

Structural properties of silicon clusters: an empirical potential study

X G Gong^{†‡}, Q Q Zheng[†] and Yi-Zhen He[‡]

[†] Centre for Theoretical Physics, Chinese Centre of Advanced Science and Technology (World Laboratory), Box 8730, Beijing, People's Republic of China

[‡] Institute of Solid-State Physics, Academia Sinica, Hefei-230031, People's Republic of China

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Abstract. By using our newly proposed empirical interatomic potential for silicon, the structure and some dynamical properties of the silicon cluster Si_n ($10 \leq n \leq 24$) have been studied. It is found that the results obtained are close to those from *ab initio* methods. From the present results, we can gain a new insight into understanding the experimental data on the Si_n clusters.

Atomic clusters exhibit various properties observed in atomic or molecular physics on one hand, and in condensed-matter physics on the other hand. Since Knight *et al* found a shell structure of alkali-metal clusters [1], which is successfully explained by the jellium model [2], the physics of atomic clusters has been studied extensively. An understanding of the structure and physical properties of small clusters can help to explain phenomena such as crystal growth, catalysts and surface reconstruction. There are many interesting problems to be solved in the studies of cluster physics. Recently many publications have been devoted to the study of the lowest-energy structures of atomic clusters. Since in clusters most of the atoms sit at the surface and do not have enough neighbours, the equilibrium structure of clusters is very complicated. Generally speaking, finding the equilibrium structure of a cluster is equivalent to globally minimizing the energy functional $E[R_i, \Psi_i]$, where R_i and Ψ_i are atomic coordinates and electronic wavefunctions respectively. In the density-functional theory, $E[R_i, \Psi_i]$ can be written down explicitly, but it is so complicated that to obtain the equilibrium structure in a more than two-atom cluster is very difficult by the conventional matrix-diagonalization method [3]. The newly developed so-called *ab initio* molecular dynamics [4] with the local-density approximation could be a good candidate to study the structural properties of clusters either at zero temperature or at finite temperature. Unfortunately, because the *ab initio* molecular dynamics relaxes ions and electrons simultaneously, the calculations become too heavy to find the global minimum among many local minima with the number of atoms more than ten. In fact, the validity of the Born–Oppenheimer approximation, which allows us to treat the electrons as if they were always in their ground state, implies that an energy functional including only positions of the nuclei with electron coordination integrated out must exist. The simplest type of description would be the form

$$E = \frac{1}{2} \sum_{ij} V_2(r_{ij}) + \frac{1}{6} \sum_{ijk} V_3(r_i, r_j, r_k) + \dots$$

where E is the total energy, and V_n are interatomic potential functions. A global description of the exact form is usually impractical. However, some approximate forms are accurate

enough in many cases; the Lennard-Jones potential with only the first term in the above equation, which has successfully modelled the inert gases and solids interacting with van der Waals forces, is a famous example. But for the tetrahedral-coordinated crystalline silicon in terms of strongly hybridized sp^3 orbitals, how to choose a suitable empirical potential is still a difficult problem nowadays. It is clear that the pair term alone could not describe the strongly hybridized system. In the past ten years or so, many attempts have been made to model the interaction in silicon and other strongly hybridized systems, most of them can be classified into two categories as proposed by Carlsson [5], cluster potential and cluster functional. Recently Balamane *et al* [6] have made extensive comparison of calculations with various model potentials on many different physical properties of silicon. They found none of those model potentials can correctly produce all the calculated physical properties with enough accuracy. The SW potential [7], proposed by Stillinger and Weber in 1985, is a cluster potential for silicon which includes a three-body contribution. It can well produce some physical properties of bulk silicon. In fact by using the SW potential, many applications have been made to study surface [8], defects in solids [9], melting [10], clusters [11] and so on. But from the results of Feuston *et al* [11], we can see that the SW potential is not accurate enough to predicate structures of silicon clusters. Feuston's results show that even for clusters of a few atoms, the structure of clusters is diamond-like, which is very much different from the *ab initio* results [12]. Consequently the experimental results on clusters cannot be explained by the SW interatomic potential.

