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# Thermal effects in the equilibrium structure and size distribution of small Si clusters

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We present the first calculation of the free energy of semiconductor clusters at nonzero temperatures. Explicit determination of electronic, vibrational, and rotational contributions to the entropy allows us to investigate the effect of temperature on the equilibrium geometric structure and size distribution of these clusters. The formalism is applied to $Si_4$, $Si_5$, and $Si_6$ clusters with symmetric geometries. We find that, in these clusters, entropy can modify relative stabilities, but does not change major trends at finite temperatures.

## I. INTRODUCTION

Recently, there has been a growing interest in the study of small clusters. Besides their potential for technological applications,[1] they close the gap in our understanding of systems ranging between isolated atoms and solids. Observation of abundances in the mass spectra,[2–4] photofragmentation,[4] Coulomb explosion,[5] and plasmon excitations[6] of small clusters have stimulated a vigorous theoretical search for equilibrium structures and electronic properties of small atomic aggregates. These studies have shown that the high stability of alkali-metal clusters with $n=2,8,20,\ldots$ atoms can be understood within the shell model of a spherical cluster.[2] In rare-gas clusters, where the cohesion is dominated by nondirectional van der Waals forces, stable sizes of $n=13,55,147,\ldots$ have been found to correspond to densely packed closed-shell icosahedra.[3] Determination of stable geometries is much less clear in materials with covalent bonding, such as semiconductors.[4] There, the strength of the directional covalent bonds depends on the atomic positions. At small cluster sizes, where most of the atoms are surface atoms, the surface tension has been found to drive the cluster geometry to metallic close-packed structures.[7,8] Recently, equilibrium geometries of $Si_n$ clusters up to $n=14$ have been determined using parametrized tight-binding and *ab initio* techniques.[7,8]

The vast majority of theoretical studies have determined the cohesive and electronic properties of small clusters at zero temperature. Without further justification, these results have been compared often to experimental data. In practice, however, clusters are created and observed at high temperatures.[9] The process of cluster formation involves condensation, fragmentation, recombination, evaporation, and finally cooling down to lower temperatures.[9] It is conceivable that entropy effects could dominate small energy differences between different geometries of a cluster and change its equilibrium structure at high enough temperatures. Indeed, a Hubbard-model study has found such a change of stable geometry from a rhombus at $T=0$ K to a tetrahedron at $T>0$ K, caused by the electronic entropy.[10]

A rough estimate of the upper bound on the cluster temperature can be obtained from calculations of the evaporation rate, which is very high even below the melting

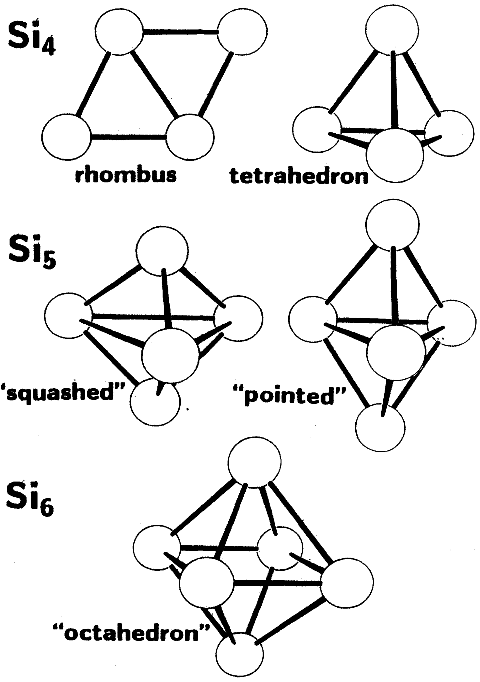

FIG. 1. Schematic diagrams of $Si_4$ (stable rhombus and metastable tetrahedron geometry), $Si_5$ (stable squashed "*S*" and metastable pointed "*P*" trigonal bipyramids), and of $Si_6$ ["octahedron" (Ref. 12) geometry].

temperature of the bulk.[11] In the present study, we explore the role of thermal effects in realistic clusters in the temperature range between 0 and 500 K and compare the results to zero temperature. We explicitly consider rotational, vibrational, and electronic contributions to entropy and apply this formalism to small silicon clusters. For $Si_4$ we consider a rhombus and tetrahedron geometry. For $Si_5$ we investigate the stable "squashed" and metastable "pointed" trigonal bipyramid geometries, which are separated by a very small energy difference.[7] Finally, we consider $Si_6$ in an "octahedron"[12] geometry. A schematic drawing of these clusters is given in Fig. 1.

