Equilibrium Structures and Finite Temperature Properties of Silicon Microclusters from *Ab Initio* Molecular-Dynamics Calculations

Pietro Ballone and Wanda Andreoni

Zurich Research Laboratory, IBM Research Division, 8803 Rüschlikon, Switzerland

and

Roberto Car and Michele Parrinello

International School for Advanced Studies, 34014 Trieste, Italy

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We show that new aspects of the physics of microclusters can be investigated accurately with *ab initio* molecular dynamics. We present results on a number of properties of Si_N aggregates (N up to 10) at both zero and finite temperatures. The results of dynamical simulated annealing for the ground state point to a complex growth sequence. Simulations at finite temperatures show the existence of two regimes, solidlike and liquidlike, with substantially different electronic and structural properties.

Understanding the behavior of covalent materials in different states of aggregation under different physical conditions is a central issue in the physics of semiconductors. Microclusters are particularly challenging since their bonding properties are expected to be rather different from those of the crystal and crucially dependent on the specific size. In fact, experiments are by now available on microclusters of Si, Ge, and GaAs,[1] which illustrate the strong size dependence of both stability and reactivity. Very recently Cheshnovsky *et al.*[2] have introduced ultraviolet photoelectron spectroscopy for mass-selected negatively charged small clusters to probe the electronic structure. These measurements have once more raised questions about the equilibrium configurations and their link to the electronic structure, as well as about the influence of temperature. So far, these questions have been investigated only partially. This was due in part to the limitations of standard theoretical approaches, i.e., *ab initio* methods of various degrees of sophistication [density-functional theory (DFT) in the local-density approximation, Hartree-Fock, etc.][3,4] and computer simulation [molecular dynamics (MD)][5] with empirical potentials for the description of the atomic interactions.[6] The former have been applied to search for the state of lowest energy by exploration of a severely limited number of configurations. The latter is more efficient in the search for the ground state and suitable for the study of the thermal behavior of the cluster since it exploits the techniques of statistical mechanics to explore large fractions of configuration space. However, it misses the link between electronic and structural properties, and the predictive capability of the potentials (usually fitted to the solid) in microclusters has still to be tested against quantum-mechanical calculations.

To achieve a reliable as well as comprehensive description of the physics of semiconductor microclusters, it is crucial to combine the accuracy of *ab initio* calculations with the advantages of statistical-mechanics approaches. This can be achieved by use of the unified approach for MD and DFT, which has been recently introduced by two of us.[7] In this scheme, a fictitious classical Lagrangean is introduced whose dynamical variables are the ionic positions and the Kohn-Sham orbitals. The dynamical trajectories generated by the Lagrangean can be used in several ways.[8,9] (i) to relax ions and electrons simultaneously to the closest local minimum; (ii) to search for the absolute minimum with the dynamical simulated annealing (DSA) strategy; (iii) to perform MD simulations, with forces calculated with DFT–local-density approximation accuracy.

Here we present results for Si_N clusters ($N = 7-10$) on the equilibrium structures and electronic properties at $T = 0$, as well as on static and dynamical properties at finite temperatures. The study at low temperatures reveals the existence of unforeseen equilibrium structures, and may lead one to modify some of the existing views on the growth of Si microclusters. The extension to higher temperatures offers, for the first time, the possibility of investigating *ab initio* the effect of thermal motion on the properties of covalent clusters. Preliminary results have been published elsewhere.[10] Calculations on Si_3, Si_4, and Si_5 were used as a successful test[8] of the ability of the DSA to reproduce their known equilibrium structures.[4]

We used a norm-conserving nonlocal pseudopotential to describe the electron-ion interaction.[11] The Kohn-Sham orbitals at Γ were expanded in plane waves with an energy cutoff of 6 Ry.[12] We assumed a fcc supercell geometry with edge $a = 35$ a.u. In the MD runs, an integration time step $\Delta t = 1.2 \times 10^{-16}$ sec was used. The fictitious mass μ of Ref. 7 was set at 300 a.u. This led to trajectories which lay on the Born-Oppenheimer surface

to within 10^{-5} a.u.

In order to obtain the most stable $T=0$ configuration, we have applied the DSA strategy. In a typical run, we heated the system to 3300 K for about $2000\Delta t$, and then cooled it down at a rate of 10^{14} K/sec. Obviously, the final result is not guaranteed to coincide with the global minimum in the potential energy surface. To enhance confidence in our findings, we also considered configurations generated by faster cooling rates and relaxation around preassigned geometries. In all cases, the stability of the resulting structures was tested by heating the clusters up to about 700 K, and monitoring whether a canonical drift was observed.