On account of the failure of the SW potential for the silicon clusters, the author has proposed a modification to the SW potential [13]. The angular part $(\cos \theta_{ijk} + \frac{1}{3})^2$ of the SW potential has been changed to $\lambda_1(\cos \theta_{ijk} + \frac{1}{3})^2[(\cos \theta_{ijk} + C_0)^2 + C_1]$. This modification can be understood as follow. Comparing the bond angle distribution of silicon clusters obtained from SW-potential and *ab initio* calculations [12], it can be found that in the *ab initio* results, there are two peaks at about 100° and 60° respectively, but in the results of the SW potential, there is only one broad peak at 90° . Furthermore in the bond angle distribution of liquid and amorphous silicon, there is also a peak at 60° . The three-body term defined in the SW potential always increases the total energy, which becomes zero only when the angle θ_{ijk} (subtended by r_{ki} and r_{ji} with the vertex at the i th site) is the perfect tetrahedron angle θ_t ($\cos \theta_t = -\frac{1}{3}$). The value of the three-body term of the SW potential at 60° is quite large, so the bond angle around 60° is not energetically favourable. That is why the bond angle distributions for non-crystalline silicon obtained from the SW potential are clearly different from what is obtained by *ab initio* methods. Because our newly proposed angle part reduced the value around 60° , it can be expected to describe non-crystalline silicon better than the SW potential. We have fitted the new parameters λ_1 , C_0 and C_1 to the bulk silicon phase diagram, the fitted numbers are 25, -0.5 and 0.45 for λ_1 , C_0 and C_1 respectively. Other parameters in the SW potential remain unchanged. Using the fitted new potential, the bulk phase diagram is calculated, the lattice constant and bulk modulus are very similar to the results of the SW potential; the diamond structure phase has the lowest energies and the total energies of the other phases are reasonably close [13].

Using this interatomic potential, the structures of Si_n clusters ($n \sim 24$) have been studied. The equilibrium structures of clusters are obtained through the simulated annealing technique. Some of the results ($n \leq 10$) have been reported previously [13]; the results from our present model potential are close to the *ab initio* results [12]. Improvement over other empirical potentials has been made. Especially reasonable energy differences of clusters with different symmetries have been obtained from our model potential.

In this paper, some structural and dynamical properties of larger Si_n clusters are presented. As the number of atoms in the cluster increases, the number of possible structures

for the cluster increases enormously: Similar to our previous work, each cluster is heated to $\sim 2500\text{--}3000\text{ K}$; after a period of relaxation, we use a molecular-dynamics simulated annealing procedure to determine the lowest-energy structure. With current computing technology, it is very difficult to explore large clusters extensively with *ab initio* molecular dynamics. However, based on our model potential, we can hope that our simulated annealing results can provide new insight into the understanding of the structure of larger silicon clusters.

For the Si_n with $n \geq 11$, the geometrical structures are very different from that of the smaller clusters, and also different from what would be expected based on the bulk structure. In the clusters of $\text{Si}_{11}\text{--}\text{Si}_{13}$, we find that the dominant structural feature is the icosahedron: Si_{11} could be considered as a distorted icosahedron with one vertex missing and Si_{12} is a regular icosahedron with a vacant centre. Different from what was obtained from Chelikowsky's results [14], the lowest-energy structure of the Si_{13} cluster is a vacant distorted icosahedron with one cap. The trigonal antiprism with seven caps has almost the same energy. The Si_{13} cluster with icosahedral symmetry is a metastable structure in our model potential, but its total energy is much higher than that of the lowest-energy structure. Moreover, even at low temperature, the icosahedral structure would transform to a lower-energy structure, which implies that only a very small barrier would be needed for the transformation. We will discuss the Si_{13} cluster more later. From Si_{14} , some hexagonal rings appear as a part of the cluster. The lowest-energy structure of Si_{14} can be considered as a trigonal antiprism (TAP) with six caps on the threefold faces and two on sixfold faces, or a hexagonal antiprism with two atoms capped at sixfold positions. Similar to the bulk diamond structure of silicon, in the larger clusters ($n \geq 14$), the hexagonal ring is not flat and it is a main building block. As pointed out above, from Si_{11} to Si_{14} there is no atom at the centre of the cluster, but beginning at the Si_{15} cluster there is one atom sitting at the centre of the cluster, with more than four neighbours at a distance larger than the average nearest-neighbour distance. It is difficult to find a simple growth pattern.

