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Abstract. The results obtained by a recently proposed empirical potential for silicon which includes four-body terms are compared with the results of quantum-mechanical tight-binding calculations. In particular, the ground-state energy and structure of the Si_{33} cluster were computed by both methods. By performing an equivalent calculation using only up to three-body interactions we demonstrate that the four-body term is absolutely necessary in order to achieve good agreement with the quantum method.

Silicon is undoubtedly one of the most technologically important materials. For this reason its properties have been studied extensively, both experimentally and theoretically. Besides its crystalline ground state (diamond structure), phases of Si with highly reduced symmetry such as amorphous Si, Si surfaces, interfaces and clusters have very interesting and distinct properties. This makes the study of such phases, both scientifically and technologically, attractive.

In this work we focus our attention on Si clusters for which both the experimental data and the theoretical information are rather limited. Experimentally the core of the information is often limited only to their mass spectrum [1, 2], whereas accurate *ab initio* calculations are restricted to clusters up to ten atoms [3, 4]. For larger clusters, one has to resort to empirical or semi-empirical methods to study their structures, cohesive energies or dynamics.

Classical model potentials, if their validity is well established, belong to this category of methods and can produce valuable information about large clusters. For this reason, several attempts have been made so far to develop a classical model potential for silicon [5–9]. Classical model potentials have the advantage over any electronic calculational methods in that molecular dynamics calculations for determining structural or dynamic properties of the material can be performed rapidly. Moreover, an analytic expression for the interactions is given, so that a precise picture of the chemical properties of the material is obtained. Each of these models can manage to simulate several of but not all the properties. For example, the Stillinger–Weber (SW) [5] model is constructed to simulate the crystalline ground state (diamond structure), the melting point and the liquid phase. On the other hand, the parameters of the Biswas–Haman [6] model are fitted to a database of quantities involving unstable periodic bulk structures, which were calculated by the local-density approximation (LDA). As a result these models have a limited range of validity and fail to simulate Si clusters.

The construction of a universal classical model is an open question at this moment. In other words, none of the models so far proposed, can reproduce structural or dynamical properties of all phases of silicon, namely bulk, surface, clusters, amorphous and liquid, without changes in its parameters.

An alternative approach to the study of the structural and dynamic properties of silicon is the tight-binding molecular dynamics (TBMD) method [10]. The tight-binding method is computationally useful because it permits the use of different parametrization schemes for the construction of the Hamiltonian, while employing a minimal basis set. The basis set used here, however, is taken to be strictly orthonormal by neglecting the overlaps. While this may reduce its accuracy, one can still obtain good agreement with *ab initio* values for small silicon clusters [16,18]. We call this orthogonal tight-binding molecular dynamics, or simply TBMD. This method can be very useful in determining the properties of large Si clusters without any particular assumption about the form and the nature (e.g. two-body, or three-body) of the potential than a classical molecular dynamics (CMD) method. Nevertheless, the TBMD method is slower and computationally more costly than the CMD method. Thus from the fundamental and the practical point of view it is useful to use the TBMD results to test the range of validity of any classical model.

Specifically in this paper, we compare the results obtained by the TBMD method [10, 11] with those produced by a recently proposed classical model [12]. This model is an improvement of the SW model and includes a next-nearest-neighbour interaction in the four-body term, so that the directionality of the covalent bonds depends not only on the bond angles but also on the dihedral angles. This model has been previously tested in simulating the $\sqrt{3} \times \sqrt{3}$ surface reconstruction on the (111) surface, and for obtaining the ground-state cohesive energies and structures of small Si clusters. The results obtained by this model are in good agreement with *ab initio* results for both clusters and surfaces. In the present work we have used this empirical potential to determine the ground-state structure of large Si clusters (Si_{33}). The results are then compared with the corresponding results obtained by the TBMD method.

