

***Ab initio* Monte Carlo simulations applied to a Si₅ cluster**

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An *ab initio* Monte Carlo (MC) program has been developed, where the total configurational energies at each MC step are obtained via density functional theory using localized numerical orbitals as basis sets. As an initial application we have investigated the structural properties of a silicon cluster (Si₅) for different temperatures and estimated its isomerization temperature. In particular, we study how this temperature depends on the particular choice of exchange-correlation functional. We performed calculations within the local density approximation (LDA), a generalized gradient approximation (GGA), and the Tao-Perdew-Staroverov-Scuseria metaGGA. The Monte Carlo method is very useful when complex exchange-correlation functionals are being used, since in these cases it is computationally difficult to evaluate the forces. From the simulations we have observed two distinct isomers, which were identified as trigonal bipyramid D_{3h} and C_2 symmetric structures. The D_{3h} was found to be the global minimum and the C_2 the first local minimum. We obtain that the isomerization temperature for the small Si₅ system has a trend opposite to what happens in the bulk, where the LDA functional provides the lowest melting temperature, whereas the one obtained using the metaGGA appears to be the highest one.

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I. INTRODUCTION

Computer simulations are essential tools in the research of physical systems at finite temperature. Basically, we can divide these simulations into three different categories: (i) situations where one would like to know the behavior of the system at a definite temperature or as a function of it (for example, phase transitions), (ii) situations where the temperature is used as a parameter in order to explore the phase space of the system, aiming to identify the global minimum or possible local minima in the potential energy surface (PES), and (iii) situations where one wants to generate representative configurations of disordered systems, such as liquid or amorphous. Monte Carlo (MC) and molecular dynamics (MD) methods are the major techniques used for those purposes.¹

In most of these simulations the nuclear degrees of freedom can be described by classical mechanics, whereas the electronic degrees of freedom must necessarily be described by quantum mechanics. Moreover, traditionally, the interactions between particles are described by means of empirical potentials. These potentials have the advantage of being easily evaluated computationally, and therefore they are appropriate to simulate (i) large systems and (ii) for long time scales. However, they are constructed (fitted) to describe with precision the system near some region of its configuration space; thus, there is no guarantee that they will provide reliable results far from these regions. For example, in many cases the results obtained for clusters using potentials fitted to the bulk are not accurate enough. Besides, there are interesting situations where empirical potentials have not yet been developed.

Therefore, there is great interest in the combination of MC and MD simulations with methods that describe the electronic structure with high precision (*ab initio* methods). Using this approach, the interactions between the constituent entities and the dynamics of the nuclear degrees of freedom are determined simultaneously and as accurate as possible as the system evolves.

The *ab initio* MD (AIMD) is already well established and implemented in a large variety of computational codes. It has been widely used to provide reliable results for various systems² since the seminal work of Car and Parrinello³ in 1985. In situations where it is necessary to follow the dynamical evolution of the system, the MD technique is obviously the best choice. However, if the interest is only in static properties and in average values, the MC method becomes an alternative choice and sometimes it is even more efficient regarding the sampling of the phase space. In this method it is not necessary to evaluate forces (only the energies), so it can be faster than the MD method. Also, the MC method has the advantage of being easily implemented in constant-temperature (or -pressure) situations.

In the case of *ab initio* MC (AIMC) some codes have been developed using different methods for the electronic structure calculations.⁴⁻⁶ In the present work, we have developed a MC program where the total configuration energies are obtained via density functional theory^{7,8} (DFT) at each MC step. One important feature of our calculations is that the Kohn-Sham equations⁸ are solved using the numerical linear combination of atomic orbitals (LCAO) basis set that are strictly localized. This method is implemented in the SIESTA package.⁹

DFT is one of the most important methods nowadays to describe the electronic structure of matter. In principle it is an exact theory, but in practice it is necessary to do some approximations. The fundamental one is the expression for the exchange-correlation energy functional E_{xc} . Many E_{xc} functionals have been proposed in the last decades and were used to study a large variety of systems and properties. The validity of these approximations depends on the systems and on the properties desired, so it should be checked every time one uses them. The functionals currently used can be classified basically as local density approximation (LDA), generalized gradient approximation (GGA), metaGGA, hybrid and exact-exchange (EXX).

