Surface and Thermodynamic Interatomic Force Fields for Silicon Clusters and Bulk Phases

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We show that when the angular dependence of three-body forces is adjusted to describe covalent-metallic phase transitions rather than small-amplitude atomic vibrations, a simple and accurate force field is obtained which is easily extended to describe energies and structures of Si_n vapor-phase clusters ($3 \leq n \leq 10$). Our model may have widespread applications to amorphous phases, melting, and extended defects.

At the atomic level our "physical intuition" concerning the nature of interatomic forces is still in its infancy. This is especially so for covalent systems which can be made metallic at modest pressures. In graphite and diamond, covalent bonding takes place through sp^2 and sp^3 hybrids, but in Si, Ge, grey and white Sn, and finally Pb, this hybridized orbital description of tetravalent structures becomes inadequate. Many properties of partially ionic diamondlike crystals have been described by dielectric theory (which includes some metallic corrections) without orbital functions,[1] but these are limited to (nearly) equilibrium configurations at low temperatures and pressures.

Interest in classical descriptions of more general configurations including different (metallic) high-pressure phases has developed because of the landmark calculation of the energies of these phases in Si and Ge by extremely accurate first-principles methods.[2] At the same time great strides have been made experimentally[3] in the measurements of many properties of vapor-phases clusters of $Si_n{}^+$ and $Ge_n{}^+$ up to $n \gtrsim 65$. Sophisticated molecular-orbital calculations[4] of Si_n clusters ($n \leq 10$) obtain the energies and atomic configurations of the ground state and several configurationally excited states and are in good agreement with these experiments, while morphological trends in cluster energies have been calculated with a semiempirical electronic quantum method[5] up to $n = 50$.

Several attempts have already been made[6-10] to model these results with classical two- and three-body forces, but all have achieved only limited success with the bulk phases and have generally failed even qualitatively to describe cluster structures and energies correctly.[11-13] The classical force fields (CFF) depend on the interatomic vectors $\mathbf{R}_{ij}$ through R_{ij}^2 and $\mathbf{R}_{ij} \cdot \mathbf{R}_{jk}$, and thus utilize the angular factor $\cos\theta_{ijk}$. The key difference between our approach and that of previous force-field models[6-13] is that we focus from the outset on an angular function

which is designed to describe the free-energy change at a first-order covalent-metallic transition, which is discontinuous. An energy function which is macroscopically discontinuous becomes S shaped on an atomic scale. The smallest angle θ_{ijk} varies from $\pi/3$ (close packed) to $2\pi/3$ (graphite) and so an appropriate angular function is actually $\cos3\theta_{ijk}$. If we sum with equal weighting over all nearest-neighbor three-body forces, the multivalued nature of $\cos3\theta$ will produce undesirable cancellations. However, we know that to obtain satisfactory results with a classical force field, it is necessary to introduce radial cutoffs to describe rapidly decreasing interatomic wave-function overlap. For consistency we do the same for angular forces with an angular cutoff, thereby suppressing such cancellations.

With this qualitative introduction, the functional form for our thermodynamic interatomic force field (TIFF) for the bulk phases of a covalent material such as Si is natural:

$$E(\{r_{ij}\}) = \sum_{ij} (Ae^{-\beta_1 r^2}/r^2 - ge^{-\beta_2 r^2}/r) , \tag{1}$$

where $r = r_{ij}$ and the three-body forces are contained in the bond-strength function g defined by

$$g(r_{ij}) = g_0 + g_1 S_{ij} S_{ji} , \tag{2}$$

$$S_{ij} = 1 + \langle \cos3\theta_{ijk} \rangle , \tag{3}$$

$$\langle f(\theta_{ijk}) \rangle = [f]/[1] , \tag{4}$$

$$[f(\theta_{ijk})] = \sum_{k \neq i,j} f(\theta_{ijk}) e^{-\gamma_1 \theta_{ijk}^4} e^{-\gamma_2 R^4} , \tag{5}$$