First, we briefly review the TBMD method. More details can be found elsewhere [11]. In the tight-binding scheme the total energy is written as a sum, namely $U = U_{el} + U_{rep} + U_{bond}$ [11, 16], with U_{el} obtained by summing the energies ϵ_i of the occupied one-electron states:

$$U_{el} = 2 \sum_i^{occ} \epsilon_i. \tag{1}$$

The electronic energies ϵ_i are obtained from a semi-empirical tight-binding Hamiltonian [13]. The Hamiltonian parameters are taken from [14]. U_{rep} is given by a repulsive pair potential:

$$U_{rep} = \sum_i \sum_{j>i} \phi(r_{ij}). \tag{2}$$

Here r_{ij} is the distance between the atoms i and j. Both the Hamiltonian matrix elements and $\phi(r)$ are taken to scale exponentially with the interatomic distance r [11]. The coefficient U_{rep} of the repulsion term is chosen so that, for a Si_2 dimer,

$$U_{rep}(d) = U_{exp}^{dimer}(d) - U_{el}(d) - U_{bond} \tag{3}$$

where $U_{exp}^{dimer}(d)$ is the experimental cohesive energy. The bond-counting term U_{bond} was introduced by Tomanek and Schluter [16] to bring cohesive energies into agreement with *ab initio* values [3,4]. It is fitted with a quadratic expression

$$U_{bond} = N[a(n_b/N)^2 + b(n_b/N) + c] \tag{4}$$

with $a = -1.33$ eV, $b = 1.76$ eV and $c = -0.49$ eV and n_b is the number of occupied bonds, obtained by including all bonds shorter than 3.4 Å.

The force F_x associated with an atomic coordinate x is given by differentiating the total energy U: $F_x = -\partial U/\partial x$.

The electronic part of the force is computed from the Hellmann–Feynman theorem:

$$F_x^{el} = -\frac{\partial U_{el}}{\partial x} = -2 \sum_i \frac{\partial \epsilon_i}{\partial x} \theta(\epsilon_F - \epsilon_i) \tag{5}$$

$$\partial \epsilon_i / \partial x = \psi_i^\dagger (\partial H / \partial x) \psi_i \tag{6}$$

where ϵ_i and ψ_i are determined from solving the eigenvalue equation for a cluster Hamiltonian: $H\psi_i = \epsilon_i \psi_i$.

Thus, using the TBMD simulation for a Si$_2$ dimer, we obtained a binding energy of -3.36 eV and a bond length of 2.28 Å. The corresponding experimental values are -3.34 eV and 2.25 Å, respectively. The experimental values were taken from [3]. The present tight-binding scheme has been used to reproduce equilibrium structures for small Si clusters [15] in agreement with the *ab initio* energy minimization calculations [3,4]. We note that a TBMD scheme [18] similar to ours has been used to obtain equilibrium geometries for the same clusters, also in agreement with *ab initio* work [3,4].

We recently proposed a classical model for silicon [12] which is an improvement of the SW model [5]. In the SW model the strength of the Si–Si covalent bond is expressed by a two-body term, while the directionality of the bonds is modelled by a three-body term. This form, where the term describing the directionality of the bonds is separate from the term describing the bond strength, is an advantage of the SW model over other models because its parameters can be selected in a natural way by fitting to important properties of silicon. It was shown in [8] that the correct description of the directionality of the bonds in Si clusters requires also the introduction of a four-body term. In more recent work [12], the study of surface reconstruction on the (111) surface showed that a four-body term with a dihedral angle dependance should be included in the model. The model, therefore, has the following form.

First a two-body term is constructed to simulate the interaction between the Si atoms in the diamond structure:

$$V_2 = A(B/r^4 - 1) \exp[\alpha/(r - R)]. \tag{7a}$$

Then the three-body and four-body terms are introduced to describe the bond angle dependance of the directionality of the covalent Si–Si bond. These many-body terms have positive (repulsive) contribution to the total energy of a Si cluster. Specifically, the form of the three-body term is $V_3 = h_{jik} + h_{ijk} + h_{ikj}$, where

$$h_{jik} = \lambda_3 f_{ij} f_{ik} \{1 - \exp[-Q(\cos\theta_{jik} + \tfrac{1}{3})^2]\}. \tag{7b}$$

The form of the four-body term is $V_4 = g_{ijkl} + g_{jikl} + g_{kijl} + g_{lijk}$, where

$$g_{ijkl} = \lambda_4 f_{ij} f_{ik} f_{il} [1 - \exp\{-Q[(\cos\theta_{jik} + \tfrac{1}{3})^2 + (\cos\theta_{jil} + \tfrac{1}{3})^2 + (\cos\theta_{kil} + \tfrac{1}{3})^2]\}]. \tag{7c}$$

The functions

$$f_{ij} = \exp[\gamma/(r_{ij} - R)] \tag{7d}$$

are cut-off functions, so that the interaction vanishes smoothly for $r_{ij} \geqslant R$.

