

Growth Regimes of Carbon Clusters

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We calculated the relative stabilities of carbon clusters with up to 60 atoms. Equilibrium geometries have been obtained by combining an adaptive simulated annealing method and a simple tight-binding-type Hamiltonian for total energies. We found that C_n clusters favor one-dimensional structures for $n \lesssim 20$. For $n \gtrsim 20$, closed fullerene cages show a larger stability than both the one- and two-dimensional structures (such as graphite flakes and buckled fullerene "caps"). Isomers with linear and "fullerene" structure should coexist near the critical cluster size $n \approx 20$. We find the C_{60} fullerene to be the most stable structure, with a binding energy of 6.99 eV/atom.

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Recent synthesis of C_{60} clusters in macroscopic quantities by Krätschmer *et al.* [1] triggered enormous scientific and public interest in this new form of carbon. The uncommon "hollow soccer ball" (or "fullerene") structure, which was originally postulated for this cluster by Kroto *et al.* [2], promises unusual properties for this cluster. While the amount of information on C_{60} is increasing very rapidly [3], much less is known about the structure and energetics of carbon clusters with fewer atoms [4]. Also, only unconfirmed speculations exist about the pathway leading to the fullerene structure [5].

In this Letter, we present a consistent picture of the different structural regimes encountered during the growth of carbon clusters with up to 60 atoms. For each cluster size, we attempt to determine the equilibrium geometry and cohesive energy which is indicative of the stability of the cluster. We have achieved this by combining an adaptive simulated annealing method with a recently developed semiempirical total-energy scheme.

Structure optimization in large C_n clusters is a non-trivial undertaking in view of the large number $3n - 6$ degrees of freedom. Carbon is very treacherous in this respect since the directionality of bonding causes a high complexity of the potential-energy surface. Consequently, total-energy minimization using standard techniques in most cases leads to local minima rather than the optimum geometry. We optimized the cluster geometries by using a modified version [6] of the adaptive simulated annealing method [7]. Starting at a "temperature" [8] which is much higher than the cluster melting temperature, we presearched the $(3n - 6)$ -dimensional coordinate space for acceptable geometries. The successful attempts, as defined by the Metropolis Monte Carlo prescription [9], converge towards a region in the coordinate space which is likely to contain the optimum geometry. The search then continues at a lower temperature, concentrating on this region. As the temperature decreases, the covariance matrix of the $3n - 6$ variables describes a gradually decreasing portion of the coordinate space.

The search is finished when the uncertainty in *all* atomic coordinates is smaller than a preset value, typically 0.1 Å.

Our energy function for the optimization is based on a parametrized tight-binding Hamiltonian. For maximum accuracy, one would prefer a first-principles scheme, based, for example, on the local-density approximation (LDA) [10,11]. A systematic survey of large systems (as done here), however, requires more computer-efficient methods at this point. Our method is several orders of magnitude faster than a corresponding LDA calculation, and has been tested successfully in a previous survey of small Si_n clusters [12]. The application to carbon is less accurate. However, important quantum-mechanical effects, such as changes in hybridization with different structural configurations, are generally well accounted for.

We write the total energy of a carbon cluster as a sum of four terms [6],

$$E_{\text{tot}} = \sum_a n_a \epsilon_a + \sum_{i < j} E_r(d_{ij}) + \sum_i \psi(Z_i) + U \sum_{i=1}^n (q_i - q_i^0)^2. \quad (1)$$

The binding energy of this cluster (with respect to isolated atoms) is then given by

$$E_{\text{coh}} = nE_{\text{tot}}(\text{C atom}) - E_{\text{tot}}(C_n). \quad (2)$$

We label the electronic states of the cluster by a and the atomic sites by i, j . The first term in Eq. (1) is the one-electron energy of the cluster, obtained using a tight-binding Hamiltonian to be described below. The second term consists of pairwise repulsive energies $E_r(d)$ arising from nuclear repulsion and electronic "overcounting" terms. As for silicon, we choose to *define* E_r as the difference of the "exact" calculated *ab initio* [13] binding energy and the tight-binding one-electron energy of C_2 , as shown in Fig. 1. The third term represents corrections to the binding energy during the transition to higher (bulklike) coordination numbers Z_i . The parameters in