where $R = (r_{ij} + r_{jk})/2$. The results depend essentially on the sharp cutoffs for which we use squared Gaussians. Outside the primary range $\pi/3 \leq \theta \leq 2\pi/3$ we replace $\cos3\theta$ by ± 1 for $\theta < \pi/2 \pm \pi/6$ and $\theta > \pi/2 \pm \pi/6$, respectively. The strength function g describes increasing covalent bonding as the bond angle increases from $\pi/3$ to
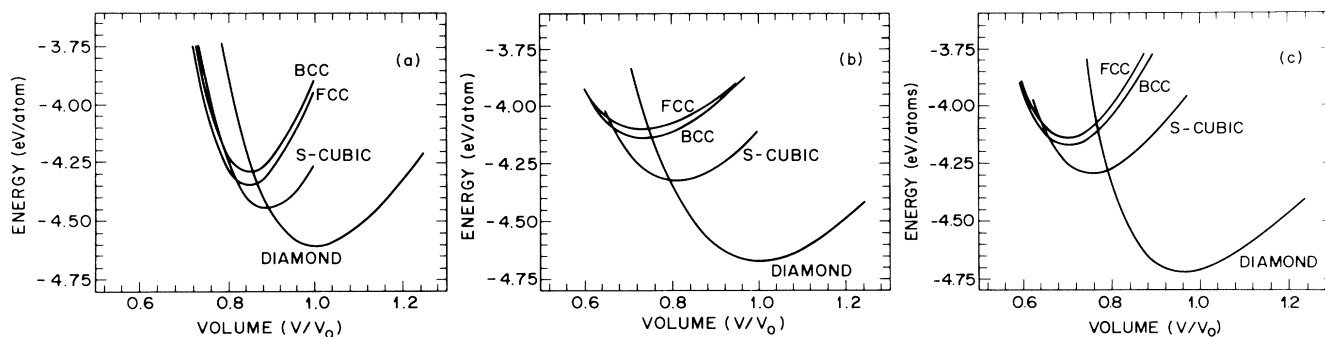
FIG. 1. Energies of simple Si bulk phases as a function of volume. (a) A previous fit (Ref. 7) without an angular cutoff for three-body forces; (b) the rigorous quantum-mechanical results (Ref. 2); and (c) our results.

$2\pi/3$.

We have fitted our seven TIFF parameters to the $E_\alpha(r)$ curves for α equal to diamond, simple, body-centered, and face-centered cubic curves for Si calculated by Yin and Cohen[2] and have obtained excellent agreement for twelve values they calculated, $E_\alpha(r_\alpha)$, r_α, and d^2E/dr_α^2, where $dE_\alpha(r_\alpha)/dr=0$. Our TIFF results, shown in Fig. 1(c), are compared to the Yin-Cohen results (b) and the Biswas-Hamann[7] CFF results (a) based on $\cos\theta$. The parameters which enter Eqs. (1)–(5) are given in Table I. The improvement obtained by use of $\cos3\theta$ with an angular cutoff instead of $\cos\theta$ without one is obvious.

When the bulk energy (1) is used to calculate the equilibrium energies and structures of small Si_n clusters ($n=5$–10), comparison with molecular-orbital (MO) theory[4] shows that the binding energies are too small and the equilibrium bond lengths are too large. The cluster topologies agree well with those previously obtained[11,12] with a CFF based on $\cos\theta$, but are much more open than those obtained quantum mechanically.[4,5] The transfer of dangling-bond strength to back bonds can produce more compact structures. This transfer depends on the angle θ_{ij} between the dangling bond and back

bond, with the dangling-bond vector $\mathbf{D}$ defined by

$$\mathbf{D}_i = -\sum_j \mathbf{r}_{ij} e^{-\gamma_3 r_{ij}^4} \Big/ \sum_j e^{-\gamma_3 r_{ij}^4}. \qquad (6)$$

Again we expect that the covalent effect of back-bond strengthening is small when the bonding is metallic ($\theta=\pi/3$). Thus we describe back-bond strengthening by the factor

$$T_{ij} = 1 + zD_i \sin[\alpha(\theta_{ij} - \pi/3)]. \qquad (7)$$

In crystals $D_i = |\mathbf{D}_i|$ is zero and it is small in clusters except for surface atoms.

TABLE I. Parameters for the bulk and surface terms of our interatomic potential for Si. See Eqs. (1)–(7) and the text for details.

Bulk parameters	
$A=182.44$ eV	
$\beta_1=0.550$ Å^{-2}	$\beta_2=0.151$ Å^{-2}
$g_0=7.08$ eV	$g_1=2.644$ eV
$\gamma_1^{-1}=(\pi/2)^4$	$\gamma_2^{-1}=5.772$ Å^4