Finally, the second four-body term, which was introduced to include next-nearest-neighbour interactions in the model by incorporating a dihedral angle dependence, has the form $V_{4n} = gn_{ijkl} + gn_{jikl} + gn_{kijl} + gn_{lijk}$, where

$$gn_{ijkl} = \lambda_{4n} f_{ij} f_{jk} f_{kl} [\![1 - \exp\{-Q[(\cos\theta_{ijk} + \tfrac{1}{3})^2 + (\cos\theta_{ijkl} - \tfrac{1}{3})^2(\cos\theta_{ijkl} + 1)^2$$
$$+ (\cos\theta_{jkl} + \tfrac{1}{3})^2]\}]\!] \tag{7e}$$

with θ_{ijkl} the angle between the vectors r_{ji} and r_{kl}. The parameters

$$A = 16.3 \text{ eV} \qquad B = 11.581 \text{ Å}^4 \qquad \alpha = 2.095 \text{ Å} \qquad R = 3.771 \text{ Å}$$
$$\lambda_3 = 2.0 \text{ eV} \qquad \gamma = 2.4 \text{ Å} \qquad \lambda_4 = 12.0 \text{ eV} \qquad \lambda_{4n} = 22.0 \text{ eV} \qquad Q = 1.7 \tag{8}$$

are selected to reproduce several geometric and dynamic properties of Si, namely the energy per atom and the structure of the crystalline ground state (diamond structure), the lattice constant, the energy difference between the diamond and the FCC structures, and the cohesive energy of the Si_{10} cluster.

As an example for testing and comparing the TBMD method and our classical model, we study the Si_{33} cluster. This cluster is an important, experimentally determined magic number, for which recent theoretical calculations based on the LDA offer a rather provocative interpretation of its stability, namely, that its ground-state structure is probably responsible for its stability. Specifically, a model for the ground-state structure of Si_{33}, which can form a structure similar to the 7×7 reconstruction of the Si(111) surface, has recently been proposed [17] (figure 1(*a*)).

It is well known that finding the lowest-energy configuration for a given size cluster by locating and comparing all the local energy minima is extremely difficult for $N > 10$ [19]. Because of the long computational time needed for the method, only a limited part of the configuration space can be scanned. On the contrary the use of a classical potential model removes this restriction and permits the scanning of a larger part of the configuration space. The model (7) was used to calculate the ground-state structure and cohesive energy of the cluster Si_{33}. To optimize the structure of the Si_{33} cluster and to obtain its ground state we used the Monte Carlo simulated annealing (MCSA) technique. The initial guess was selected to be the structure given in [17] as a probable ground state (figure 1(*a*)). Then the MCSA method converged to a new structure after 3×10^5 trials.

The structure obtained by this model as the ground state for the Si_{33} cluster exhibits important differences from the initial guess (figure 1(*b*)). Specifically, the average bond length is 2.65 Å and the average coordination number is 6.8, while, in the structure proposed in [17], the average bond length is 2.4 Å and the average coordination number is 3.5. Therefore the structure obtained by the classical model (7) has a structure similar to glass or liquid silicon, while the structure of the initial guess is more diamond like. The cohesive energy of the new structure is 3.89 eV atom^{-1}, while the cohesive energy of the metastable state (1*a*) as calcualted by the same classical model is 3.51 eV atom^{-1}. We also note that other workers employing the tight-binding energy minimization scheme of Tomanek and Schluter [20] for Si_{45} have obtained a more close-packed structure than proposed by Kaxiras [17].