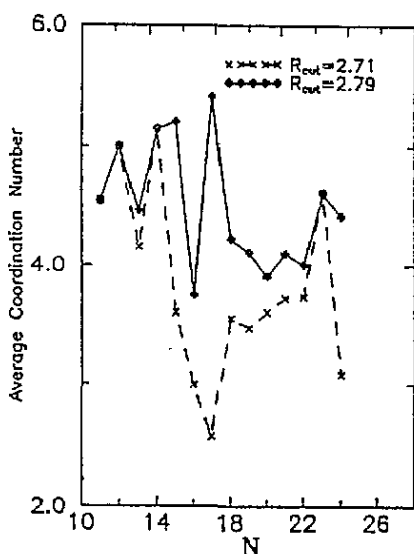


Figure 1. Size dependence of average coordination number with different distance cut-offs for silicon clusters.

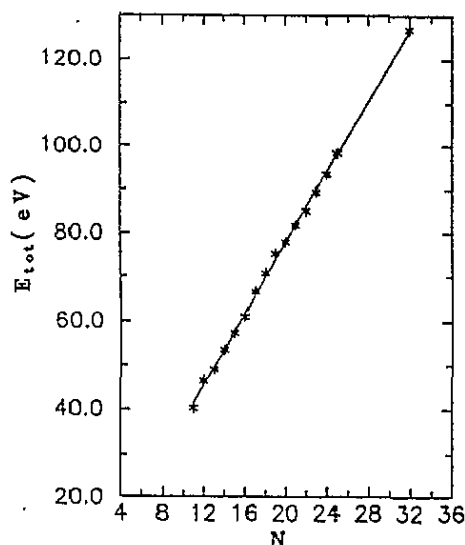


Figure 2. Total energies of the calculated silicon clusters.

We have calculated the average coordination number for all calculated clusters with two distance cut-offs R_{cut} . We can see from figure 1 that in the smaller clusters, the coordination number is close to five, but as the size of the cluster increases the coordination number decreases to about four. In the Si_{17} cluster, the coordination number changes from about two to five, as the R_{cut} changes from 2.71 Å to 2.79 Å. This is because there are five atoms loosely connected to their neighbours. In figure 2 the total energies for all calculated clusters are plotted as a function of the number of atoms n . On the scale shown in this figure, the size dependence of the energy is almost linear. We fit our calculated values of $E(n)$ against n to $E(n) = a + bn$, and get $b = 4.10$ eV/atom; the fitted result is shown in the figure by the solid line. One can compare b with the cohesive energy of the bulk silicon phase in the diamond structure. The cohesive energy of the diamond silicon phase is 4.6 eV/atom: we can see that there is about a 13% difference between our extrapolated value and the experimental cohesive energy of the bulk structure. We have also tried to fit the energy against n by using $E(n) = C_1 + C_2n + C_3n^{2/3}$; normally the C_2 represents the *bulk-like* contributions, and the C_3 represents a *surface-like* contributions. We find C_2 to be 3.91, and C_3 to be 0.59 which is a very small number. This is not surprising because, in the calculated clusters, nearly all the atoms sit at the surface and the number of atoms at surface is almost linearly dependent on the total number of atoms in the clusters, so the contributions from surface atoms are included in C_2 . But we believe that, going to larger clusters in which there are many bulk-like atoms and surface-like atoms, it is important to include a surface term in the energy function.

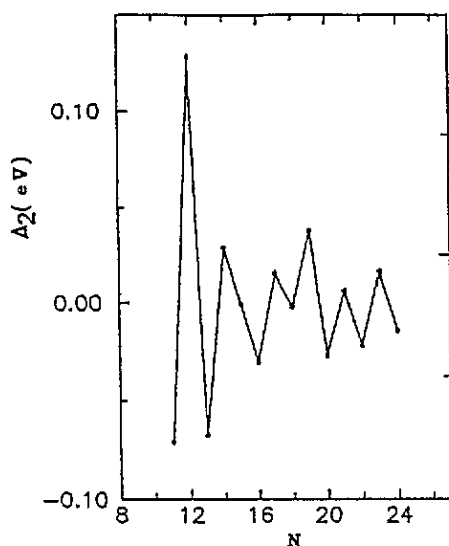


Figure 3. The second energy difference as a function of n for silicon clusters.