The objective of this study is to find the role of temperature in free-energy (rather than internal-energy) differences between different clusters. We are especially interested in the possibility of entropy contributions being significantly different for (a) clusters with the same number of atoms but a different geometry, and (b) for different cluster sizes. In those cases, temperature could change the equilibrium geometry and size distribution of clusters.

## II. THEORY

We consider an ensemble of identical clusters in thermal contact and equilibrium with a surrounding carrier gas of temperature $T$. Its equilibrium geometry is obtained by minimizing the free energy, which is given by

$$F = -kT \ln Z \ . \tag{1}$$

Here, $Z$ is the total partition function. In the following, we consider the contribution associated with electronic, vibrational, and rotational degrees of freedom to be separable as long as there is no coupling between these degrees of freedom. Then, the partition function of the cluster factorizes as

$$Z = Z_t Z_r Z_v Z_e Z_s \ . \tag{2}$$

The subscripts $t$, $r$, $v$, $e$, and $s$ correspond to translational, rotational, vibrational, electronic and structural degrees of freedom.

The translational motion, though important for the thermal equilibration of the cluster with its environment, does not depend on the geometry of the cluster, and is the same for clusters with the same mass. In the free energy, $Z_t$ adds an uninteresting constant, which depends on the temperature but not the structure, and we do not consider it further.

Since the moment of inertia of silicon clusters is very large, the rotational motion can be treated classically and the corresponding partition function for a nonlinear asymmetric cluster is given by[13]

$$Z_r = \sqrt{\pi}(8\pi^2 kT/h^2)^{3/2}(I_x I_y I_z)^{1/2} \ . \tag{3}$$

$I_x$, $I_y$, and $I_z$ are the moments of inertia of the cluster about its three principal axes. They are obtained by diagonalizing the inertia tensor

$$I_{ij} = \sum_{l=1}^{n} M[r^2(l)\delta_{ij} - r_i(l) r_j(l)] \ . \tag{4}$$

Here the sum is over the constituent atoms $l$ of the cluster with mass $M$.

We treat the vibrational degrees of freedom in the harmonic approximation, which is justified in the temperature range of interest, i.e., below the melting point. Then the vibrational partition function is given by

$$Z_v = \prod_i \frac{e^{-\hbar\omega_i/2kT}}{1 - e^{-\hbar\omega_i/kT}} \ , \tag{5}$$

where $\omega_i$ are the $3n-6$ normal mode frequencies of the $n$-atom cluster.

The electronic partition function $Z_e$ can be written as

$$Z_e = \sum g(E) e^{-\Delta E(n_1, n_2, \ldots)/kT} \ , \tag{6}$$

where

$$\Delta E(n_1, n_2, \ldots) = \sum_\alpha (n_\alpha - n_\alpha^g)\varepsilon_\alpha, \quad n_\alpha, n_\alpha^g = 0,1,2 \tag{7}$$

is the electronic excitation energy and $n_\alpha$ ($n_\alpha^g$) are the occupation numbers of the level $\alpha$ in the excited state (ground state) of the cluster. $g(E)$ is the degeneracy of the electronic energy level $E$, and $\varepsilon_1, \varepsilon_2, \ldots$ are the one-electron energies. The energy required to excite an electron in a small cluster is typically of the order of one electron volt with a corresponding temperature of about $10^4$ K. Hence in the temperature range of interest, only very few lowest excitations need to be considered.

