Potential model for silicon clusters

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An interatomic potential for silicon is proposed, which is a significant improvement over the Stillinger-Weber model. This potential is valid for clusters with more than six atoms, where π bonding is not significant because of the large degree of coordination. Guided by *ab initio* electronic calculations, we introduced four-body interactions to the potential, which were essential to give good agreement with the melting point of the crystal and the geometries and the energies of the ground and low metastable states of silicon clusters.

I. INTRODUCTION

Clusters constitute an intermediate state for a material between the atom and crystal. Their study becomes increasingly interesting because their structure and dynamical behavior can explain phenomena as crystal growth, surface reconstruction, and properties of the corresponding amorphous material.

A model which describes the interaction between the atoms by an empirical potential has the advantage that the dynamical behavior of the clusters can be studied. In other words, numerical experiments can be conducted which simulate collisions between clusters, their fragmentation, or the deposition of clusters on a substrate of the same or other material, at different temperatures. Therefore the development of such analytical models is particularly useful.

Unfortunately, the construction of the proper analytical potential is not easy. Any potential-energy function F, which describes the interactions among N identical particles, can be written as an N-body expansion of the form¹

$$F(1,2,...,N) = \sum_{1 \le i \le N} V_1(i) + \sum_{1 \le i < j \le N} V_2(i,j) + \sum_{1 \le i < j < k \le N} V_3(i,j,k) + \dots + V_N(1,2,...,N) .$$
(1)

We hope that only a small number of terms of this expansion will be needed to successfully approximate the real interactions. In some cases (e.g., rare gases) only the two-body term is required. On the contrary, this is not true for semiconductors, where the strong covalent bonds cannot be described by a two-body term.

Several attempts have been made to develop an analytical model for silicon. Pearson, Takai, Halicioglu, and Tiller proposed a potential with a long-range two-body term, and a nonseparable three-body term.² The Stillinger-Weber potential has also a nonseparable threebody term which is short ranged.³ This potential has been used to reproduce the melting of the silicon crystal, and its advantages will be discussed later in detail. More recently, Tersoff has developed a potential with only a two-body term, which depends on the coordination number of the atom.⁴ In this way the other many-body terms are effectively expressed by the two-body term. A modification of this model was proposed by Dodson.⁵ These models succeeded in reproducing some of the bulk and surface properties of the crystal.

Finally, Biswas and Hamann developed a potential for silicon which fits the local-density approximation (LDA) results for several different lattice structures. They have also tested this potential in small Si clusters.⁶ Their results show that this model can only coarsely fit the energies and the structures of the Si clusters, which have been found from *ab initio* calculations. The Stillinger-Weber potential has also been used for dynamic calculations in small clusters of silicon,^{7,8} but it has not proved to be a successful approximation in this case. More specifically, if the Stillinger-Weber potential is used, the ground states of the small clusters have qualitatively different structures than those found from *ab initio* calculations.^{9,10}

In this study we develop a potential which models primarily the small silicon clusters (7–100 atoms in size) without losing some important properties of the crystal. In other words, our potential produces ground states (absolute minima) of the small neutral clusters with structure and energy, which are very close to the *ab initio* results.⁹ The same potential yields the correct crystalline structure for the ground state of the solid silicon (in the diamond structure), and approximates its melting point.

There are only few experimental results for silicon clusters to compare with the computations. These include the mass spectra of charged clusters Si_x^{+} , ¹¹ or Si_x^{-} , where magic numbers are observed. Also, the energies of the ground state of the dimer Si_2 , and the trimer Si_3 , have been found experimentally.^{12,13} These values are used to properly scale the energies of the larger clusters which were computed by Hartree-Fock calculations.

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This paper is organized as following. In Sec. II we present the form of the new potential, and analyze the qualitative features of the interatomic interaction which are included in the form of the function describing this interaction. In Sec. III we discuss the strategy which is followed to select the parameters of the potential. Finally, in Sec. IV we present the results concerning the ground states of the clusters, which are found when our potential is used.