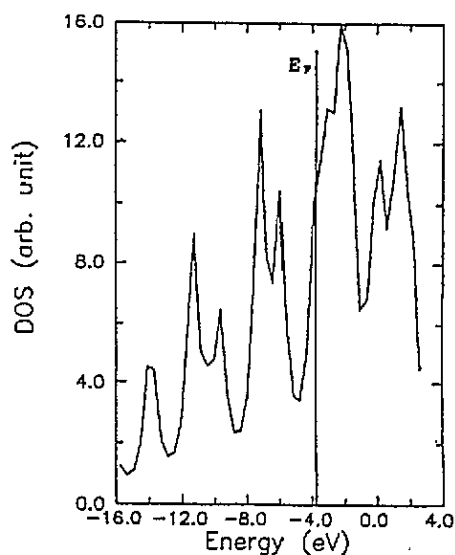


Figure 4. Electronic density of states for icosahedral Si_{13} cluster from density-functional calculation.

The second energy difference defined by $\Delta_2(n) = E(n+1) + E(n-1) - 2E(n)$ is presented in figure 3: we can see clearly that at $n = 12, 14, 17, 19$ and 23 there are peaks in $\Delta_2(n)$, which implies that, at these numbers, the silicon clusters should have relatively higher stability than their neighbours. In the experiment of the addition reaction of Si_n^+ to C_2H_4 , Jarrold *et al* [15] have found that Si_{13}^+ , Si_{19}^+ and Si_{23}^+ have relatively lower reactivity.

Except for Si_{13}^+ , our results are in agreement with the experiment data. But when we compare the stability just from the energy point of view with the chemical reactivity, it is important to notice that there is no reason to expect direct correspondence between the thermodynamical stability and chemical reactivity, because experimental results suggest the stable isomer may have high chemical reactivity [16]. So the relatively lower reactivity for the Si_{13}^+ cluster obtained by Jarrold does not necessarily mean that Si_{13} should have high binding energy [15]. The thirteen-atom clusters are very interesting clusters. In the inert-gas cluster, many studies suggest that the thirteen-atom cluster has an icosahedral structure. The *ab initio* molecular-dynamics studies show that the structure of Al_{13} is a distorted icosahedron, and it has been argued that Al_{13} should be a perfect icosahedron, because the highest occupied state is completely filled and no Jahn–Teller effect exists [17]. In the work of Chelikowsky *et al* on the interatomic force field [14], the icosahedral structure is also obtained for the Si_{13} , which has the highest binding energy. In fact in icosahedral Si_{13} , the centre silicon atom has twelve neighbours and other vertex atoms have six neighbours. As we know, each atom in the lowest-energy phase of silicon has only four neighbours; the close-packed phases with more neighbours have very low binding energy. So it is hard to imagine that Si_{13} with an icosahedral structure would have high binding energy. For further confirmation, we have calculated the electronic structure of icosahedral Si_{13} . The equilibrium distance between atoms is obtained by total-energy calculation in the scheme of the density-functional theory with the local-density approximation to the exchange–correlation of electrons [18, 19]. In figure 4, the total electronic density of states obtained is shown. We can see that at the Fermi level, the density of states is quite high, the highest occupied molecular state is not completely filled, so at least some Jahn–Teller distortion would increase the binding energy. This calculation suggests that the perfect icosahedron is not a stable structure for the Si_{13} cluster. As a matter of fact the results from more efficient *ab initio* molecular-dynamics simulations by Rothlisberger *et al* [20] also support our argument. They found that the lowest-energy structure of Si_{13} can be described as a trigonal antiprism (TAP) with six caps on the threefold faces and one cap on one sixfold face, the coordination number is between four and five; the icosahedral Si_{13} was found to have an energy 5.3 eV above the ground state. In our model potential, we obtain a TAP in our simulated annealing calculation. The total energy is only 0.025 eV/atom higher than that of the lowest-energy structure: this small energy difference should be within the error of our model potential. The lowest-energy structure of Si_{14} that we obtained can be considered as one atom capped at the second sixfold position in the ground-state structure of Si_{13} obtained by Rothlisberger *et al* [20].