Finally, the structural partition function $Z_s$ is given by

$$Z_s = e^{-E_{\text{total}}/kT} \ , \tag{8}$$

where $E_{\text{total}}$ is the total internal energy of the cluster at zero temperature, which depends only on the structure. This is obtained from a total energy calculation discussed in the following section.

## III. CALCULATIONS

We determine the zero-temperature equilibrium geometries within an optimized tight-binding (TB) formalism which has been successfully used previously[7] to predict stable geometries of small Si clusters in agreement with experiments[4] and *ab initio* calculations.[7,8] For a given cluster geometry, the total energy of the cluster (with respect to isolated atoms) is given by[7]

$$\begin{aligned} E_{\text{total}} = \sum_\alpha n_\alpha^g \varepsilon_\alpha - n \sum_{\beta=s,p} n_\beta^0 \varepsilon_\beta^0 + \sum_{1 \le i < j \le n} E_r(d_{ij}) \\ - n[\psi_1(n_b/n)^2 + \psi_2(n_b/n) + \psi_3] \\ + U \sum_{i=1}^{n} (q_i - q_i^0)^2 \ . \end{aligned} \tag{9}$$

In our notation, $\alpha$ and $\beta$ refer to electronic levels of the cluster and isolated atoms, respectively, and Latin-letter indices denote atomic sites. The one-electron energy levels $\varepsilon_\alpha$ of the cluster are the eigenvalues of the nearest-neighbor TB Hamiltonian

$$H_{\mathrm{TB}} = \sum_{1 \le i \le n} \sum_{\beta} \varepsilon^0_{i\beta} \alpha^\dagger_{i\beta} \alpha_{i\beta} + \sum_{1 \le i < j \le n} \sum_{\beta,\beta'} t_{i\beta,j\beta'} (\alpha^\dagger_{i\beta} \alpha_{j\beta'} + \text{c.c.}) \ . \tag{10}$$

In the TB calculation of Si clusters, we use four orbitals of $s$, $p_x$, $p_y$, and $p_z$ character on each of the $n$ atomic sites. The energies of the electronic levels of the isolated atoms are $\varepsilon_s^0 = -5.25$ eV and $\varepsilon_p^0 = 1.2$ eV. The Slater-Koster parametrized hopping integrals $t_{i\beta,j\beta'}$ show an $r^{-2}$ distance dependence. Their values at the bulk equilibrium nearest-neighbor distance are[7] $t_{ss\sigma} = -1.938$ eV, $t_{sp\sigma} = 1.745$ eV, $t_{pp\sigma} = 3.050$ eV, and $t_{pp\pi} = -1.075$ eV. The third term in $E_{\mathrm{total}}$ is a semiempirical expression for the ion-ion repulsive energy, exchange-correlation energy, and correction to the double counting of electron-electron interactions. The fourth term in Eq. (9), with $\psi_1 = 0.225$ eV, $\psi_2 = 1.945$ eV, and $\psi_3 = -1.03$ eV, corrects the total energy in case of different coordination numbers. The last term, an intra-atomic Coulomb interaction with $U = 1$ eV, makes geometric arrangements with large charge transfers $(q_i - q_i^0)$ less favorable.

In the harmonic approximation, the cluster vibration frequencies $\omega_i$ are given by

$$\omega_i = \left[ \frac{\lambda_i}{M} \right]^{1/2} \ . \tag{11}$$

There are $3n-6$ nonzero vibration frequencies in an $n$-atom cluster. $M$ is the atomic mass and $\lambda_i$ are the eigenvalues of the force-constant matrix

$$D_{ij} = \frac{\partial^2 E_{\mathrm{total}}}{\partial u_i \partial u_j} \ , \tag{12}$$

where $u_i$ and $u_j$ are displacements of $i$th and $j$th coordinates from their equilibrium values.