II. THE NEW POTENTIAL

It was explained in Sec. I that we are interested in building a potential which will be a good approximation for medium-size clusters of silicon, containing up to 100 atoms. We expect that this new potential will also fit the dynamical properties of the crystal at least to the degree that they were reproduced by the other potentials proposed so far. In this spirit of the many-body expansion method¹ we could use *ab initio* and experimental data of Si₂ (Ref. 13) and Si₃ (Ref. 10) to construct the two- and three-body terms in Eq. (1). Indeed, a three-body term was obtained in the form of Sorbie-Murrell function from the ab initio data of Si₃. Then the structures and energies of larger clusters were obtained and compared with available data.9 A disagreement was found and this is attributed to the predominance of the π bonding in small clusters (2-4 atoms). In contrast, for clusters with more than six atoms, the bonds are better described with sp^3 orbitals. Therefore the use of a three-body term constructed from Si3 in clusters with more than six atoms it is bound to lead to unsatisfactory results. For this reason we decided to produce a potential which is valid for clusters with more than four atoms, surfaces, and the bulk silicon. In particular, we modify the Stillinger-Weber potential which gives good results for the crystal so that it will fit cluster properties as well.

The Stillinger-Weber potential consists of a two-body and a three-body term. The two-body term has the form

$$V_2(r) = \begin{cases} A \left[\frac{B}{r^4} - 1 \right] e^{\alpha/(r-R)}, & r < R \\ 0, & r \ge R \end{cases}$$
(2)

where A, B, α , and R are parameters properly chosen to fit dynamic properties of the crystal. The exponential term is a cutoff function, which smoothly vanishes at r=R. This greatly reduces the computation time for molecular-dynamics simulations, because the two-body interaction between atoms, which have a distance between them larger than R, are neglected. The same cutoff is also applied in the three-body term, which is of the form

$$V_{3}(r_{i},r_{j},r_{k}) = h(r_{ij},r_{ik},\theta_{jik}) + h(r_{ji},r_{jk},\theta_{ijk}) + h(r_{ki},r_{kj},\theta_{ikj}), \qquad (3)$$

where r_{ij} is the distance between the atoms *i* and *j*, and θ_{jik} is the angle between the vectors \mathbf{r}_{ij} and \mathbf{r}_{ik} . The function *h* is given by the formula

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp[\gamma(r_{ij} - R)^{-1} + \gamma(r_{ik} - R)^{-1}](\cos\theta_{jik} + \frac{1}{3})^2,$$
(4)

where λ and γ are two more parameters of the model. This three-body term is repulsive, and vanishes for $\cos \theta_{jik} = -\frac{1}{3}$. Therefore, the three-body term of the Stillinger-Weber potential expresses the tendency of silicon atoms to form four sp_3 covalent bonds.

This simple model succeeded in reproducing some basic properties of silicon crystal. In other words, it gives the correct ground state of the crystal (diamond structure), approximates the melting point of silicon,³ and gives good estimates for some elastic properties of the bulk.¹⁴ Nevertheless, it is not a good potential for modeling small silicon clusters. More specifically, it fails to reproduce the energy and the correct structure of the ground state of silicon clusters,^{7,8} which have been found from *ab initio* calculations.⁹

The new potential which we have developed, even though it retains the advantages of the Stillinger-Weber model, also gives good results for small clusters. The modifications we made on the Stillinger-Weber potential are guided by the following two observations.

(a) The angle dependence of the three-body term is of the form

$$\lambda(\cos\theta + \frac{1}{2})^2 . \tag{5}$$

The function (5) has only one parameter λ , which is used to control its second derivative at the minimum $\theta = 109.47^{\circ}$. The proper choice of this parameter is essential for finding a value for the melting point of the crystal close to the experimental one. The same parameter λ also determines the amplitude of the repulsive three-body term for small values of the angle θ ($\approx 60^{\circ}$). Note that if the Stillinger-Weber potential is applied to the structure of the ground state of small clusters which were found by *ab initio* calculations, many three-body terms with the angle θ at about 60° appear. Therefore a choice of λ which gives good results for the melting point of the crystal may not produce the correct ground states for the clusters. For this reason we replace the term (5) by another of the form

$$\lambda \{1 - \exp\left[-Q\left(\cos\theta + \frac{1}{3}\right)^2\right]\}.$$
 (6)