Although DFT has provided satisfactory results for a large range of problems, some situations are still not very well

described by its approximations. One example is the melting temperature of silicon at zero pressure, where the results obtained with different functionals are not very accurate when compared to the experimental ones. It is known that in this case in particular, the GGA improves the LDA results.^{10,11} However, the theoretical transition temperature is still smaller than the experimental result by approximately 200 K. Therefore, it is an interesting question to see if improvements over the E_{xc} functional, such as the metaGGA functional, would provide a better result for the silicon bulk melting temperature.¹²

The improvement of the melting temperature as the E_{xc} functional is changed from the LDA to the GGA is mostly attributed to an improvement in the calculation of the relative enthalpies of the two phases. This is related to a better cancellation of exchange-correlation errors between the liquid and solid phases for the GGA when compared to the LDA.¹¹ If one looks at the local configurations in a liquid as dynamical structural fluctuations, it is interesting to see the effect of different functionals on the relative energies between distinct stable isomers of Si clusters.

Semiconductor clusters (such as the silicon ones) have received considerable attention for the past decades,¹³ both theoretically¹⁴ and experimentally. One reason for that is the desire to understand the properties of materials as a function of their size. Moreover, these clusters have an important role in a number of industrial applications such as fabrication of microelectronic devices or catalysis. Also, in the last decade the experimental techniques for production and analysis of clusters have improved significantly, allowing the study of clusters with preselected size and composition.^{15,16}

Most of these works with clusters are related to the study of the geometries and electronic properties of the systems. The thermal properties of small clusters are much less investigated. Usually empirical potentials are used and only recently have there also been some works using tight-binding MD (TBMD) (Refs. 17 and 18) and AIMD (Ref. 19). These studies have revealed interesting features about the melting properties of clusters. For instance, they have shown that the isomerization usually occurs at a higher temperature than the bulk melting point for clusters of tin,¹⁹ in agreement with experimental evidence.²⁰

As an initial application of our methodology we have investigated the structural and energetic properties of a silicon cluster (Si_5) for different E_{xc} functionals and temperatures. Indeed, the study of small clusters by first-principles simulations is interesting for many reasons. First of all, empirical potentials (fitted to bulk phase) do not usually describe them well. Also, the properties of clusters are often peculiar, being qualitatively different from their constituent parts (either atoms or molecules) and from the bulk. One of the aims of the present work is to study the structural changes of the Si_5 cluster as a function of temperature in order to obtain the “melting temperature.” Strictly speaking, these changes cannot be considered as a real phase transition, since this happens only at the macroscopic limit. Actually, the cluster phase transition can be viewed as a transition between distinct isomers, an isomerization. It has the important characteristic that it is not a sharp transition occurring at a definite temperature, as happens in the bulk phase. Instead, it takes

place smoothly over a finite temperature range, where two or more isomers can coexist dynamically. Also, the thermal properties can be strongly size dependent. With this caveat in mind, we will refer to this isomerization transition as a phase transition throughout the paper.

In the following, we briefly describe the computational method used (Sec. II). Then, in Sec. III, we describe our results of AIMC simulations for Si_5 , focusing on the phase transition for different E_{xc} functionals. Finally, in Sec. IV we present our main conclusions.

II. COMPUTATIONAL METHODS

A. Monte Carlo simulation

The standard Metropolis algorithm²¹ was used in our *ab initio* MC simulations. Before starting the simulation some parameters related to the MC method must be chosen: the initial configuration, the temperature, and the maximum displacement of the particles. After this, the simulation evolves according to the following steps: (i) given a configuration μ and its energy E_μ a new configuration ν is generated by random displacements of all particles simultaneously. All configuration energies are obtained from an *ab initio* calculation, as explained below. (ii) The energy of the new configuration (E_ν) is then obtained, and the acceptance probability is determined by

$$P(\mu \rightarrow \nu) = \begin{cases} 1 & \text{if } E_\nu \leq E_\mu, \\ e^{-\beta\Delta E} & \text{if } E_\nu > E_\mu, \end{cases} \quad (1)$$

where $\Delta E = E_\nu - E_\mu$ and $\beta = (k_B T)^{-1}$ (k_B is the Boltzmann constant and T the temperature). (iii) If the configuration ν is rejected, the old one is maintained, and if accepted, it serves as the configuration μ in the next step. At the end of the simulation, the sampled configurations are then used to obtain the equilibrium properties of the system. The acceptance ratio is maintained at about 50% by adjusting periodically the maximum displacement of the atoms.