## IV. RESULTS

The equilibrium geometries for the rhombohedral $R$-$\mathrm{Si}_4$ and tetragonal $T$-$\mathrm{Si}_4$, the "squashed" $S$-$\mathrm{Si}_5$ and the "pointed" $P$-$\mathrm{Si}_5$ bipyramid, and the "octahedral"[12] $O$-$\mathrm{Si}_6$ clusters are given in Fig. 1. The typical interatomic distance is close to the bulk nearest-neighbor distance of 2.35 Å. We have considered symmetric geometries and found that the different contributions to the entropy are nearly independent of possible Jahn-Teller distortions. For symmetric structures with fewer degrees of freedom, it is simple to represent potential-energy surfaces as contour plots, such as in Fig. 2 for $\mathrm{Si}_5$.

For these equilibrium cluster geometries, the rotational partition function $Z_r$ can be evaluated in a straightforward way using Eq. (3). The vibrational partition function $Z_v$ requires the determination of interatomic force constants $c$ and the $3n-6$ vibration frequencies $\omega_i$ first. For $T$-$\mathrm{Si}_4$ the force constant $c = 6.01$ eV Å$^{-2}$ gives rise to the softest vibration frequency $\omega_1 = 30$ meV. The values of the force constants in $R$-$\mathrm{Si}_4$ which is energetically favored over $T$-$\mathrm{Si}_4$ by 2.0 eV, are $c_s = 10.91$ eV Å$^{-2}$ for the side and $c_d = 9.47$ eV Å$^{-2}$ for the short diagonal.

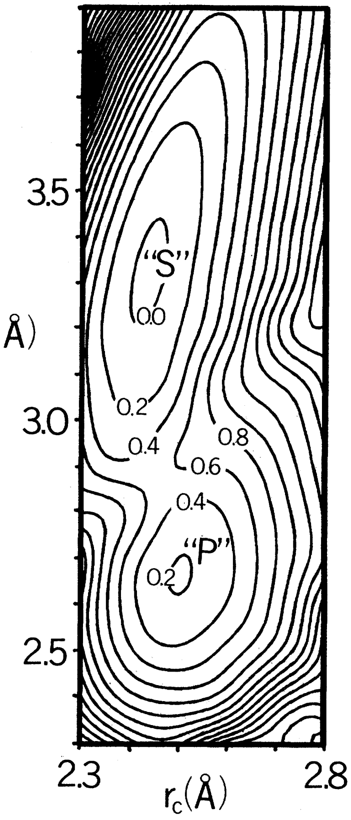

FIG. 2. Contour plot of the total energy $E_{\mathrm{total}}$ (with respect to an arbitrary reference energy) at $T = 0$ K, given by Eq. (9), for symmetric $\mathrm{Si}_5$ clusters. Cluster geometry is defined by the bond length of the base trimmer, $r_b$, and the cap-to-base atom bond length, $r_c$. Energy minima correspond to the "pointed" and "squashed" geometries shown in Fig. 1. Adjacent energy contours are separated by 0.2 eV.

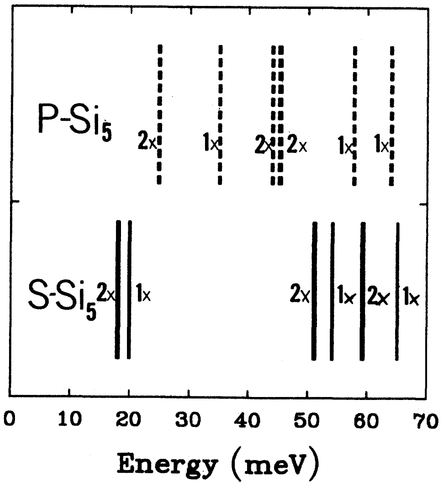

FIG. 3. Normal vibration frequencies $\omega_i$ of $\mathrm{Si}_5$ clusters in the "squashed" (solid lines) and "pointed" (dashed lines) geometry.