The structures of minimum energy are invariably the result of DSA and are displayed in Fig. 1. Si_7 is a pentagonal bipyramid,[13] Si_8 is a bicapped octahedron,[3] Si_9 can be viewed as a strongly reconstructed tricapped octahedron, and Si_{10} is a distorted tetracapped triangular prism (TTP). Some of these structures, most noticeably the TTP, have so far escaped the attention of other investigators. It would be very interesting to have fully *ab initio* calculations for these new geometries in order to test the accuracy of our predictions. Within our model, the growth pattern in this size range appears to be more complex than previously speculated.[3]

As expected, the number of stable isomers increases rapidly with cluster size. In the case of Si_{10}, in order of increasing energy from the TTP state we find, among others, (i) the tetracapped octahedron proposed as ground state in Ref. 3, $E \lesssim 0.01$ eV/atom (i.e., essentially degenerate with the TTP within the accuracy of the calculations); (ii) a bicapped tetragonal antiprism, $E=0.05$ eV/atom; and (iii) two parallel but shifted planar zigzag chains of five atoms, $E=0.07$ eV/atom. Relaxing these configurations in a larger cell ($a=40$ a.u.) and using an energy cutoff of 8 Ry preserves the energy ordering. Moreover, the structural energy differences increase slightly ($E=0.03$, 0.06, and 0.09 eV/atom, respectively).
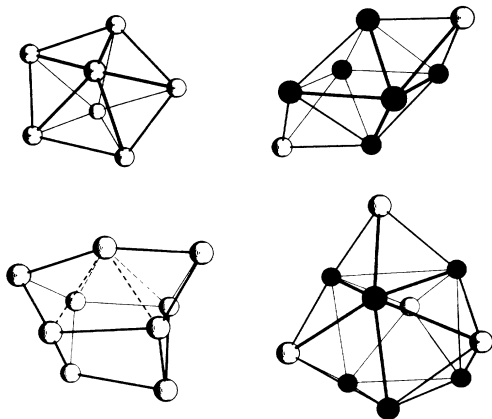
In agreement with previous studies, all low-energy structures are quite different from crystalline fragments which have open configurations. Instead, they are very compact, with the majority of bond angles in the range of 60°, an average coordination number higher than four, and the atomic positions confined within a narrow shell at $\simeq 4.5$ a.u. from the center of mass of the cluster. The spherical average $\bar{\rho}_e(r)$ of the electronic density for these structures looks very similar, i.e., peaking around the ionic shell with a tail mostly due to the highest-energy orbitals.

It would be interesting to compare the electronic structure of the different low-energy geometries with the ultraviolet photoelectron spectroscopy data.[2] This re-

FIG. 1. Ground-state geometries of Si_7–Si_{10} obtained by simulated annealing.
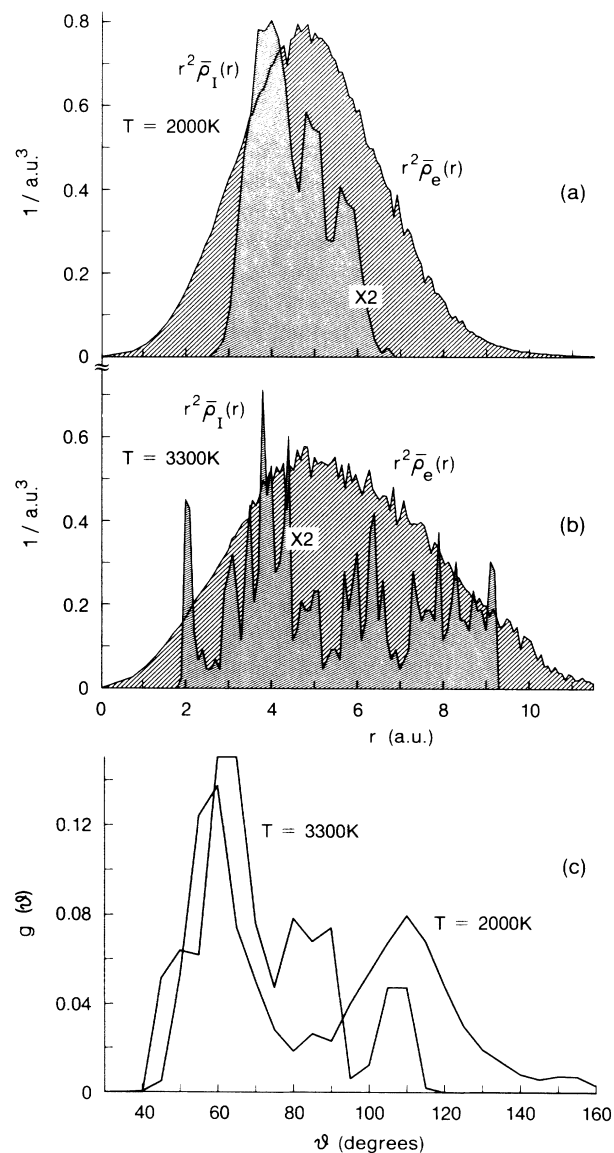