The simulation can be divided into two stages. The first one is the *equilibration* period, where the sampled configurations do not reflect an equilibrium distribution and, therefore, are not considered in the calculation of the averages. Thus, before moving to the second stage, it is necessary to simulate for enough MC steps until quantities like the energy have started to perform oscillations around their mean values. The second period is the *equilibrium* or *stationary* phase, where the mean probability of finding the system in a particular state is proportional to the Boltzmann weight of this state. In this stage, there is not a simple way to determine for how many steps one should perform the simulation. It is necessary to simulate a given system until one obtains converged mean values within a certain error bar. Besides that, it is also important to analyze the energy autocorrelation function to obtain statistically independent configurations, which were calculated for all simulations performed. In our case, the number of MC steps was chosen such that the average fluctuation of the bond lengths, described in detail below, had approximately reached convergence.

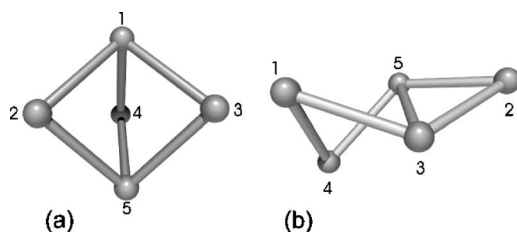


FIG. 1. Si_5 isomers: (a) global minimum-energy configuration (symmetry D_{3h}) and (b) first local minimum-energy configuration (symmetry C_2).

B. Total energy calculation

All total configurational energies were obtained via DFT using the SIESTA package.⁹ We have considered three different exchange-correlation functionals: LDA⁸ parametrized by Perdew and Zunger,²² GGA as proposed by Perdew, Burke, and Ernzerhof (PBE),²³ and metaGGA in the form known as TPSS²⁴ (proposed by Tao, Perdew, Staroverov, and Scuseria).²⁵ They were used both for the AIMC simulations and for the geometry optimization. The calculations done using the LDA and GGA were self-consistent; however, for the metaGGA approximation we have a post-self-consistent implementation, in which a GGA (PBE) self-consistent calculation is performed previously, and the resulting orbitals and densities are then substituted in the metaGGA E_{xc} expression.²⁶ In this way, it is only possible to evaluate the metaGGA total energy, which then makes the MC method a natural choice to sample the phase space.

The DFT calculations were done considering a cubic supercell with 15 Å length. One k point (Γ) was used to sample the Brillouin zone. For quantities that are calculated in real space we have used an energy cutoff of 200 Ry for the grid where the electronic wave function and density are projected. We have also used norm-conserving Troullier-Martins pseudopotentials.²⁸ For the valence electrons of Si atoms we have employed a double- ζ basis set with polarization function (DZP) to describe the Kohn-Sham orbitals.

When necessary, the geometry optimizations were performed using the conjugate gradient method, also calculated with the SIESTA code. These were done without any symmetry constraints until all the forces were smaller than 0.015 eV/Å. In the case of the metaGGA functional the optimization was done via a quenching process starting from the final geometry obtained using the GGA. This was necessary because in our implementation it is still not possible to efficiently evaluate computationally the forces using the metaGGA approximation.²⁶ The quenching process was performed using our MC code modified to accept only configura-

TABLE I. Bond lengths (in Å) and angles (in degrees) for the D_{3h} Si_5 isomer, calculated using different E_{xc} functionals. ΔE (in eV) is the difference in total energy with respect to the global energy minimum.

Sym.	d_{23}	d_{13}	d_{15}	θ_{2-1-3}	θ_{4-1-5}	ΔE	
D_{3h}	LDA	3.04	2.28	2.92	83.4	50.2	–
	GGA	3.09	2.32	2.95	83.8	50.4	–
	metaGGA	3.08	2.31	2.95	83.8	50.4	–

tions with lower energy than the previous one and the temperature was slowly decreased during the simulation, from $T=100$ K until it reached the minimum-energy state—i.e., $T \approx 0$ K.