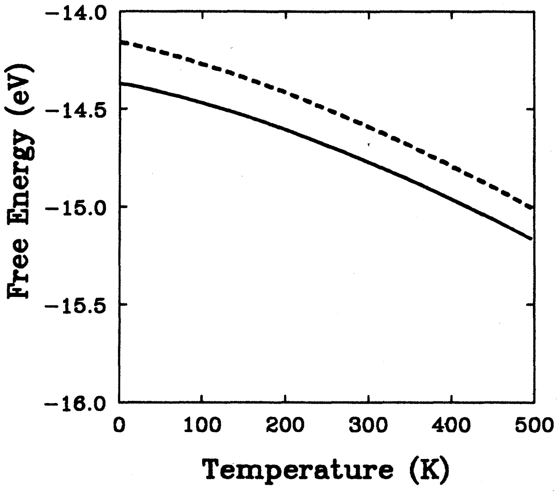

FIG. 4. Free energy $F$ as a function of temperature $T$ for the squashed (solid line) and pointed (dashed line) geometries of $Si_5$.

This would leave one zero-frequency floppy mode (about the short diagonal), the frequency of which is shifted to $\omega_1=13$ meV due to an angular restoring force. For $P$-$Si_5$, the force constants are $c_b=5.70$ eV Å$^{-2}$ and $c_c=7.22$ eV Å$^{-2}$ for the base and the cap-to-base bonds, respectively. In $S$-$Si_5$, which is energetically favored over $P$-$Si_5$ by only 0.2 eV, the corresponding force constants are $c_b=2.16$ eV Å$^{-2}$ and $c_c=10.44$ eV Å$^{-2}$. The vibration spectrum of $P$- and $S$-$Si_5$ is given in Fig. 3, with the softest frequencies $\omega_1\approx 20$ meV. Force constants for $O$-$Si_6$ are $c_b=6.54$ eV Å$^{-2}$ and $c_c=9.97$ eV Å$^{-2}$ and the softest vibration frequency is $\omega_1=28$ meV.

The electronic partition function $Z_e$ depends primarily on the occupancy $n_h$ and degeneracy of the highest occupied cluster orbital $\varepsilon_h$ as well as the gap $\Delta_{hl}$ between $\varepsilon_h$ and the lowest unoccupied orbital $\varepsilon_l$. In $T$-$Si_4$ ($R$-$Si_4$), $\varepsilon_h$ is threefold degenerate (nondegenerate) and filled; $\Delta_{hl}$ is 1.3 eV (2.6 eV). In $P$-$Si_5$ ($S$-$Si_5$), $\varepsilon_h$ is twofold degenerate and half-filled (filled); $\Delta_{hl}$ is 2.6 eV (1.4 eV). In $O$-$Si_6$, $\varepsilon_h$ is twofold degenerate and filled; $\Delta_{hl}$ is 1.5 eV.

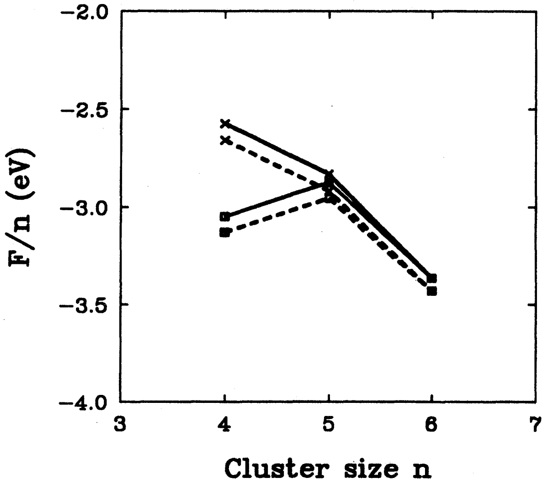

FIG. 5. Free energy per atom $F/n$ at $T=0$ K (solid line) and at $T=300$ K (dashed line). Stable geometries are denoted by □ and metastable geometries by ×.

This information allows us to plot the free energy $F$ of each cluster as a function of temperature, which is done in Fig. 4 for $P$- and $S$-$Si_5$. A comparison of free energies per atom $F/n$ of $Si_4$, $Si_5$, and $Si_6$ clusters is given in Fig. 5 for $T=0$ and 500 K.