To study the structural properties of Si_n clusters at finite temperature, we start with the lowest-energy structure at zero temperature. We give a small random displacement to each atom, then let the atoms keep moving, keeping the temperature at about 500 K. In figure 5 and figure 6, the bond angle distributions and pair-correlation functions for Si_n clusters ($11 \leq n \leq 23$) are shown. We can compare the results with what was obtained from the SW potential [11]: the qualitative changes can be clearly observed. In the results of the SW potential, the bond angles distribute only around θ_t , which is obviously contrary to the results of the *ab initio* molecular-dynamics calculation [12]. But in the present calculation, the bond angles distributed mainly around 60° and 110° . Chelikowsky *et al* have also obtained a similar bond angle distribution for Si_n , but clearly they got a peak at 60° much higher than the peak at about 110° : this is because they predicated an icosahedral-like structure for Si_n clusters. In our previous work [13], the bond angle distribution of Si_{10} has been compared with the results of the *ab initio* method: a very good agreement has been obtained. It is interesting to look at the pair-correlation functions shown in figure 6:

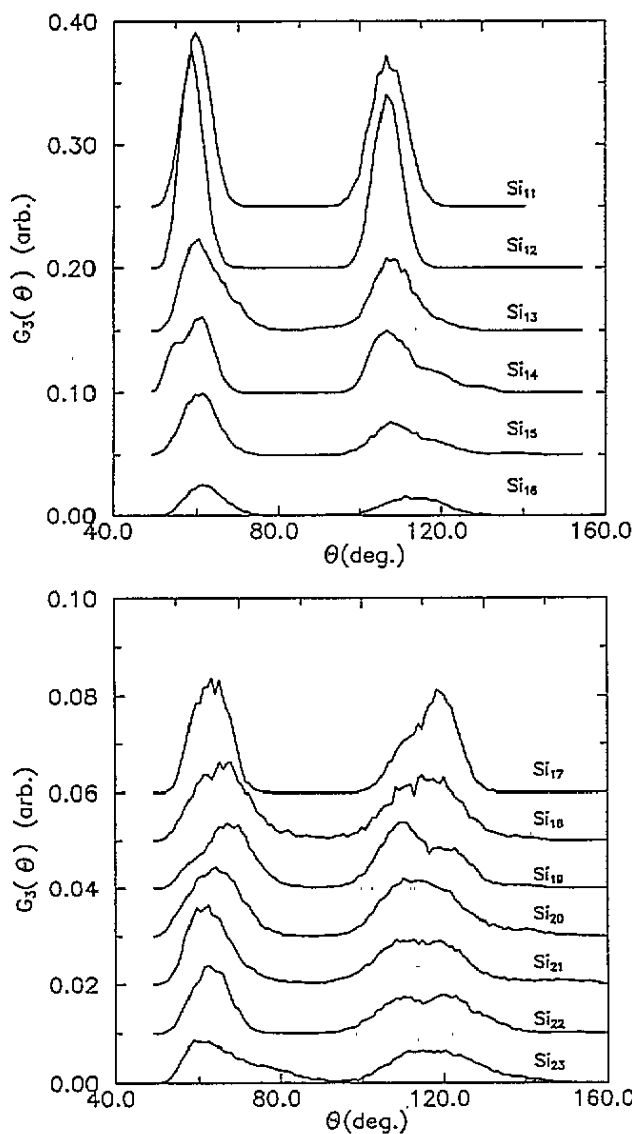


Figure 5. The bond-angle distribution $G_3(\theta)$ for the silicon clusters at about 500 K.

although it is not so meaningful far away from the second peak, we can still find some structural information in the first peak. Beginning with the Si_{17} cluster, there is a shoulder appearing on the right of the first peak, and in Si_{19} , the shoulder grows into a peak. But in Si_{20} this peak disappears again. This shoulder is also reflected in the bond angle distribution: we can see, in Si_{19} , the bond angle at the larger angle becomes the major part, and the two peaks at 110° and 120° can clearly be seen. From the bond-angle distributions, it can be seen that the contribution to the θ_i is increased as the size of the clusters increases, which might imply that the transition to the bulk diamond structure is in process.