III. RESULTS AND DISCUSSION

A. Isomer geometries

As we will discuss later, we have observed two distinct Si_5 isomers during the MC simulations. Thus, before we present the results of the simulations, we discuss the zero-temperature properties of these isomers. The ground state of Si_5 is a trigonal bipyramid, with symmetry D_{3h} [see Fig. 1(a)], as was reported before in the literature.^{29,30} In Table I we present our results for the nonequivalent bond lengths and bond angles of this structure for the three E_{xc} functionals used, which are in good agreement with previous calculations.^{29,30}

The other isomer observed during the simulations corresponds to the first local minimum, with symmetry C_2 , shown in Fig. 1(b) and characterized in Table II. We have found that this isomer has an energy 0.66 eV above the global minimum for the metaGGA approximation (for the GGA it is 0.69 eV and for the LDA 0.75 eV). Tight-binding calculations¹⁷ have previously encountered this structure; it was, however, described as the global minimum configuration, with the D_{3h} trigonal bipyramid being the first local minimum. We believe that this is related to the difficulty of the tight-binding method, which always has to employ a particular parametrization, to describe clusters that have isomers with quite distinct local atomic configurations.

In addition to the energetic and structural properties, we also show our results for the vibrational frequencies of the two structures in Table III. We calculated them only for the LDA and GGA functionals because the dynamical matrix is not easily evaluated for the metaGGA approximation and we do not expect large variations when compared to the GGA

TABLE II. Bond lengths (in Å) and angles (in degrees) for the C_2 Si_5 isomer, calculated using different E_{xc} functionals. ΔE (in eV) is the difference in total energy with respect to the global energy minimum.

Sym.	d_{12}	d_{13}	d_{14}	d_{15}	d_{35}	θ_{1-3-2}	θ_{1-3-4}	ΔE	
C_2	LDA	3.99	2.26	2.31	2.76	2.44	123.2	53.6	0.75
	GGA	4.04	2.29	2.34	2.80	2.47	123.2	53.6	0.69
	metaGGA	4.04	2.29	2.34	2.80	2.47	123.2	53.6	0.66

TABLE III. Vibrational frequencies (in cm^{-1}) calculated for the two Si_5 isomers using different E_{xc} functionals (L stands for the LDA and G for the GGA).

D_{3h}	L	187 (e')	228 (a'_1)	368 (e')	411 (a''_2)	439 (e'')	467 (a'_1)			
	G	194 (e')	213 (a'_1)	351 (e')	408 (a''_2)	437 (e'')	458 (a'_1)			
C_2	L	87	149	215	282	323	378	440	444	506
	G	86	143	207	275	318	372	436	437	499

results. Our calculated vibrational frequencies are in reasonably good agreement with previous results,³⁰ within approximately 10 cm^{-1} . The exceptions are for the a'_1 and the e' modes, which are lower in our case by more than 30 cm^{-1} . From the MC simulation, we observe that the lowest-frequency mode (e') is associated with the transition from the D_{3h} to the C_2 structure. The C_2 configuration has an overall softening of the modes, with the appearance of a particularly low-energy mode ($\sim 90 \text{ cm}^{-1}$) which is associated with the backward conversion to the D_{3h} . All these results will be used later to obtain the isomerization temperature.

B. Monte Carlo simulations

All MC simulations were started from the global minimum geometry [see Fig. 1(a)]. For each functional (LDA, GGA, and metaGGA) we performed simulations in the range of 1500–2200 K. After the period of equilibration ($\sim 10\,000$ MC steps), we have performed 45 000 MC steps for each simulation. It is important to emphasize that in one MC step in our simulations all atoms are displaced (suppressing cluster global rotation and translation). This should be contrasted to what is usually done in empirical potential simulations, where atoms are displaced one at a time.

In Fig. 2 we show the total energy variation relative to its

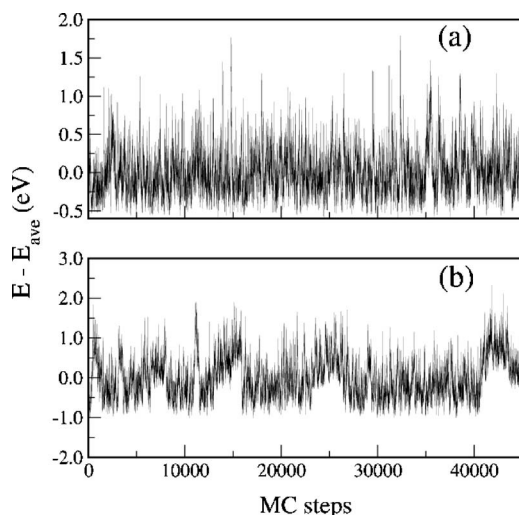


FIG. 2. Variation of the total energy E relative to its mean value E_{ave} as a function of MC steps, illustrated by the simulation done using the metaGGA E_{xc} functional. In the upper picture (a), $T=1500 \text{ K}$, and in case (b), $T=2000 \text{ K}$.