The above result offers the possibility for a test of the validity of the classical model (7). In other words, the cohesive energy of both structures (figures 1(*a*) and 1(*b*)) can be computed by the TBMD method. Using as an initial condition the structure in figure 1(*b*), the TBMD calculation converged to the structure shown in figure 1(*c*). The cohesive energy of the new structure is 4.09 eV atom^{-1}, the average bond length is 2.5 Å and the average
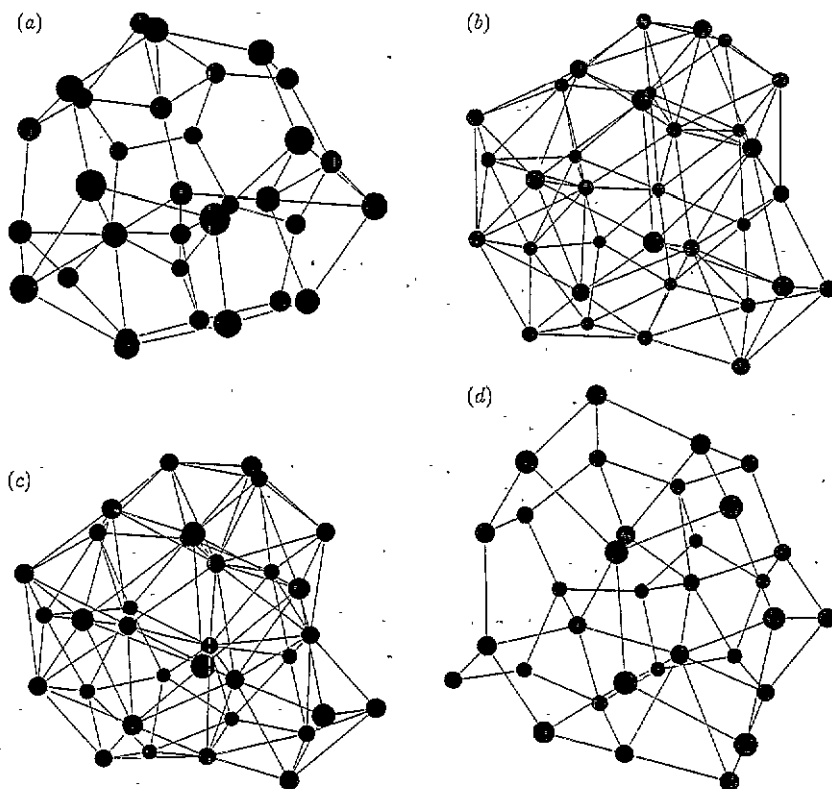
Figure 1. Ground-state structures for the Si$_{33}$ cluster obtained by (a) the LDA method [17], (b) the present classical model, (c) the TBMD method and (d) the classical SW model. The structure shown in (a) was used as an initial guess for obtaining the structure in (b) using the present classical model.

coordination number is 6.2. Therefore, this structure has the same qualitative characteristics as the ground-state structure obtained by the classical model (7). The striking agreement between the results of the TBMD method and the classical model strongly suggests the proposed structure to be a genuine ground state for Si$_{33}$.

Furthermore, we studied the same problem using the SW model as a typical three-body potential, in order to demonstrate the importance of the four-body terms. The ground-state structure obtained by the MCSA method is shown in figure $1(d)$ and it has similar qualitative features to the structure in figure $1(a)$. Therefore, we have verified that the introduction of the four-body terms is essential for simulating the quantum results. Table 1 presents all the results for the Si$_{33}$ cluster obtained by the SW three-body model, the present four-body model and the TBMD method.

Table 1. Comparison of the ground-state structures of Si$_{33}$ produced by the present four-body potential model, the TBMD method, the LDA method and the three-body classical SW model.

Method	Average bond length (Å)	Coordination number	Cohesive energy per atom (eV)
LDA	2.40	3.5	—
SW	2.45	3.7	3.35
Present model	2.65	6.8	4.23
TBMD	2.50	6.2	4.09

The tight-binding method can also provide some information about the electronic structure of the Si_{33} cluster. Specifically, the energy gap was found to be 0.52 eV. The same set of tight-binding parameters gives a gap of 1.13 eV for bulk silicon. Therefore, the cluster has a considerably stronger conducting character than the crystalline silicon.

In conclusion we note that the inclusion of the four-body interaction is absolutely necessary to achieve good agreement between the classical and quantum descriptions of Si clusters. Moreover, the structural properties of the Si_{33} ground state obtained by both the classical and the TBMD methods are qualitatively the same, i.e. the ground state of Si_{33} is found to be not diamond like, contrary to previous suggestions.

The successful simulation of cluster properties by the present model together with previous results on surface properties give a strong indication that this model could be considered to be closest to universal, which can be used to simulate, within acceptable limits of accuracy, the properties of all phases of silicon. Moreover, the verification of the Si_{33} ground-state structure, determined by the present model using the TBMD method, suggests important predictive possibilities for this model. The tight-binding model used here, although simple, still retains all the salient features of other tight-binding schemes [16, 18] used to obtain good agreement with *ab initio* results for small clusters. Tight-binding methods generally seem to favour close-packed structures for these clusters, indicating a need to go to larger clusters to obtain bulk-like coordination. The inclusion of non-orthogonality may favour more open structures for small clusters than obtained using the orthogonal scheme. More work is needed in this area.

Acknowledgments

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