FIG. 2. Si_{10}: Temperature effects (a),(b) on ionic and electronic densities and (c) on the angular correlation function.

quires the computation of transition probabilities between ground and excited states of Si_N and Si_N^-. Here we only look at the energy distribution of the final states, i.e., neutral configurations corresponding to the removal of one electron from the occupied states of the anion. We have calculated these energies for Si_{10}, keeping the ionic positions fixed at the two lowest minima of the neutral cluster (TTP and tetracapped octahedron) but allowing for full electron relaxation. This amounts to the assumption that the extra electron does not substantially modify the geometry. Both structures exhibit a large lowest unoccupied–highest occupied molecular orbital energy gap of $\simeq 2$ eV, to be compared with the experimental value of $\simeq 1.7$ eV for the distance between the two highest peaks. The remaining part of the quasiparticle spectra is rather different for the two structures, with the TTP resembling the experimental results more closely. However, an unambiguous identification of the structure from the experimental data requires higher experimental resolution and more elaborate theoretical analysis.

We have studied the changes with temperature of several properties of Si_{10}. The averages were typically taken over a time interval of 1 ps, after equilibration runs of 0.2 ps. In Fig. 2, the spherically averaged electronic and ionic densities $\bar{\rho}_e(r)$ and $\bar{\rho}_I(r)$ are plotted versus the distance from the center of mass, (a) at
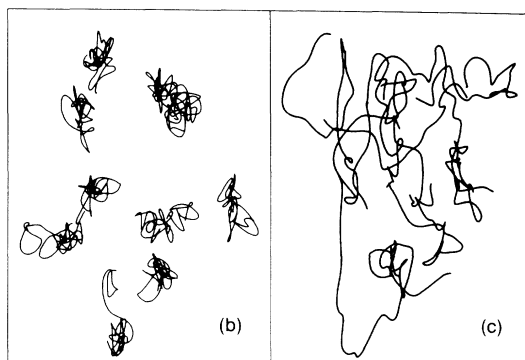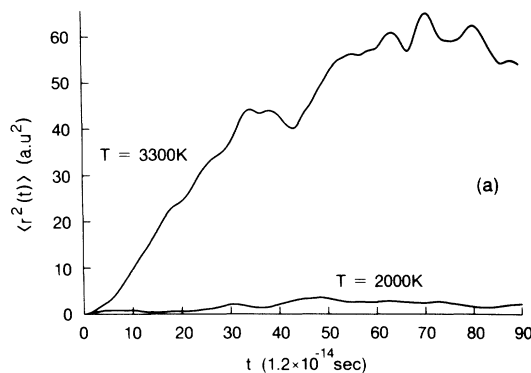
$T_1 = 2000$ K and (b) at $T_2 = 3300$ K. At T_1, both densities are only slightly broadened relative to low temperatures. In contrast, at T_2 more pronounced effects are observed: $\bar{\rho}_e(r)$ becomes much smoother and $\bar{\rho}_I(r)$ shows an approximate ionic shell structure with three atoms moving from the main shell, one inwards and two outwards.

In this temperature range, the two-body ionic correlation function shows only some thermal broadening. More striking structural changes are revealed by the bond-angle distribution [Fig. 2(c)], which shows that angles in the range $80°-90°$ become more likely at higher temperatures. Significant variations are also observed in the density of the valence-electron states, which extends invariably over $\simeq 12$ eV. At T_1 it shows four well-separated peaks, whereas at T_2 only the high-energy peak can be distinguished.