mean value as a function of MC steps, illustrated by the simulations done with metaGGA for two temperatures: 1500 K and 2000 K. In the upper picture [Fig. 2(a)] we can observe that the energy fluctuates around only one average value, and this is related to fluctuations of the bond distances of the global minimum geometry. On the other hand, in the lower picture [Fig. 2(b)] it is possible to observe basically two distinct regions. These are related to fluctuations of the structures of two isomers: the region with lower energy is related to the D_{3h} isomer and the region with higher energy is related to the fluctuations of the first local minima isomer C_2 . At high temperatures the system can cross the energy barriers separating the global minimum from the local minima. Therefore, the C_2 minimum becomes populated and there is a dynamical coexistence of the two isomers.

One way to monitor the isomerization is analyzing structural changes in the bond-length and bond-angle distributions (BLD and BAD, respectively), as a function of temperature. We illustrate our results for these properties in Figs. 3 and 4, respectively, calculated using the metaGGA approximation. In the BLD the peaks around 2.3 and 3 Å correspond to the distances between the first and second neighbors in the D_{3h} structure. With increasing temperature these peaks decrease and a third peak appears around 4 Å. This bond length is typical of the first local minimum (C_2 structure). In the same way, we see in the BAD that initially there is no peak around 120° , and then for higher temperatures it appears. Also, the peak around 80° decreases as the temperature increases, and in the region close to 55° we observe the opposite. A similar trend in both the BLD and BAD is observed for all the other E_{xc} functionals.

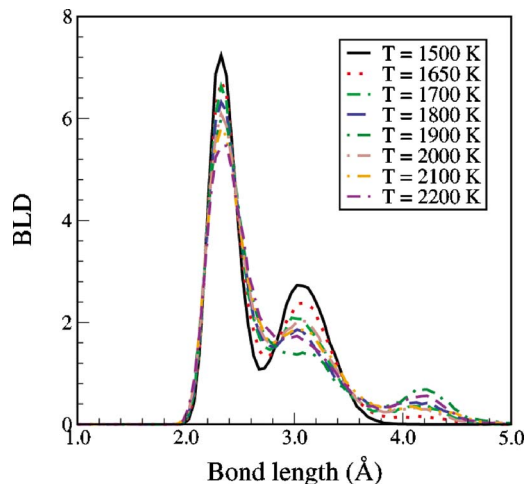


FIG. 3. (Color online) Bond-length distribution for different temperatures obtained using the metaGGA approximation.

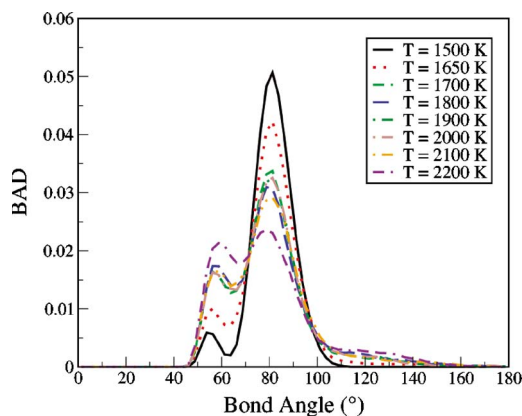


FIG. 4. (Color online) Bond-angle distribution for different temperatures obtained using the metaGGA approximation.

The other property monitored aiming at characterizing the isomerization was the bond-length root-mean-square fluctuation (BLF), defined by

$$BLF = \frac{2}{N(N-1)} \sum_{i < j} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle}, \quad (2)$$

where r_{ij} denotes the distance between atoms i and j , N is the total number of atoms in the cluster, and $\langle \dots \rangle$ indicates the average over all configurations in the simulation (only for the equilibrium period). This quantity is related to the mobility of the atoms and therefore is sensitive to structural changes. Thus, a sudden increase of its value can be associated with a phase transition.