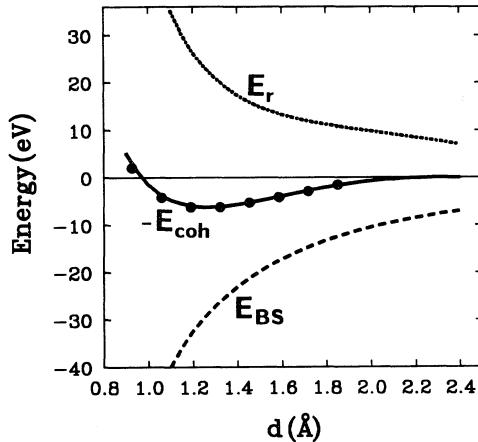


FIG. 1. Binding energy E_{coh} (solid line), repulsive energy E_r (dotted line), and band-structure energy E_{BS} (dashed line) for a C_2 molecule, as a function of the bond length. The *ab initio* CI results [13] are indicated by \bullet .

this term are chosen to reproduce binding energies of selected bulklike structures. The final fourth term is an intra-atomic Coulomb repulsion arising from possible charge transfers between inequivalent sites. Zero-point vibrational energies are neglected.

This tight-binding energy formula contains the essential physics which governs bonding in carbon structures. It is easily applicable to very large carbon clusters which are inaccessible to *ab initio* techniques, at the expense of avoiding an explicit treatment of multicenter integrals which can be important in small structures. Where applicable, however, it provides a more detailed insight into rehybridization energetics than more empirical schemes (such as the Tersoff potentials [14]), which have recently been applied to this system [15], since it treats the kinetic energy quantum mechanically and thus correctly reproduces electronic-shell-structure effects. Furthermore, it yields Jahn-Teller distortions of symmetric geometries due to partially occupied degenerate levels at the "Fermi energy." We expect it to give a reasonably accurate interpolation between the dimer and selected bulk structures.

We have used a simple two-center Slater-Koster parametrization [16] for our four-state (s, p_x, p_y, p_z) nearest-neighbor tight-binding Hamiltonian [12]. The parameters have been obtained from a global fit to local-density approximation [10] calculations for the electronic structure of C_2 , a graphite monolayer, and bulk diamond for different nearest-neighbor distances [17]. The diagonal elements of the Hamiltonian are s - and p -level energies $E_s = -7.3$ eV and $E_p = 0.0$ eV. The off-diagonal matrix elements are the hopping integrals with a d^{-2} distance dependence. Their values for $d = 1.546$ Å, which is the equilibrium nearest-neighbor distance in diamond [18], are $V_{ss\sigma} = -3.63$ eV, $V_{sp\sigma} = 4.20$ eV, $V_{pp\sigma} = 5.38$ eV, and $V_{pp\pi} = -2.24$ eV. Similar to silicon, we use $U = 1$ eV

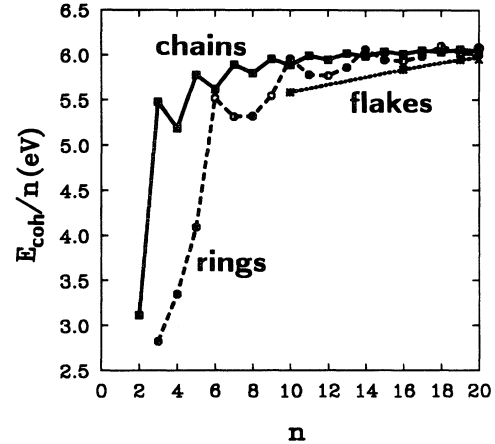


FIG. 2. Binding energy E_{coh} of small carbon clusters as a function of cluster size n , for $n \leq 20$. Results for chains (\blacksquare) are connected by a solid line, results for rings (\circ) are connected by a dashed line, and results for planar graphite flakes (\star) are connected by a dotted line.

for the intra-atomic Coulomb interaction as suggested by Auger spectroscopy. In our Hamiltonian, we consider those atoms as nearest neighbors which are closer than the cutoff distance $d_c = 1.67$ Å. This is the average of the nearest- and second-nearest-neighbor distances in bulk diamond, and hence near the minimum of the radial distribution function.