New information comes from the study of the dynamical properties of the clusters. We have calculated the atomic mean square displacement for Si_{10} as a function of time different temperatures. This shows a diffusive behavior at T_2, while at T_1 only sporadic jumplike diffusion processes were observed (Fig. 3). Since at T_2 the ionic shell structure is still maintained over relatively long times, we could analyze the mean square displacement for atoms in different shells. We find (i) marked increased in the ionic mobility on passing from the inner to the outer shell, (ii) predominance of tangential over radial motion, and (iii) strong correlation of the two outermost atoms, which tend to sit on opposite sides of the cluster.

When one is interested only in ionic properties, empirical potentials offer an efficient scheme for computer simulations, especially if one wants to extend our studies to large clusters. By using a DSA strategy similar to that described above, we have checked the accuracy of a recently improved potential.[14] The results found are at variance with ours. For instance, in the case of Si_{10}, the bicapped tetragonal antiprism is the ground state, and the tetracapped octahedron is much too high (by 0.6 eV/atom). The results published for other potentials[5] point to even larger discrepancies.

In conclusion, new results can be obtained in the physics of microclusters with the unified MD-DFT approach. On the basis of our present calculations, we can make two remarks:

(i) The success of DSA in generating ordered configurations suggests that the experimental clusters, which are obtained after cooling on a time scale presumably longer by several orders of magnitude, are likely to be in the ground state.

(ii) The study of dissociation processes requires simulation runs longer than the ones used in this work, but is feasible. On the basis of our experience at high temperatures, we expect that the dissociation products are not simply related to the $T = 0$ structures, as already sug-

FIG. 3. Si_{10}: (a) Time dependence of mean square displacement and (b),(c) ionic trajectories at $T = 2000$ and 3300 K.

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[12]In the case of Si_{10} the dispersion turns out to be at most 0.5 eV for the levels of highest energy.

[13]This is in agreement with recent configuration-interaction calculations by K. Raghavachari (private communication) and with the proposal in Ref. 4.

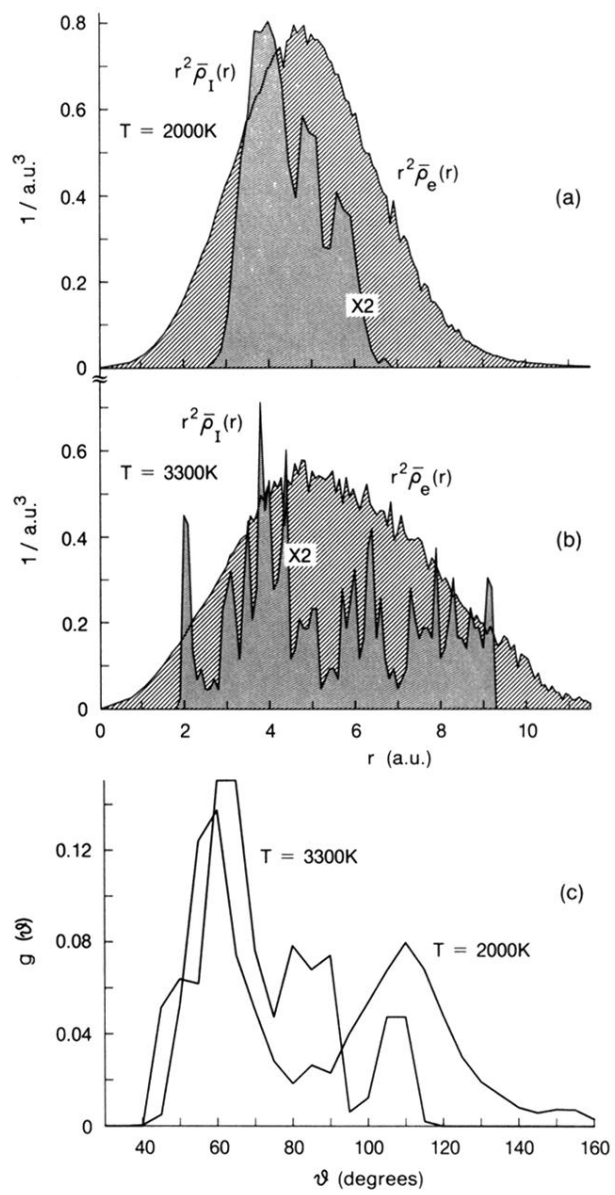[14]J. Tersoff, private communication.

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