

First-principles molecular-dynamics study of carbon clusters

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(Received 13 November 1992; revised manuscript received 30 March 1993)

A generalized tight-binding molecular-dynamics technique that correctly treats interactions in nontetrahedral as well as multicoordinated covalent systems is used to obtain equilibrium geometries for carbon clusters of arbitrary size. For $N \leq 10$ the ground states are determined to be linear chains for odd N and closed rings for even N . The minimum-energy cyclic structures exhibit symmetry-lowering in-plane distortions rather than being regular polygons. These findings are in complete agreement with available *ab initio* results. Large clusters of atoms are used to demonstrate the validity of the method to simulate bulklike diamond and single-layer graphitic structures. The well-known 2×1 reconstruction for the (001) face is observed for the diamond cluster.

I. INTRODUCTION

The interest in pure carbon clusters has received a tremendous boost by the recent discovery of the C_{60} molecule.¹ There have been extensive studies of small carbon clusters.² These clusters also occur as a by-product in several chemical reactions and also in astrophysical objects.

Various theoretical tools have been used to study the equilibrium geometries of these clusters.³⁻¹⁰ The determination of equilibrium structures of carbon clusters poses a severe challenge on account of the special chemistry of the C-C bond. It is therefore perhaps not surprising that the predictions of structural properties reveal significant disagreements, even while using similar methods. Some of these give conflicting results with respect to whether the ground-state structures of carbon clusters from C_4 through C_{10} are linear chains or rings. It is well known that the bond lengths for carbon compounds can be significantly different from the sum of the covalent radii of the components forming these bonds.¹¹ Therefore, while performing geometry optimization, structures with widely differing bond lengths even within a linear chain or a ring cannot be excluded. It is quite easy to miss some low-symmetry structures on account of this. The in-plane distortions for rings can result in many interesting geometries that are unique to carbon clusters. The planar ground-state geometries can persist for $N > 10$. The small covalent radius of carbon can generate considerable strain energy for small N , preventing the formation of close-packed structures with larger coordination found in clusters of covalent elements with larger radii like silicon.

A useful approach to the determination of the structural properties of covalent clusters is the recently developed nonorthogonal tight-binding molecular-dynamics scheme of Menon and Subbaswamy.^{12,13} This approach has been applied to obtain equilibrium geometries for small silicon clusters.¹³ Complete agreement has been obtained with *ab initio* results^{14,15} for the lowest-energy

structures of silicon clusters of size up to $N = 10$ (for which *ab initio* results are available). The method is a generalization of the conventional tight-binding molecular dynamics formulation^{16,17} so as to apply to nontetrahedral and multicoordinated systems. In this approach the atoms are taken to interact with each other without any cutoff, eliminating the introduction of any spurious forces associated with abrupt termination of the interactions. The method is computationally efficient, requiring no additional cost over the conventional orthogonal tight-binding method. The method is orders of magnitude faster than *ab initio* schemes and can handle much larger clusters while treating the physics of covalent bonding correctly.

In this paper we present our results for small carbon clusters for which *ab initio* results are available for comparison. This establishes the applicability of our scheme to the study of carbon clusters. We also consider large diamondlike and graphitic clusters to test the applicability of the method to obtain bulk properties. The details of our technique have been published elsewhere.^{12,13} As described in our earlier work, the total energy consists of the electronic part (determined from the tight-binding Hamiltonian), a pair-wise repulsion term, and a bond-counting term. The electronic tight-binding parameters (e.g., $V_{ss\sigma}$, $V_{pp\pi}$, etc.) for carbon are generated using Harrison's¹⁸ universal parameter scheme and are listed in Table I. We emphasize that to preserve the a

TABLE I. Carbon parameters derived from the universal scheme from Ref. 18.

Parameters	eV
ϵ_s	-17.52
ϵ_p	-8.97
$V_{ss\sigma}$	-6.73
$V_{sp\sigma}$	7.15
$V_{pp\sigma}$	9.41
$V_{pp\pi}$	-3.03

priori nature of the calculation we have chosen not to use other parametrization schemes known to yield better results for bulk C, e.g., that of Chadi and Cohen.¹⁹ There are only two additional parameters that enter our molecular-dynamics scheme. One is the coefficient of the pairwise repulsive term χ_0 . Since our scheme treats the nonorthogonality of the basis explicitly by making the overlap integrals proportional to the Hamiltonian matrix elements (in the spirit of extended Hückel theory²⁰), an additional overlap proportionality parameter K , also enters our scheme. In this work we use $K = 2.7$ and $\chi_0 = 2.14$ eV, which are the same as in our earlier work on $C_{60}O_2$.²¹ With these values we obtain a bond length of 1.32 Å for the carbon dimer, compared to the experimental value of 1.25 Å.^{22,23}