As a first step, we have analyzed the evolution of the BLF as a function of MC steps, illustrated in Fig. 5 for the metaGGA simulations (for the other functionals the trend is similar). At low temperatures (for example, 1500 K) there is no significant change during the simulations. This nearly constant BLF is indicative of purely vibrational motion. However, for the higher temperatures the BLF increases until it converges to a higher value. For intermediary temperatures (such as 1800 K) there is an oscillatory behavior, related to a

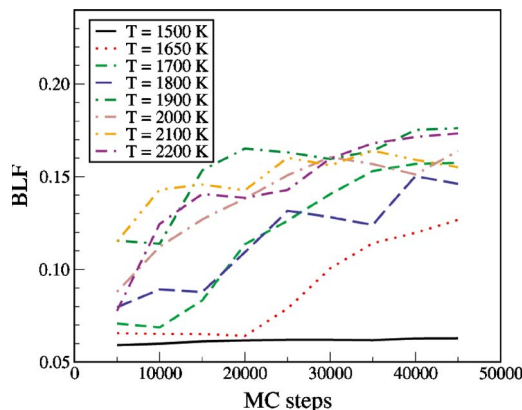


FIG. 5. (Color online) Bond-length fluctuation (BLF) at different temperatures as a function of MC steps, obtained using the metaGGA approximation.

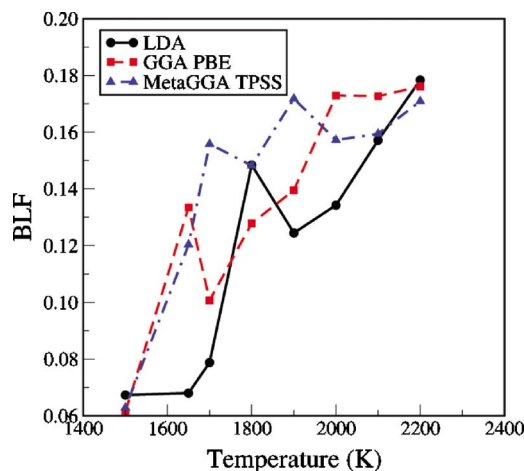


FIG. 6. (Color online) Bond-length fluctuation (BLF) as a function of temperature for the three E_{xc} functionals (LDA, GGA, and metaGGA) considered.

highly fluctuating dynamical coexistence of the two isomers in these temperatures. We can also see that at $T=1650$ K the BLF already increases, which is an indication that the melting starts at this temperature. Thus, as the temperature increases the cluster spends more time in the C_2 configuration. Another important feature is that for both low and high temperatures the number of MC steps seems to be sufficient; however, for the transition region it might be necessary to perform longer simulations in order to get better convergence. However, for the main conclusions of our work, this is not necessary.

Finally, to get the range of temperatures related to the phase transition, we have plotted the average value of the BLF in the last 5000 MC steps as a function of temperature for all E_{xc} functionals considered (see Fig. 6). In this graph we can see that the BLF for the lowest temperature is small; then, it rises as the temperature increases. In Table IV we present the isomerization temperatures extracted from the BLF data for each functional. We have considered the onset temperature, where the BLF is equal to 0.01, which is when it starts to increase. We can also observe that the melting starts at higher temperatures for the LDA when compared with the GGA and metaGGA. There is basically no difference between the GGA and metaGGA, but it seems that the initial melting temperature is a little bit lower for the GGA functional.

C. T_m via PES

We have also calculated the melting temperature using a model based on the probability of occurrence of a new iso-

TABLE IV. Phase transition temperatures for Si_5 ; T_B are the ones obtained via BLF, whereas T_m are the ones obtained from the model based on the probability of occurrence of a given isomer (see text for more details).

	LDA	GGA	metaGGA
T_B (K)	1730	1580	1600
T_m (K)	2770	2476	2370

mer, related to their partition function Z_s (the index s refers to the isomer).¹³ This probability can be written as

$$p_s = \frac{n_s Z_s}{Z}, \quad (3)$$

where Z is the total partition function and $n_s = 2N! / h_s$ is the number of equivalent permutational isomers for homogeneous clusters (N is the number of atoms and h_s is the order of the symmetry group for the minimum s). If the coupling of rotational and vibrational motions can be neglected, we can factor Z_s as $Z_s = Z_s^{tr} Z_s^{rot} Z_s^{vib}$, and using a harmonic approximation for Z_s^{vib} we have

$$Z_s^{vib} = e^{-\beta E_s^0} \prod_{i=1}^{\kappa} \left(\frac{kT}{\hbar \omega_{s,i}} \right),$$

$$Z_s^{tr} = V \left(\frac{MkT}{2\pi\hbar^2} \right)^{3/2}, \quad Z_s^{rot} = \left(\frac{2\pi kT \bar{I}_s}{\hbar^2} \right)^{3/2}, \quad (4)$$

where E_s^0 is the minimum energy of isomer s , $\omega_{s,i}$ are the normal-mode frequencies, V is the volume of the box where the clusters are confined, M is the total cluster mass, and \bar{I}_s is the average inertial moment in s [$\bar{I}_s = (I_s^{xx} I_s^{yy} I_s^{zz})^{1/3}$, with I_s^{xx} , I_s^{yy} , and I_s^{zz} the principal moments of inertia].