Our Hamiltonian is rather simplified and does not treat explicitly the multicenter as well as longer-range interactions. To account for those, we introduce a simple bond-counting term. We determine the bond-number function $\psi(Z)$ by fitting the value $E_{\text{coh}} = 7.37$ eV for the cohesive energy [18,19] of bulk diamond ($Z=4$) and graphite ($Z=3$) as well as the binding energy (per atom) in an infinite linear chain [20] ($Z=2$) $E_{\text{coh}} = 6.12$ eV [21]. We have $\psi(1) = 0$ eV by definition (C_2 is reference with $Z=1$), $\psi(2) = -0.94$ eV, $\psi(3) = -2.69$ eV, and $\psi(4) = -5.11$ eV. With these parameters we calculate the other bulk properties such as the lattice constant of C(diamond), $a_0 = 3.17$ Å (expt. 3.57 Å) [18], and the in-plane nearest-neighbor distance of C(graphite), $d_0 = 1.30$ Å (expt. 1.42 Å) [19]. The degree of agreement between the calculated and the experimental values is sufficient and remarkable in view of the fact that the dependence of E_{tot} on geometry in our Hamiltonian is based predominantly on the C_2 molecule.

In order to understand the growth of large clusters, we compared the energy of the optimum annealed structures to regular geometries such as chains, planar rings, graphite flakes, selected "fullerenes" (or hollow cages), as well as "caps" (or fragments) of the most stable C_{60} fullerene. Our results are summarized in Figs. 2 and 3 and reflect a large variation of the binding energy per atom from 3.1 eV in C_2 to 7.0 eV in C_{60} . These values are in overall

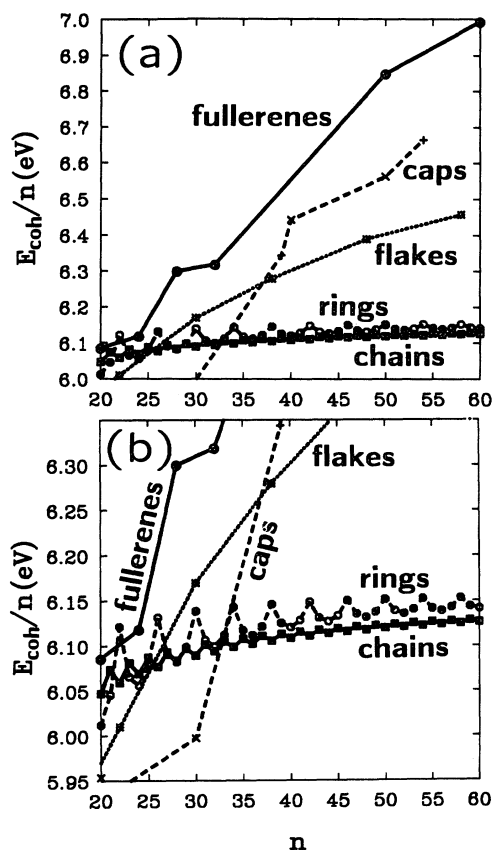


FIG. 3. Binding energy E_{coh} of small carbon clusters as a function of cluster size n , for $n \geq 20$. Results for chains (\blacksquare) are connected by a solid line, results for rings (\circ) are connected by a dashed line, and results for planar graphite flakes (\star) are connected by a dotted line. Results for buckled fullerene caps with a pentagonal (\times) or a hexagonal basis ($+$) are connected by a dashed line. Results for hollow fullerene cages (\bullet) are connected by a solid line. The full energy region is given in (a). The critical transition region near $n=20$ is shown on an expanded energy scale in (b).

general agreement with available *ab initio* results [3].

As shown in Fig. 2, the strong $pp\sigma$ bond is very effective in stabilizing the linear structures in small carbon clusters. Clearly, our parametrized energy expression in Eq. (1) cannot resolve the standing controversy between different *ab initio* calculations [4], whether the tetramer [22–25] C_4 and the six- and eight-membered clusters [23,24] C_6 and C_8 are cyclic or linear. In fact, our fit to C_2 biases us towards linear, open-ended structures. Only for larger clusters do we find that the creation of one extra bond in the cyclic structure outweighs the energy loss due to bond bending, such as for cluster sizes $n=10, 14, 18, \dots$ and $n > 30$. The stability maxima at $n=10+4k$ ($k=0, 1, 2, 3, \dots$) result from an electronic effect and have been discussed previously [23,24]. Even at these relatively small cluster sizes, however, planar and three-dimensional structures start to pre-

vail, as shown in Fig. 3.