As described in our earlier work, the bond-counting contribution to the total energy is needed in tight-binding treatment of multicoordinated systems to account for the promotion, polar, and other electronic energy contributions.¹³ To fix the bond-counting term we use a linear polynomial with a smooth cutoff in our nonorthogonal scheme:

$$U_{\text{bond}} = N[a(n_b/N) + b], \quad (1)$$

where

$$n_b = \sum_i \left[\exp \left(\frac{d_i - R_c}{\Delta} \right) + 1 \right]^{-1}, \quad (2)$$

N is the number of atoms in the cluster, and the sum is over all bonds. For the present work on carbon clusters we take $R_c = 1.7$ Å and $\Delta = 0.1$ Å. We emphasize that R_c is not an interaction cutoff, but rather a parameter that is needed to calibrate total energies. The determination of the parameters a and b is discussed in the following section.

II. RESULTS

A. Chains and rings

We have carried out calculations for carbon clusters of size up to ten atoms both in the form of linear chains and rings. In our starting configuration all the nearest-neighbor C-C bond lengths are taken to be identical. Molecular dynamics is then performed to obtain the final equilibrium geometry. The atoms are allowed to relax by removing a small fraction ($\leq 1\%$) of each of the velocity components at every time step, and the simulation is stopped when atoms no longer move.

As outlined above, total-energy calibration requires the determination of the coefficients a and b in Eq. (1). They were determined so as to bring our total energies for the clusters in overall reasonable agreement with the corresponding available experimental values. We get $a = 1.86$ eV and $b = 2.70$ eV. Table II shows our calculated energies (per atom) for each N . The corresponding experimental energies, where available, are shown in parentheses. With this energy scheme, we get complete agreement

TABLE II. Binding energy per atom in eV for C_N . The experimental values are shown in parentheses.

N	Linear	Cyclic
2	2.82 (3.10 ^a)	
3	4.85 (4.63 ^b)	4.85
4	4.80	4.90 (4.75 ^b)
5	5.38 (5.30 ^c)	5.08
6	5.29	5.39
7	5.56	
8		5.27
9	5.50	
10		5.69

^aReference 22.

^bReference 24.

^cReference 23.

with *ab initio* results for the ground state of carbon clusters up to $N = 10$ as discussed below. We note in passing that *ab initio* results for larger carbon clusters are not available.

Figure 1 shows the equilibrium bond lengths for carbon chains for $N = 3, 5, 7,$ and 9 . These ground-state linear chains are found to be of cumulene type rather than polyacetylene type (i.e., the bond length differences are small rather than having bond conjugation), in agreement with *ab initio* results.³ We also find the stable C_4 chain to be of cumulene type, in agreement with *ab initio* theory.^{3,4} We find that for large, even N (> 6), the linear chains are unstable, breaking up into components containing C_3 and C_5 . A linear chain for $N = 8$ is observed to break up into $N = 3$ and $N = 5$ chains; similarly a C_{10} is found to break up into two C_5 chains. We find that the bond-length variations within a structure are in complete agreement with *ab initio* results; our equilibrium bond lengths are on average 5% larger in absolute value, however.

In Fig. 2 we show all the stable final equilibrium geometries obtained by molecular-dynamics simulations for carbon rings. These structures were obtained by starting with a regular polygon configuration with identical bond lengths. After molecular-dynamics relaxation we

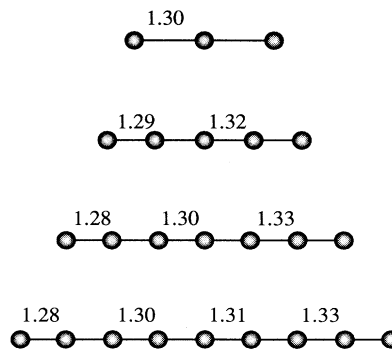


FIG. 1. Geometries of the low-energy structures of small linear carbon chains from $N = 3$ to $N = 9$ obtained using the present molecular-dynamics scheme. The bond lengths are in angstroms.