The melting temperature is then obtained equating the probability of occurrence of each isomer ($p_{s'} = p_s$):

$$T_m = \frac{\Delta E}{k} \left[\ln \left(\frac{n_{s'}}{n_s} \right) + \frac{3}{2} \ln \left(\frac{\bar{I}_{s'}}{\bar{I}_s} \right) + \ln \left(\frac{\prod_i \omega_{s,i}}{\prod_i \omega_{s',i}} \right) \right]^{-1}, \quad (5)$$

where $\Delta E = E_{s'}^0 - E_s^0$. This temperature can be viewed as a threshold, above which the isomer s' becomes more probable than the isomer s , and for temperatures below it the opposite is true.

Using our results for these quantities (for each isomer and each functional) we have obtained $T_m^{LDA} = 2270$ K for the LDA approximation and $T_m^{GGA} = 2470$ K for the GGA. As we did not calculate the vibrational frequencies for the metaGGA functional, we cannot evaluate T_m . However, if we suppose that there is not a big difference between the frequencies obtained using either the GGA or metaGGA, we can use the ones obtained for the GGA to estimate T_m for the metaGGA as a first approximation. In this way, we have $T_m^{MGGA} = 2370$ K. All results are collected in Table IV.

IV. CONCLUSIONS

We have implemented a Monte Carlo method where the total configurational energies are calculated using an *ab initio* density functional theory approach. In the present work we have used this implementation to study the isomerization of a Si₅ cluster. We have performed simulations for a variety of temperatures, in the range between 1500 K and 2200 K, and for the LDA, GGA, and metaGGA E_{xc} functionals.

From the simulations performed, we have observed two distinct isomers, which were identified as trigonal bipyramid D_{3h} and C_2 symmetric structures. The D_{3h} was found to be the global minimum and the C_2 the first local minimum in the PES. This is contrary to what has been found in tight-binding simulations,¹⁷ indicating the importance of using *ab initio* calculations in the description of small covalent systems such as Si clusters. The energy difference between these two isomers is lower for the metaGGA; then, we have the GGA and the highest value is for the LDA functional. On the other hand, the geometrical parameters for the two structures are very similar for all three functionals considered and are in agreement with previous results.^{29,30}

We have also obtained the bond-length fluctuation using the results of the MC simulations. The graph of this quantity as a function of temperature can provide an estimate of the isomerization temperature; for the GGA, the isomerization begins at $T_B^{GGA} = 1580$ K, which is basically the same as the metaGGA result $T_B^{MGGA} = 1600$ K. For the LDA we have obtained a higher temperature $T_B^{LDA} = 1730$ K, which is consistent with the higher energy value of the C_2 isomer at the LDA level.

As a second approach to determine the phase transition temperature, we have considered a theoretical model using some information of the PES of the system, such as the probability of occurrence of a given isomer. Using this model we still obtain the highest temperature for the LDA functional, $T_m^{LDA} = 2770$ K. In this case the metaGGA ($T_m^{MGGA} = 2370$ K) functional has a slightly lower temperature when compared to the GGA ($T_m^{GGA} = 2476$ K).

However, it is important to notice that this temperature (T_m) is obtained equating the probability of occurrence of two isomers, whereas the BLF estimate of the isomerization temperature looks at the onset of the transition. Therefore, T_m will certainly provide a higher temperature than the one obtained using the BLF since it indicates where the two isomers will coexist dynamically.

Another interesting feature in the phase transition of a small Si system is that we have obtained a trend opposite to what happens in the bulk. In the latter, the LDA functional provides the lowest melting temperature, whereas the one obtained using the metaGGA appears to be the highest one.¹²

Finally, we would like to emphasize that the MC method allows more complex functionals, such as metaGGA, to be studied as a function of temperature without the necessity of evaluating forces. Furthermore, the MC method can be more efficient than molecular dynamics regarding the sampling of the phase space, which may be very useful when studying phase diagrams and phase transition temperatures.

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