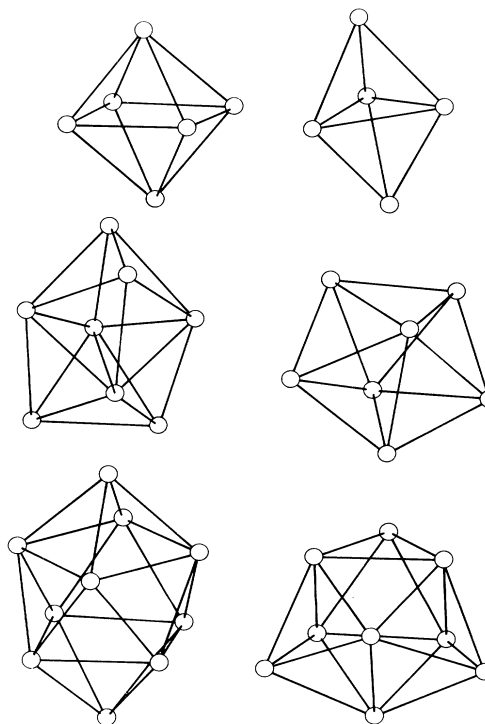| Surface parameters	
$\gamma_3^{-1}=30.498$ Å^4	$z=0.0851$ Å^{-1}
$u=4.0$ eV	$\alpha=1.70$

FIG. 2. Lowest-energy cluster topologies ($5 \le n \le 10$) for Si_n clusters derived from our TIFF including back bonding.
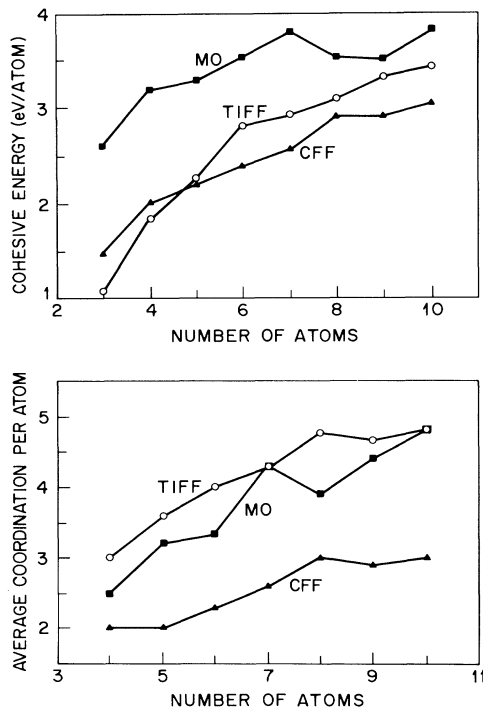
FIG. 3. Comparison of MO cluster energies and average coordination numbers with previous CFF results and our present TIFF results including back bonding.

Back-bond strengthing effects the attractive metallic and covalent as well as the repulsive interactions. To minimize the number of parameters, we assume that for each bond ij,

$$\Delta g_0/g_0 = -\Delta g_1/g_1 = u(T_{ij}T_{ji} - 1).\qquad (8)$$

To evaluate our results we compare them with those obtained in MO calculations[4] and those obtained[11,12] using an earlier force field[6] without dangling-bond corrections. The MO cluster structures exhibit many generalized Jahn-Teller or surface reconstruction effects. Especially for small clusters Si_n with $n < 10$ these effects may be significant (energy shifts of order 1 eV per cluster) and may depend on valence-electron filling of specific MO's. With increasing n steric hindrance reduces the Jahn-Teller distortion energies and surface reconstruction transition temperatures towards bulk values (of order 10^3 K or less, so that we expect that our method really comes into its own for $n \geq 10$.

We have constructed two sets of parameters, both of which generate compact structures similar to those obtained in molecular-orbital calculations and radically superior to the open structures obtained with previous potentials[11,12] based on $\cos\theta$ and no back-bonding enhancement. In both sets for $n = 7$ the lowest-energy structure is a bicapped pentagon, with either a short[4] or long bond

between the caps; the latter gives for $n = 10$ a bicapped staggered octahedron, and its molecular geometries are shown in Fig. 2. Generally, these structures are similar to the ground states calculated quantum mechanically,[4] but the classical model omits the π symmetry energy which favors unaxial structures, and so the results are not identical. The disagreements are generally in the range ≤ 0.2 eV/atom, which we take to represent the limiting accuracy achievable without quantum methods for small clusters. Comparisons are made for energy E_n and topology {mean coordination number $[N_c(n)]$} in Fig. 3 for our second parameter set. The parameters which enter Eqs. (6) and (7) are given in Table I. Also, for $N = 3$ and 4 we obtain an equilateral triangle and a regular tetrahedron. These structures are not displayed in Fig. 2, but the energy and average coordination for $N = 3$ and 4 are given where appropriate in Fig. 3.

In conclusion, we have developed a new interatomic force field for Si which we believe contains two vital improvements—an angular cutoff in three-body interactions, and a back-bonding term which represents an $(n+1)$-body force for an n-fold coordinate atom. Applications to many problems, such as simulations of the structure of a-Si,[14] appear promising.

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