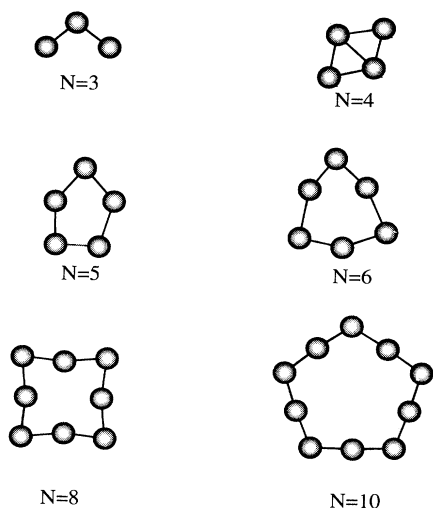


FIG. 2. Lowest-energy cyclic carbon structures for N up to 10, excluding $N = 7$ and $N = 9$, which are found to be unstable.

find the final configurations to deviate from the initial regular polygon structures, attaining lesser symmetry geometries. This allows for more overlap of the π electrons, lowering the electronic energy. These findings are in complete agreement with available *ab initio* results.³ For $N = 3$ we obtain an open triangle with D_{2h} symmetry rather than a closed triangle. This is because the small covalent radius of carbon generates sufficient strain energy to offset the energy gain from the additional bonding due to ring closure. This effect persists up to $N = 5$, after which the ring diameter is large enough to make the closed rings energetically favorable. For C_3 the C-C bond length is 1.37 Å and the bond angle is 98°.

For $N = 4$ we find the most stable structure to be a rhombus (D_{2h} symmetry). This structure is lower in energy than the linear chain, in agreement with previous *ab initio* theories³⁻⁵ and in disagreement with previous conventional tight-binding results.^{9,10} The equilibrium bond length and bond angle are 1.40 Å and 69.6°, respectively [compared to the *ab initio* values 1.425 Å and 61.5° (Ref. 3)].

A distorted pentagonal ring (Fig. 2) is found to be a stable energy minimum for $N = 5$, although higher in energy (0.68 eV/atom) than the linear chain for the same N . The bond lengths for this structure lie between 1.36 Å and 1.56 Å. The ring structure for $N = 5$ has not been considered previously by *ab initio* methods.

For $N = 6$ we obtain a cyclic structure (Fig. 2) to be the ground state which has the same symmetry (D_{3h}) as the one obtained by *ab initio* methods,³ with a side length of 1.36 Å and a vertex angle of 80°, compared to the *ab initio* values of 1.316 Å and 90.4°, respectively). For $N = 8$ and $N = 10$ also the minimum-energy structures we find have the same symmetry as those found in *ab initio* work.³ We note that other workers using conventional tight-binding schemes have found the ground state for these rings to be regular polygons^{9,10} rather than lower symmetry rings.

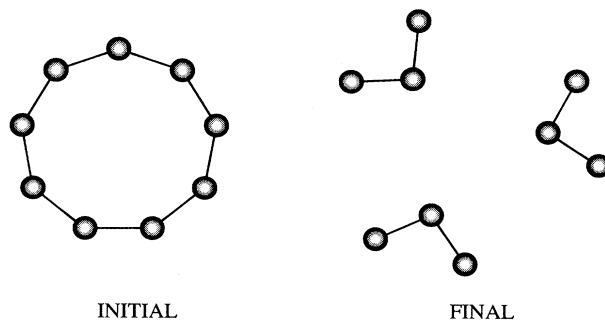


FIG. 3. Simulation showing the breakup of a $N = 9$ carbon ring into three C_3 rings. All the odd numbered cyclic carbon structures are found to be unstable for $N > 5$.

The odd N rings are unstable for $N \geq 7$. Figure 3 shows a simulation demonstrating this instability for C_9 . Here the initial cyclic structure breaks up into three open triangles, each identical to the geometry obtained for $N = 3$ (and shown in Fig. 2).

B. Diamond and graphite

Since the method is several orders of magnitude faster than *ab initio* methods, it can be used more easily in the simulation of larger clusters than is presently possible with *ab initio* methods. With conventional programming techniques we estimate that we can presently treat several hundred atoms with our molecular-dynamics scheme. Using the latest numerical techniques and with parallelization we should be able to significantly increase the number of atoms we can handle. The present scheme has already been used to treat clusters such as the C_{60} molecule.^{12,21} To test the applicability of our method for bulklike clusters we have studied large adamantane and graphitic carbon clusters.