Figure 1 shows the plot of the function (6) where Q=5 and $\lambda=0.3$. The parameter Q of the new form controls the second derivative of the function (6) at its minimum, while λ determines the amplitude of the three-body term. After this replacement the energies of the ground states of the clusters approach those found from the *ab initio* calculations.⁹

(b) The contribution of the repulsive three-body term to the energy of the clusters increases slower than what is expected from the *ab initio* results, as the average coordination number per atom is increasing. This is explained if an important contribution from a four-body term is considered, because the number of four-body terms between N atoms is N(N-1)(N-2)(N-3)/24, while the



FIG. 1. Angle dependence of the three-body and four-body terms of the new potential which is expressed by Eq. (6). The parameters λ and Q are selected to be equal to 0.3 and 5.0, respectively.

three-body terms corresponding to the same N atoms are N(N-1)(N-2)/6. Therefore the number of the fourbody terms increases with N faster than the number of the three-body terms. For this reason we add to the potential a four-body term, which is built from quantities which have already been computed for the calculation of the three-body terms. In this way the computation time for molecular-dynamics simulations does not increase too much. Thus the four-body term introduces a better counting of the three-body terms including some correlation between them. After the four-body term was introduced, the new potential provides a good approximation for several properties of small clusters even though it has only one extra parameter. These results are presented and discussed in Sec. IV.

Hence we developed a potential which has the same two-body term as the Stillinger-Weber potential (formula 2), but its three-body term has the form (3), where

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda_3 \exp[\gamma(r_{ij} - R)^{-1} + \gamma(r_{ik} - R)^{-1}] \\ \times \{1 - \exp[-Q(\cos\theta_{jik} + \frac{1}{3})^2]\}.$$
(7)

Moreover, a four-body term was added of the form

$$V_{4}(r_{i}, r_{j}, r_{k}, r_{l}) = g(r_{ij}, r_{ik}, r_{il}, \theta_{jik}, \theta_{jil}, \theta_{kil})$$

$$+ g(r_{ji}, r_{jk}, r_{jl}, \theta_{ijk}, \theta_{ijl}, \theta_{kjl})$$

$$+ g(r_{ki}, r_{kj}, r_{kl}, \theta_{ikj}, \theta_{ikl}, \theta_{jkl})$$

$$+ g(r_{li}, r_{lj}, r_{lk}, \theta_{ilj}, \theta_{ilk}, \theta_{jlk}), \qquad (8)$$

where

$$g(\mathbf{r}_{ij}, \mathbf{r}_{ik}, \mathbf{r}_{il}, \theta_{jik}, \theta_{jil}, \theta_{kil}) = \lambda_4 \exp\{\gamma[(\mathbf{r}_{ij} - \mathbf{R})^{-1} + (\mathbf{r}_{ik} - \mathbf{R})^{-1} + (\mathbf{r}_{il} - \mathbf{R})^{-1}]\} \times (1 - \exp\{-Q[(\cos\theta_{jik} + \frac{1}{3})^2 + (\cos\theta_{jil} + \frac{1}{3})^2 + (\cos\theta_{kil} + \frac{1}{3})^2]\}).$$
(9)

In Sec. III we choose the parameters of the potential so that the dynamic properties of the crystal are reproduced as successfully as by the Stillinger-Weber potential. Finally, in Sec. IV the new potential with the parameters found in Sec. III is applied in the case of small clusters. Our calculations show that several properties of silicon clusters are fitted.

III. A STRATEGY FOR SELECTING THE PARAMETERS OF THE NEW POTENTIAL

To determine a good set of parameters for our model, we followed the method used by Stillinger and Weber to determine the parameters of their potential. More specifically, the parameters of the two-body term are selected such that the energy per atom E_0 and the lattice constant D of the crystal at zero temperature are equal to the experimental values, namely, $E_0 = -4.63$ eV and D = 5.43 Å.