Our results for binding energies of clusters with $n \geq 20$ atoms are summarized in Fig. 3. We find that planar graphite flakes become more stable than linear chain or ring structures for $n > 26$. One way to regain energy stored in dangling bonds is to reduce the fraction of twofold-coordinated atoms in graphite flakes. This can be achieved by buckling the flakes, by substituting pentagons for hexagons. The corresponding strain energy is very large in the small caps with only few atoms, but diminishes rapidly with increasing cluster size and makes caps more favorable than planar arrangements for structures with $n > 38$ atoms.

A rather surprising result of our study is the relatively high stability of closed fullerene cages with $n \geq 20$ atoms. We find that the stability of these cages exceeds by far any other comparable structures [26]. Except for the C_{60} and C_{70} fullerenes, which we find to be only $\lesssim 0.4$ eV (per atom) less stable than graphite, there is no experimental evidence confirming or denying the existence of three-dimensional structures. We concentrated our study on the most stable fullerene cages which have been postulated previously by Kroto [27]. These are polyhedra with twelve pentagons and a varying number of hexagons, and start at $n=20$ with the dodecahedron. While the $n=20$ and $n=24$ structures are comparable in energy to the corresponding rings, the larger structures with $n=28$, $n=32$, and $n=50$ atoms are significantly more stable than the linear or planar structures. The C_{60} fullerene is the first low-strain structure where all pentagons are separated by hexagons. This is reflected in the high binding energy of 6.99 eV per atom. The next regular fullerene is C_{70} with larger regions of connected hexagons which are reminiscent of graphite sheets. Accordingly, the binding energy of 7.02 eV per atom is higher than in C_{60} and is approaching the graphite value [18] of 7.37 eV per atom.

The relative stabilities of the clusters can be understood using one-electron energy and hybridization arguments. The linear structures result from the stable $pp\sigma$ bond which maximizes hybridization in small carbon clusters. The large sp^2 -type hybridization which stabilizes bulk graphite is again responsible for the graphitic structures which we found in large carbon clusters. Especially stable structures also tend to show a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). We found the extraordinarily large stability of C_{60} reflected in the large value $E_g=2.4$ eV of the gap between fivefold degenerate h_u HOMO and the threefold degenerate t_{1u} LUMO [3]. This occurrence of “shell structure” is a result of the quantum-mechanical nature of the kinetic energy.

The equilibrium carbon-carbon nearest-neighbor distances d_{C-C} in all C_n clusters lie in the range between 1.2 and 1.42 Å, which is the value for bulk graphite. They follow the general scheme that fewer nearest neighbors

shorten the bond length, while a decreasing nearest-neighbor overlap (e.g., due to changing angles between bonds) tends to increase the bond lengths. In planar graphite flakes, in the above discussed favorable fullerene cages, and in caps of the C_{60} fullerene structure, the bond lengths approach the graphite value of d_{C-C} . Twofold-coordinated atoms at the boundary of caps or flakes show a bond-length contraction which affects the average bond length in the cluster only in case of small clusters. Our Hamiltonian also predicts the length difference of 0.03 Å between “single” and “double” bonds in the C_{60} fullerene [3].

Results presented in this study narrow down the possibilities for the growth mechanism of carbon clusters. Based on our $T=0$ results, we postulate initial growth as one-dimensional structures (chains or rings) for $n \lesssim 20$ atoms. We find that in the intermediate regime for $20 \lesssim n \lesssim 60$ or larger, closed fullerene cages show a larger stability than both the one-dimensional and two-dimensional structures (such as graphite flakes and buckled fullerene caps). For large systems, of course, diamond and layered graphite structures will prevail. The crossover from “huge” fullerenes to these structures has not been studied.

Unfortunately, our $T=0$ results offer little help in understanding the pathway in which the C_{60} fullerene is formed. The idea [5] that caps would accrete carbon and grow into the C_{60} fullerene seems unrealistic since these structures should convert spontaneously into the more stable closed fullerene cages. We can think of specific accretion channels being singled out by entropy under $T > 0$ conditions. Another possibility for the generation of the C_{60} structure is a fusion of two smaller fullerenes, such as C_{24} and C_{36} , which is highly exothermic. Obviously, further study of the smaller carbon clusters, especially at nonzero temperature, is needed to answer these questions.

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