In Fig. 4 we show the initial and final configurations of a cluster of 123 carbon atoms in the diamond structure. The starting cluster consists of a central atom and all

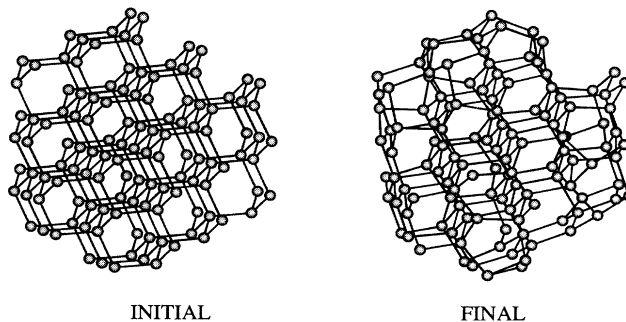


FIG. 4. Initial and final stages of simulation for a 123-atom adamantane cluster. Surface atoms have undergone strong relaxation and reconstruction at the end of the simulation. Note the 2×1 reconstruction for the (001) face (upper right-hand face).

other atoms in the crystalline diamond structure within a radius of 5.45 Å. Using very conventional numerical techniques the first-principles molecular-dynamics optimization of this carbon cluster required about 30 CPU h on our in-house IBM 3090. As can be seen from the final geometry, the most interior atoms are almost unaffected while most of the surface atoms undergo strong relaxation and reconstruction. The average bond length for the fourfold coordinated (i.e., bulk) atoms is 1.593 Å, while the average for threefold coordinated atoms is 1.587 Å; for the twofold coordinated surface atoms the average bond length is found to be 1.533 Å. Considering that we have used universal parameters for the electronic structure and fitted the overlap and repulsive parameters to the carbon dimer value, the agreement for bulk is excellent. Since the ratio of the numbers of surface atoms to bulk atoms in this cluster is 1.08, the cohesive energy for this cluster is not expected to approach the bulk cohesive energy. Indeed, the binding energy in this cluster is found to be 5.70 eV/atom while the bulk value is 7.37 eV/atom.

Due to the absence of an artificial cutoff in the interactions in our scheme, the surface atoms experience unbalanced forces which naturally leads to relaxation and reconstructions. In Fig. 4 the upper right-hand face in the initial configuration corresponds to the unreconstructed 1×1 (001) face. We note from the final configuration in the same figure the formation of surface dimers, i.e., the well-known 2×1 reconstruction of the (001) surface.²⁵ The C-C bond length for the surface dimers is found to be 1.606 Å. The recent scanning tunneling microscopy experiment performed on the surface of diamond epitaxial film has shown that this film grows through 2×1 reconstruction.²⁶ Note that this reconstruction comes about through next-nearest and farther neighbor interactions which are present in our scheme.

Clearly, our scheme can readily be used to study large sp^2 -bonded planar structures like graphite layers. In Fig. 5 we show the final equilibrium geometry of a 126-atom single layer graphitic cluster. Note the absence of any strong distortion at the edges. We find the average bond length for the threefold-coordinated ("bulk") atoms to be 1.393 Å and for the twofold-coordinated atoms to be 1.404 Å. The cohesive energy for this cluster is found to be 6.84 eV/atom, compared to the experimental value of 7.37 eV/atom. We have also estimated the frequency of the in-plane, E_2 vibrational mode frequency of the two-dimensional graphite layer by giving an appropriate displacement to the two innermost atoms in the cluster and recording the resulting periodic motion of the atoms. We find the frequency to be 1959 cm^{-1} , which is about 25% higher than the experimental value (1582 cm^{-1}) (Ref. 27) for the Γ -point E_{2g_2} mode in three-dimensional graphite. The agreement with experiment is excellent considering that we are using the universal scheme for the electronic parameters and have fitted the repulsive parameters in the dimer regime. It is consistent with the degree of accuracy found in our earlier C_{60} work.¹²

We next turn to the applicability of the present scheme to study interlayer interactions in graphite. The interlayer separation in three-dimensional graphite is 3.35 Å.

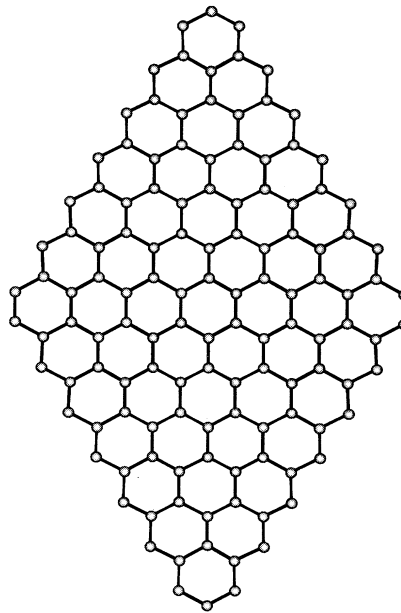


FIG. 5. Final equilibrium geometry for a 126-atom single-layer graphitic cluster obtained in our simulation. There are no strong distortions at the edges.