The fitting of these two values determines two of the parameters of the two-body term, preferably the A and B, of which the potential is a linear function. The other two parameters are kept the same as in the Stillinger-Weber model, but they are expressed in standard units eV and angstroms, instead of the reduced units which are used by Stillinger and Weber. In other words, $\alpha = 2.0951$ Å and R = 3.77118 Å. If these values are given, A and B can be found to fit the experimental values of E_0 and D. Therefore, A = 16.30076 and B = 11.58113. Figure 2

shows the plot of the two-body term for the above values of the parameters. Note that the two-body term of the Stillinger-Weber potential does not reproduce the experimental value for the energy of the crystal. More specifically, the energy per atom for the diamond structure is -4.33 eV if the Stillinger-Weber potential is used, which is 0.3 eV higher than the experimental one.

The three-body and four-body terms does not contribute to the energy of the diamond lattice because of the special form of their dependence on the angle θ . The parameters λ_3 , λ_4 , γ , and Q are chosen such that first, the diamond structure is the ground state of the silicon crys-



FIG. 2. Plot of the two-body term of the new potential [Eq. (2)]. Its parameters are A = 16.30076 eV, B = 11.58113 Å⁴, $\alpha = 2.0951$ Å, and R = 3.77118 Å.

Using these values of the parameters, the energy per atom as a function of the volume of the lattice is calculated for several structures. Figure 4 shows that the diamond structure corresponds to the lowest energy per atom. The fcc and bcc structures also have a low energy per atom, which is only 0.1 eV higher than the diamond structure. Even though the energy difference between the diamond lattice and the structures with large coordination number (fcc and bcc) is small compared to the results found from local density approximation (LDA) calculations,¹⁵ this is necessary for finding a good estimate for the melting point of silicon.

The numerical simulation of the melting of the silicon crystal is conducted on a cubic cell of silicon with 64 atoms, where periodic boundary conditions are considered. The volume of this cell is not constant as in the work of Stillinger and Weber, but can change under constant pressure. This molecular-dynamics simulation under constant pressure is done following the method of Andersen.¹⁶ This method considers the volume as one more coordinate of the system. Therefore a term of the form PV is added to the potential energy of the system, and the corresponding term $(M/2)[d(V^{1/3})/dt]^2$ is added to the kinetic energy of the system. The factor M is a mass corresponding to the mass of the piston which applies the constant pressure on the crystal. It can be shown that the values of quantities which are calculated during a numerical experiment of this type as time averages are independent of the value of M.¹⁶ The advantage of doing the numerical experiment under constant pressure is that not only does it become more realistic, but also it simulates quantities (e.g., specific heat under constant pressure) which can be measured experimentally.

The melting of the crystal cell with 64 silicon atoms was studied under constant pressure of 1 atm. The



FIG. 4. Energies per atom for several crystal structures as a function of the relative volume V/V_0 . V_0 is the experimental volume of the silicon crystal at zero temperature.

dependence of the melting point on two of the parameters λ_4 and Q of our model was examined. The phase diagram where the average potential energy $\langle \Phi \rangle$ is plotted as a function of the temperature T is constructed for two cases. In the case (i) $\lambda_4 = 50$ and Q = 7, while in case (ii) $\lambda_4 = 47$ and Q = 5. Figure 5 shows the phase diagrams corresponding to these two cases. The local minimum of each of these curves, noted by MP, is considered as the melting point of the crystal, while the local maximum, noted by SH, is considered as the maximum temperature where superheated solid exists. Note that the second choice of parameters has decreased the melting point by 650 K compared to case (i).

The melting point for the case (ii), which corresponds to our final choice of parameters, is about 2050 K. This value is similar to the one found by Stillinger and Weber. Moreover, our estimate for the latent heat for melting is 0.3 eV/atom, while Stillinger-Weber's value is 0.31 eV/atom, and the experimental value is 0.52 eV/atom. These results show the similarities of our model to the one of Stillinger and Weber. The differences with the experimental values (the melting point of silicon is 1683 K) may be attributed to both this strategy for constructing a model for silicon and the unrealistic conditions for the numerical simulation of melting. Indeed, the periodic boundary conditions which are valid even after the melt-



FIG. 3. Equipotential lines close to the equilibrium position of an atom in the crystal. The distances are measured in angstroms and the energies in eV.



FIG. 5. Phase diagrams which show the melting of silicon crystal. Curve (i) corresponds to the choice of parameters $\lambda_4 = 50$ and Q = 7, and curve (ii) corresponds to $\lambda_4 = 47$ and Q = 5, mean potential vs temperature.

ing, for a small size crystal can cause a considerable overestimation for the melting point.