## V. DISCUSSION

The fact that the total energies of the stable $S$-$Si_5$ and the metastable $P$-$Si_5$ clusters (Fig. 1) differ only by $\approx 0.2$ eV suggests that their relative stability could possibly be modified by thermal effects. One way to stabilize $P$-$Si_5$ would be through vibrational entropy. This does not seem unreasonable in view of the differences in the potential-energy surfaces (Fig. 2) and force constants between $P$-$Si_5$ and $S$-$Si_5$. An inspection of the vibration modes, given in Fig. 3, does not allow any simple predictions. Our calculation shows that the vibrational entropy lowers the free energy of $Si_5$ by 0.4 eV from $T=0$–500 K. However, the difference of the vibration free energies between $S$- and $P$-$Si_5$ remains below 0.01 eV and hence does not affect the relative stability in the temperature range considered.

Another contribution to the free energy comes from rotational modes, which depend on moments of inertia. In the elongated $P$-$Si_5$, we find that the increase in the largest moment of inertia with respect to $S$-$Si_5$ is nearly compensated by decreases of the other moments in the expression for the rotational partition function in Eq. (3). We find that rotational entropy lowers the free energy of $Si_5$ by 0.6 eV from $T=0$–500 K. As in the case of vibrational entropy, the difference of the rotational free energies between $S$- and $P$-$Si_5$ remains negligible in this temperature range.

The only significant contribution to entropy differences between $S$-$Si_5$ and $P$-$Si_5$ comes from electronic entropy, due to a degeneracy of the highest partly occupied molecular orbital of $P$-$Si_5$. The electronic entropy lowers the free energy of $P$-$Si_5$ by 0.06 eV at $T=500$ K with respect to $T=0$ K. This contribution stabilizes $P$-$Si_5$ with respect to $S$-$Si_5$, since the electronic entropy for the $S$ geometry is negligible.

The total free energy $F$ of $Si_5$ is given in Fig. 4. As a result of different entropy contributions, $F$ is lowered by $\approx 1$ eV in the temperature range $T=0$–500 K. While the free energies of $P$-$Si_5$ and $S$-$Si_5$ get closer at higher temperatures, the relatively small difference in the electronic entropies is not sufficient to make the two curves cross and hence to make $P$-$Si_5$ the stable geometry at reasonably high temperatures. Also in $Si_4$, which at $T=0$ K prefers a rhombus geometry over a tetrahedron arrangement by as much as 2.0 eV, thermal effects do not affect the equilibrium geometry at higher temperatures.

If thermal contributions to $F$ of clusters with a different number of atoms are very different, they can significantly modify the size distribution in the mass spectra. We studied this effect by comparing the free energy per atom, $F/n$, of $Si_4$, $Si_5$, and $Si_6$, at $T=0$ and 500 K. The results are given in Fig. 5. In $Si_4$ and $Si_5$, entropy contributions to $F/n$ are nearly the same and much larger than in the more compact $Si_6$. These differences due to thermal effects are, however, negligible when compared to total energy differences. For this reason, we do not expect a change in the abundances of $Si_4$, $Si_5$, and $Si_6$ clusters due to entropy.

The magnitude of the entropy contributions to $F$ suggest that thermal effects could still play a significant role in the stability of clusters other than $Si_n$. One very prospective candidate is carbon clusters with a strongly varying number of bonds per atom and a large number of soft vibration modes. These clusters are the subject of ongoing research.[14]

## VI. SUMMARY AND CONCLUSIONS

We have presented the first calculation of the free energy of small semiconductor clusters at nonzero temperature. We evaluated electronic, vibrational and rotational contributions to the free energy $F$ of $Si_4$, $Si_5$, and $Si_6$ in different geometries in the temperature range $T=0-500$ K. We found a general decrease of $F$ in this temperature range by typically 1 eV for all these clusters. The calculated small differences in the entropy between the different clusters should have only a moderate effect on their relative stability and size distribution. In the temperature range considered, we did not find any thermally induced stabilization of metastable cluster geometries, nor any large changes in the entropy with changing cluster size which would change the abundances. Hence, our results for small $Si_n$ clusters indicate that the presently available $T=0$ calculations can indeed be used to interpret experimental data, which are obtained at usually much higher temperatures.

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