Structure and Energetics of Single and Multilayer Fullerene Cages

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Minimum energy structures for large carbon cages are investigated using realistic atomic potentials. Above a critical size of ~6000 there is a stability crossover from single to multilayer cages. The lowest energy atomic configuration of a cage of any size consists only of hexagons and pentagons and is polyhedral in shape. Lowest energy defects involve either rearrangements between pentagons and hexagons or 5-7-5 triplets. Simulated transmission electron microscopy images show that a polyhedral onion appears spheroidal when viewed along its highest symmetry axis, and polyhedral when viewed from a more general direction.

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Recent experimental breakthroughs in the production of macroscopic quantities of C_{60} in a graphite arc and the direct confirmation of the molecule's spheroidal nature [1] have added a new family of stable forms of solid carbon. Graphitic sheets, the lowest energy form in the bulk, are energetically less favorable in finite-sized samples. This is because the presence of dangling bonds results in a tendency for the hexagonal sheets to patch up loose ends by curling up [2–4]. Experimental isolation of large carbon cages [5–7] and the unexpected discovery of concentric carbon nanotubes [8–10] have stimulated detailed theoretical studies [11,12] of energetics, electronic structure, and nucleation mechanisms of different kinds of fullerenes. Very recently yet another structure of carbon has been discovered in soot annealed by intense electron-beam radiation [13]. These new fullerenes, called "onions," consist of nearly spherical, concentric shells, and are extremely stable under further irradiation [13,14]. The existence and stability of carbon onions have added to the excitement of unraveling the lowest energy allotrope of carbon in systems of limited size.

This Letter presents scaling arguments and explicit energetic considerations for the existence of a critical size of carbon clusters below which single cages are favored energetically and above which multilayer cages, or onions, are stable. The critical size marking this stability change is estimated from total energy calculations. Among the single-layer cages, the ones with icosahedral symmetry are found to be energetically the most stable. *We also find that the ground state corresponding to the most stable cage consisting of an even number of atoms always involves only hexagons and exactly twelve pentagons.* (Odd-atom cages cannot form a fully threefold-coordinated network.) The lowest energy cages are thus always polyhedral. Low energy topological defects in large cages ($N > 200$) are possible, but the polyhedral shape of the cage still remains. Simulated transmission electron microscopy (TEM) pictures show that polyhedral cages can appear spheroidal when viewed from a particular high symmetry direction, and polyhedral when viewed from a more general direction.

The method of calculation is based on a conjugate gradient minimization of a three-valent atomic network. The interatomic forces are calculated from a three-body Tersoff potential [15] as modified by Brenner [16] (henceforth referred to as the Tersoff-Brenner potential). Simulated annealing performed directly on an initially random atomic cage almost always gives rise to fullerenes with defects [17,18], due to strong directional bonding that results in high barriers for bond rearrangements [19]. A simulated annealing search of sufficient duration to find the true ground state or the low energy metastable states is too demanding computationally at this time. A feasible shortcut is to minimize first the network of face centers, the so-called face-dual network, interacting through a pairwise repulsive potential and constrained to move on a closed surface [20]. For concreteness, a pairwise $1/r^2$ potential is used in all calculations reported here, and the constraining surface is chosen to be spherical. The resulting face-dual network is a spherical tessellation of triangles, with five or more sides meeting at each vertex. Following Coxeter [21,22], we denote such a network by the symbol $\{3,5+\}$. Dualizing this face-dual network yields a tessellation $\{5+,3\}$ of an atomic network: a three-valent cage structure with five or more sided faces, which forms a suitable initial configuration to be relaxed with the Tersoff-Brenner potential. This procedure provides an efficient method for generating low energy structures of cages with any even number of atoms. For an "onion," the starting configuration is obtained by generating each concentric onion shell separately by the face-dual minimization procedure described above. A conjugate gradient relaxation is then performed using the Tersoff-Brenner potential within each shell, and a van der Waals (vdW) potential between pairs of consecutive shells. The vdW potential has been taken directly from previous studies of bulk graphite [23]. The results were also checked with another parametrization of the vdW interaction [24].

The results for the ground state total energy per atom for single cages are shown in Fig. 1, as a function of cage size. A convex hull is constructed through the energies of the most stable cages [25]. The cages whose energies are on the hull turn out to be the ones with icosahedral sym-

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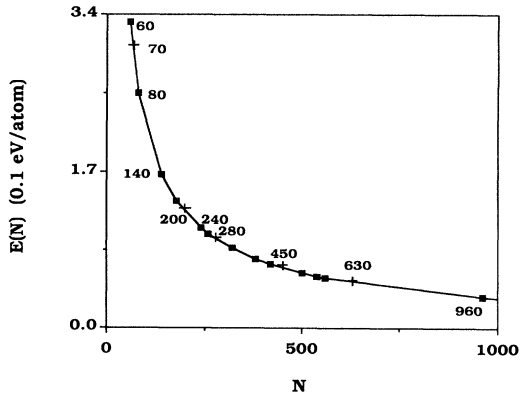

FIG. 1. The ground state energy $E(N)$ (per atom) of single cages as a function of cage size N. The zero is chosen at $E_{\text{graphene}} = -7.3768$ eV/atom. The convex hull (bold line) passes through the icosahedral cages (black squares). Some stable cages of lower symmetry (crosses) are also shown.