It is also interesting that our model reproduces some properties of liquid silicon. More specifically, the specific heat of the liquid is found to be 6.8 kcal/mol, while the experimental value is 7.4 kcal/mol.

Another interesting property of the liquid is that its atoms have an average number of first neighbors greater than 6, while the first neighbors for an atom in the solid is 4. To check if this property is reproduced by our model, we considered successive shells of increasing radius and width 0.2 Å around each atom, and count the number of the neighboring atoms in them. Then the average number of particles N in a shell of radius r is plotted as a function of r. The integral of the function N(r) for $r \leq r_0$, where r_0 is the value of r corresponding to the first minimum of the function N(r), is the average number of first neighbors for an atom of the system. Figure 6 shows that if the system is in the solid state, the average number of the first neighbors of its atoms is about 4, while if the system is in the liquid phase this number becomes about 6.5.

Therefore our model reproduces many of the properties of the solid and the liquid silicon as successfully as the Stillinger-Weber model does. Several of the quantities which are determined by these numerical experiments compare well with experimental values, even though some properties of the liquid are very much influenced by the periodic boundary conditions which are used to facilitate the computation. This potential with the set of parameters which are selected to fit properties of the bulk is used in Sec. IV to simulate some properties of small clusters of silicon.



FIG. 6. Average number of neighboring particles per atom as a function of the distance between them for (a) the solid state and (b) the liquid state of silicon at temperature T = 2050 K.

IV. GROUND STATES OF SMALL SILICON CLUSTERS

The great advantage of our potential over the Stillinger-Weber model and the other model potentials, which were proposed so far to simulate silicon, is that it gives good results for small clusters (larger than 6 atoms). More specifically, it produces ground states for the small clusters with energies and structures similar to those found from Hartree-Fock⁹ or LDA (Ref. 15) calculations. Moreover, it gives energies for other structures of metastable states which are also in agreement with the *ab initio* results. Therefore this potential is a good model for simulating dynamic properties of the clusters.

In this section our results for the ground state of small silicon clusters are compared to the *ab initio* results and the ground states found from other analytical models. We used the method of simulated annealing to determine the minimum of the clusters. This method determines the global minimum of a function with many variables if a sufficiently large number of trials is done. The number of trials needed depends on the number of variables of the function. Therefore if the number of variables is large it may be required that an extremely large number of trials be computed. Nevertheless the method tends to give a structure with energy close to the energy of the absolute minimum even in the cases where it fails to produce this minimum itself.

In this way we determine the energy and the structure of the ground state for 7 to 15 atoms. Figure 7 shows the structure of the absolute minima for the clusters with 7, 8, 9, and 10 atoms. These are very similar to the structures published in Ref. 17, where the ground states were found by the Car-Parinello method. This method is a combination of the local density approximation and molecular dynamics. More specifically, we found a structure of the absolute minimum of Si₇ which is exactly the same as in Ref. 17. The ground state of Si_8 is described in Ref. 17 as a bicapped tetragonal bipyramid. We found this structure, too, but in our result the two extra atoms which cap two of the sides of the bipyramid are close to each other so there is an interaction between them. The ground state of Si₉ is described in Ref. 17 as a strongly distorted tricapped octahedron. The same figure can also be described as a distorted tetracapped triagonal bipyramid, which is a structure similar to what we found as the ground state of Si₉.

Finally the absolute minimum of Si₁₀ which is given in Ref. 17 is a tetracapped triagonal prism. Our results show a slightly different ground state for Si₁₀. More specifically, the structure we found is a distorted tricapped triangular prism with one more atom interacting with the two atoms of an edge of the prism and the two nearby extra atoms, which are not elements of the prism. Therefore the structure of the ground state of Si₁₀ is basically the same as that found by the Car-Parinello method, but the tenth atom is not placed over one of the triangular basis of the prism, preferring to interact with four atoms instead of three. Note that in Fig. 7 lines are drawn between atoms which are less than R = 3.77118 Å apart.