The binding of layers in graphite is assumed to be a van der Waals type of interaction which results entirely from exchange-correlation effects. Clearly, such effects are not included in any non-self-consistent schemes, including ours. While correlation effects must certainly be important, there are π electron overlap effects as well, as shown by DiVincenzo, Mele, and Holzwarth,²⁸ within a simplified local-density-functional scheme. We have studied interlayer interactions in graphitic layers (42 atoms in each layer) by letting the layers approach one another from a large distance. We find that a weak repulsive barrier develops as the π overlap increases, with no minimum in the interlayer potential for separations greater than 2.5 Å. The inclusion of the attractive exchange-correlation effects is essential for obtaining interlayer binding at these distances.

The present method has already been proven successful in its application to C_{60} and its complexes.^{12,21} Based on this technique we had predicted that the lowest-energy configuration for an oxygen atom chemisorbed on this molecule is one where the oxygen is bonded over the short bond in C_{60} that is shared by two adjoining hexagons. The underlying double bond is weakened into a single bond in the process, giving rise to the "epoxide" structure, and its formation has now been established experimentally.^{29,30} We have also studied $C_{60}O_2$ complexes by this method.²¹

III. CONCLUSION

We have applied an efficient nonorthogonal tight-binding molecular-dynamics scheme to study equilibrium

geometries of carbon clusters of arbitrary size. The number of adjustable parameters has been kept to a minimum in our technique by the use of Harrison's universal scheme.¹⁸ This allows us to preserve the *a priori* nature of the theory and treat a wide range of covalent systems with differing environments within a unified scheme.

The method is computationally efficient, requiring no additional cost over the conventional orthogonal tight-binding method, while greatly extending the scope of the conventional scheme by providing more accurate treatment of structures with arbitrary coordination. The method is orders of magnitude more economical than *ab initio* schemes while treating the physics of the covalent bonding in nontetrahedral and multicoordinated systems correctly. Complete agreement with *ab initio* results has been obtained for clusters of size up to $N = 10$, both for the ground-state geometries and with regard to the symmetry-lowering in-plane distortions for the ring structures. The latter feature has not been obtained by previous works employing conventional tight-binding schemes.^{9,10}

For small carbon clusters ($N \leq 10$), cyclic rings are determined to be the ground state for even N , while linear chains are found to be the ground state for odd N . The linear chains are determined to be of cumulene type rather than polyacetylene type. These results are in complete agreement with *ab initio* results. We have also shown the instability of odd numbered rings for $N > 5$. In addition, we also show that chains with large, even N prefer to fragment into smaller components.

The results for carbon clusters show important differences from silicon. The persistence of linear and ring structures with low coordination indicates the presence of considerable strain energy on account of the smaller

covalent radius of carbon. This seems to be responsible for preventing the formation of closed-pack structures ($n_b/N > 2$) found in clusters of atoms with larger covalent radii such as silicon for $N \leq 10$. The symmetry-lowering in-plane distortions for the closed rings, on the other hand, can relieve some of this strain energy by allowing better overlap of the π orbitals, resulting in interesting two-dimensional structures unique to carbon.

We have obtained excellent agreement with experiment for structures and bond lengths for large adamantane and graphitic carbon clusters, simulating bulk diamond and graphite (single layer). For the (001) face of the diamond cluster we have obtained the well-known 2×1 reconstruction.

By using the universal scheme for the electronic parameters and fitting the repulsive parameters in the dimer regime we have demonstrated that it is possible to treat carbon clusters of arbitrary size and different phases within a simplified molecular-dynamics scheme. Carbon is generally considered to be a difficult element to treat since it readily forms structures with widely differing bond lengths and our results clearly show the importance of including the effects of nonorthogonality in obtaining agreement with *ab initio* and experimental results for carbon clusters.

ACKNOWLEDGMENTS

This research was supported in part by U.S. DOE Contract No. DE-FC22-90PC90029, by NSF Grant No. EHR 91-08764, and by the University of Kentucky Center for Computational Sciences. One author (M.S.) acknowledges financial support from the Pew Charitable Trust.

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