As discussed above, the structures of silicon clusters with $n = 11-24$ are very complicated; the growth pattern is not very clear. We did not see a pentagonal growth pattern for Si_n as obtained by Chelikowsky *et al.* In their results, the low reactivity of some Si_n^+ to C_2H_4 was explained by a completely capped pentagon. From the energy point of view,

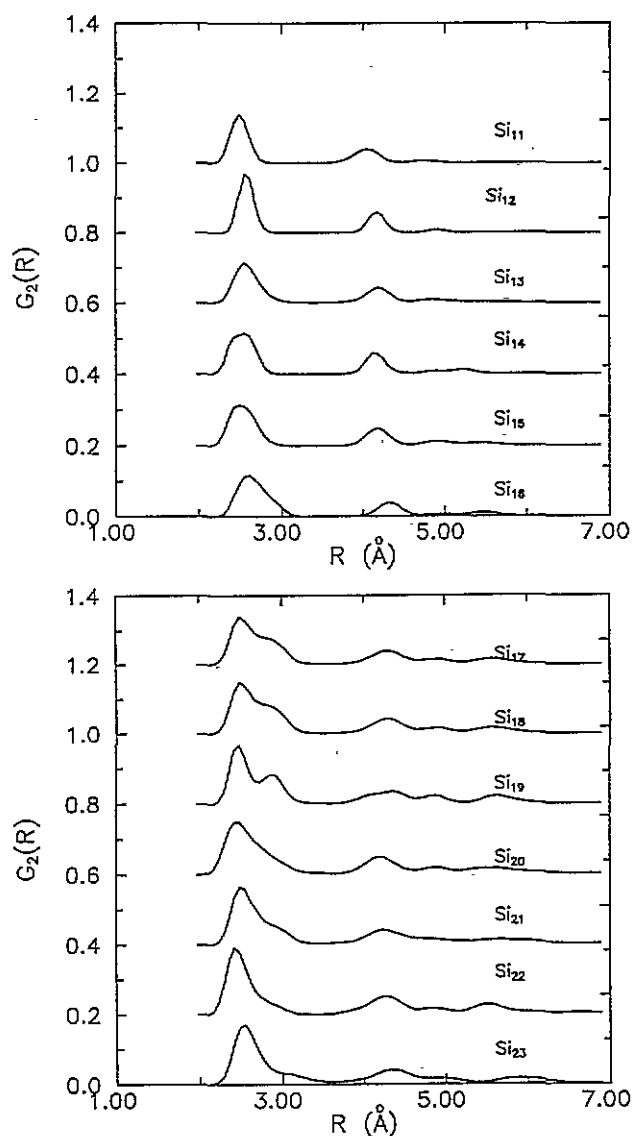


Figure 6. The pair-correlation functions for the silicon clusters at about 500 K.

we find Si_{12} , Si_{14} , Si_{17} , Si_{19} and Si_{23} clusters to be more stable than their neighbours. In fact it is evident from our electronic-structure calculation and from *ab initio* molecular dynamics that Si_{13} with the icosahedral structure is not stable. To explain the discrepancy between the *ab initio* calculation and the experimental chemical reactivity, Phillips [21] has tried to argue that Si_{13} is a very strongly electronically correlated system with a correlation energy underestimated by as much as 10 eV by the various *ab initio* methods, which makes Si_{13} a metallic system. In fact understanding the relatively low reactivity of Si_{13} is very difficult, because, as found by Jarrold, the energetically stable structure may have higher reactivity, so *ab initio* results on the instability of icosahedral Si_{13} do not exclude the possibility of low reactivity. On the other hand, the mass spectrum of Si_n clusters does not show any high stability of Si_{13} [22]: instead the energetically stable Si_6 and Si_{10} clusters found in the mass spectrum have been observed in the fragmentation of larger clusters [15, 23].

We found an average coordination number approaching four in the larger clusters which is close to the value in bulk silicon, instead of six as obtained by Chelikowsky *et al* because of the pentagonal structure. Although some hexagonal rings, which may be considered as fragments of bulk silicon structures, have been found in the large clusters, it seems far away from the convergence of the bulk structure. The equilibrium structures of the Si clusters from our model potential are in agreement with the available results of *ab initio* molecular-dynamics simulation. All these results suggest that the present interatomic potential gives us reasonable results for Si_n clusters. Some further application to the silicon surface and defects in solids is being performed.

Acknowledgment

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