The energies per atom for the clusters of size 5 to 15



FIG. 7. Ground state of silicon clusters with 7, 8, 9, and 10 atoms. Lines are drawn between atoms which are less than R = 3.77118 Å apart.

are shown in Fig. 8. Our results are noted by a +, while an * marks the corresponding values for the Stillinger-Weber potential as it is given in Ref. 8. The mark \times shows the values found by the new Biswas-Hamann model. The # notes the *ab initio* values found by Raghavashari, and \bigcirc notes the same results after they have been scaled to fit the experimental values for Si₂ and Si₃. Our results not only approach very much the scaled *ab initio* values, but also they show a similar to the *ab initio* results increase for the energy per atom as the size of the clusters grows.

Figure 9 shows the fragmentation energy for the clusters with 5–15 atoms, which were determined from our potential (solid). The fragmentation energies for clusters of the same size which are calculated from the Stillinger-Weber potential are also presented in the same figure (dashed line). Note that the two higher peaks of the curve corresponding to the new potential coincide with the two of the magic numbers which are shown in the mass spectrum in Ref. 11 for the range of masses between 5 and 15 atoms. On the contrary, the fragmentation energies corresponding to the Stillinger-Weber potential do not correlate with these magic numbers.

The third peak of the solid curve of Fig. 9, which corresponds to a cluster with 12 atoms, does not correspond to a magic number. It is not certain what is the reason for this disagreement between our model and the experimental results. First it should be noted that we treat neutral clusters, while the mass spectrum in Ref. 11 is produced from positively charged particles. Another possible explanation, which is also discussed in Ref. 8, is that the magic numbers correspond to clusters with maximum fragmentation temperature and not to maximum fragmentation energy. In other words, the stability of clusters should be studied in relationship to the dynamics. Finally we must keep in mind that the method of simulated annealing does not necessarily determine the absolute minimum of the clusters, but it probably gives a state with energy close to the ground state. Hence this peak in the fragmentation energy for the Si_{12} may be artificial.



FIG. 8. Comparison of the energy per atom for the ground state of clusters between the different classical models and the *ab initio* results. The marks \circ and # correspond to the *ab initio* results after scaling and before scaling, respectively. The marks *, \times , and + correspond to the Stillinger-Weber potential, Biswas-Hamann potential, and the new potential proposed in this paper, respectively.



FIG. 9. Fragmentation energy for silicon clusters. The dashed curve corresponds to the results of the Stillinger-Weber potential. The solid curve corresponds to our results.

Therefore we developed a potential which describes the structure and energy of silicon clusters more successfully than any of the other analytical models proposed so far. We plan to use this potential for doing moleculardynamics simulations for clusters the results of which may be compared with future experimental data.

V. CONCLUSIONS

In this study we propose an analytical potential for silicon which gives good results for small clusters. Moreover, the same classical potential fits some dynamic properties of the bulk silicon. Therefore, it can be used to describe the growth and the first fragmentation of silicon clusters $(Si_n \rightarrow Si_{n-1} + Si)$.

The new potential, which is presented in this paper, is a modification of the Stillinger-Weber model. In other words, a four-body term is added to their model, and the angle dependence of the three-body and four-body terms has been changed. These modifications result in a qualitative improvement over the previous models for silicon. More specifically, good values for the energy of the ground states of the clusters obtained for a large range of the parameters of the three-body and four-body terms. Therefore these parameters can be selected to fit properties of the crystal.

We choose to select the values of these parameters such that the melting point of the bulk silicon can be approximated. The validity of the numerical experiment which simulates the melting of the crystal can be questioned. Nevertheless, this strategy for selecting the parameters is probably the best if the dynamical properties of silicon are to be studied.

After the parameters of the potential are chosen to fit properties of the crystal, the model is used to determine the energies and structures of the ground states of small silicon clusters, where a good agreement with the results of *ab initio* electronic calculations is observed.

Several parameters of our potential were taken from previous studies of the Stillinger-Weber model. We have not attempted to vary these parameters but we expect that more satisfactory results could be obtained by slightly different values for the parameters. The study of the influence of these parameters on dynamical properties of silicon clusters is left for future work and to this effect new experimental measurements will be very useful.

It is very important that by introducing only two extra parameters we have succeeded to fit a large number of new properties, i.e., the structure and energies of the ground state and low metastable states of small clusters.

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