher temperatures. There is also the question as to whether harmonic models are valid at high temperatures. The potential is short ranged, thus it is tractable for computer simulations. Furthermore, the values of the potential, force and the acceleration at the cut-off distance are all zero, which is an advantage when performing molecular dynamics simulations.

To date, several many-body potentials for silicon have been introduced. Each of these have been developed with emphasis on different aspects of silicon. The simplest of these potentials has been used by Pearson, Takai, Haliçoglu, and Tiller to model Si and SiC surfaces.⁷ The two-body potentials used were of the familiar Lennard-Jones form,⁸ while the three-body interactions were modeled by an Axilrod-Teller potential.⁹ As stated by the authors, the potential forms were used because they favored open crystal structures and not because of any direct theoretical justification. Stillinger and Weber have introduced another model potential which was developed to study the local structure of both solid and liquid silicon around its melting point.¹⁰ While this potential accurately describes the structure of silicon, it was not developed nor parametrized to yield an accurate description of other bulk properties, such as the vibrational dispersion relations. Biswas and Hamann have also recently introduced a many-body potential which yields an excellent description of the structural energies of silicon arranged in several lat-

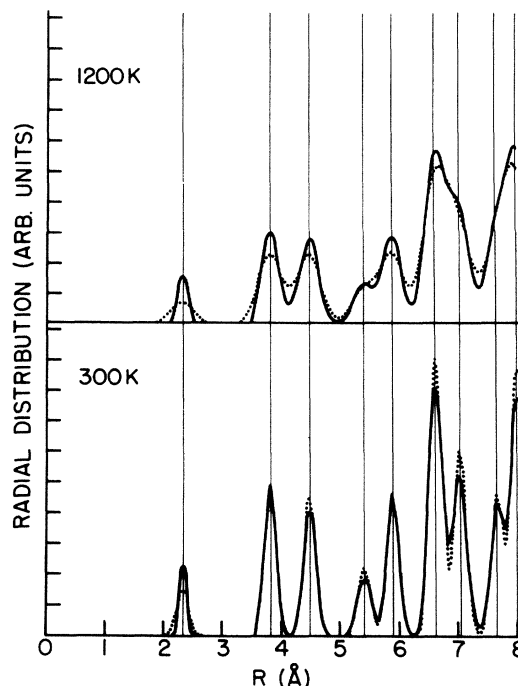


FIG. 2. Radial distribution from two different temperature-constant volume simulations of 216 atoms with periodic boundary conditions in all directions. This function represents the average number of neighbors a given distance from a central atom. The area under the peaks gives the relative number of neighbors in each shell. The vertical lines indicate the positions of the peaks in an undeformed lattice. The dotted lines show the expected result derived from the experimental room temperature Debye-Waller factor (Ref. 6), assuming a harmonic lattice.

tices.¹¹ The potential forms used, however, were not intended for temperature-dependent classical dynamics simulations. Furthermore, the authors report that the dynamical properties of bulk silicon are not well reproduced, with some phonon frequencies being as much as 25% to 50% too high. Recent calculations by Noorbachta, Raff, and Thompson¹² have shown that the diffusion of single silicon adatoms on a silicon surface is surprisingly dependent on the bulk force constants. This seems to indicate that an accurate description of the bulk dispersion relations is essential in order to model dynamic processes on silicon surfaces.

The dissociative valence force-field potential for silicon presented here contains virtually all of the features that we believe are necessary for modeling dynamic processes. The vibrational properties and energetics are well described. The symmetric dimer reconstruction of the Si{100} surface is predicted. The appeal of this dissociative VFF potential is that it is based on a prescription that fits our chemical concepts of bond stretches and bends. Furthermore, while this potential was parametrized for silicon, the dissociative properties of the expansion functions, Eqs. (6)–(12), should be applicable to other systems where VFF potentials have traditionally been used. Work is currently underway using these potential forms to model heteroatomic solids where the Keating functions have already proved successful.¹³

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