metry and correspond to sizes given by the formula [26]

$$N = 20(b^2 + bc + c^2)\,, \tag{1}$$

where b and c are non-negative integers. The lowest few numbers in this series are 20, 60, 80, 140, 180, 240, and so on. *However, many clusters of lower symmetry, although not exactly on the hull, are surprisingly close to it, and are also quite stable.* The energies of a few of these stable clusters with $N = 70,200,280,450,630$ are also shown in Fig. 1. For cages with $N > 100$ a face-dual minimization run often gets trapped in local minima, always with a lower symmetry than the ground state. The ground state of any given cage is always found to involve only pentagonal and hexagonal faces with the maximum possible separation between pentagons, in accord with similar conclusions drawn from chemical arguments [27]. The lowest energy defect state of any given cage has the same number of pentagons and hexagons as the ground state, but with a different atomic arrangement that results in a slight deformation from the ground state structure. There are several topologically allowed ways of inserting heptagons into a $\{5+,3\}$ tessellation, e.g., those seen in the buckling pattern of a spherical honeycomb structure [22]. For large cages ($N > 200$) low energy metastable states exist, involving one or more heptagons. Some of the lowest energy candidates are (a) a pentagon-heptagon pair; (b) a pentagon-heptagon-pentagon triplet with nonadjacent pentagons; (c) more complicated morphologies involving a larger number of nonadjacent pentagons and heptagons. In a low energy metastable fullerene structure, however, a heptagon always appears in the triplet morphology of the case (b) above. This structural unit replaces an isolated pentagon of the ground state structure, thereby automatically satisfying the constraints of Euler's equation: (No. pentagons) − (No. heptagons) = 12. In large clusters ($N > 200$) we find that the defect energy scales almost linearly with the number of heptagons in the system. This implies that the defects are approximately noninteracting and that the effects of a heptagon insertion are short ranged. The defect energy per heptagon is practically independent of the cage size and is about 0.5 eV/defect. Other kinds of more extended topological defects can be artificially introduced and their energetics is currently under investigation.

The convex hull of Fig. 1 is accurately fitted by the curve

$$E(N) = E_{\text{graphene}} + 4.6164 N^{-(0.561 + 0.022 \ln N)}\,, \tag{2}$$

where $E_{\text{graphene}} = -7.3768$ is the energy per atom for the infinite graphene layer [16] and all the units are in eV/atom. The above fit is extremely accurate in the range $200 < N < 10000$. [The asymptotic behavior of $E(N)$ was not considered.] Although Eq. (2) was only fitted to the icosahedral cages, it turns out that cages of lower symmetry are quite close in ground state energy to the convex hull of Fig. 1. The fit given by Eq. (2) is thus a very good approximation (within 0.2% for $N > 200$) to the ground state energies of all large cages.

In order to address the issue of stability of onion structures it is necessary to compare energetics of an onion with that of an isolated cage of equal size. Previous calculations indicated that *closed* finite-sized tubules are higher in energy than isolated cages [28]. Therefore, tubular structures are not considered in this Letter, although open tubes might become energetically important at sizes well beyond the range considered in this Letter. In order to estimate the critical size above which onions could become energetically favorable, it is convenient to calculate the quantity ΔE, defined, for a two-shell onion, by

$$\Delta E = E(N_1 + N_2) - \frac{N_1 E(N_1) + N_2 E(N_2)}{N_1 + N_2}\,, \tag{3}$$

where N_1 (N_2) is the number of atoms in the inner (outer) shell of an $[N_1,N_2]$ onion and $E(N)$ is the energy per atom of a single cage of size N (henceforth referred to as E^{cage}). Physically ΔE corresonds to the fragmentation energy per atom of a single cage of size $(N_1 + N_2)$ into two smaller cages of sizes N_1 and N_2. The effective vdW attraction per atom of the $[N_1,N_2]$ onion is given by

$$E^{\text{vdW}}[N_1,N_2] = E^{\text{onion}}[N_1,N_2] - \frac{N_1 E(N_1) + N_2 E(N_2)}{N_1 + N_2}\,, \tag{4}$$

where $E^{\text{onion}}[N_1,N_2]$ is the total energy per atom of the $[N_1,N_2]$ onion. Equations (3) and (4) can be generalized to the case of more than two shells in a straightforward fashion. The crossover in stability from single cages to onions occurs when the energy loss due to smaller radii of curvature in an onion (as compared to a single cage with the same *total* number of atoms) is overcompensated by a

TABLE I. A comparison of the ground state energies of a few icosahedral onions with those of single cages of equal size. The units are eV/atom.

Onion size	E^{onion}	E^{cage}	ΔE	E^{vdW}
[60,240]	−7.2260	−7.2852	−0.0622	−0.0030
[240,540]	−7.3069	−7.3355	−0.0314	−0.0028
[540,960]	−7.3373	−7.3535	−0.0190	−0.0028
[960,1500]	−7.3520	−7.3618	−0.0127	−0.0029
[2160,2940]	−7.3653	−7.3691	−0.0068	−0.0030
[6000,7260]	−7.3739	−7.3737	−0.0029	−0.0031
[60,240,540]	−7.2893	−7.3381	−0.0525	−0.0037
[60,240,540,960]	−7.3199	−7.3569	−0.0410	−0.0040

gain in energy due to the attractive vdW force between the onion layers. This happens when the fragmentation energy ΔE is smaller in magnitude than the vdW energy E^{vdW}. Our results for E^{onion}, E^{cage}, ΔE, and E^{vdW} for a few onions, using the vdW interaction of Ref. [23], are displayed in Table I. Figure 2 shows ΔE and E^{vdW} for the two-layer icosahedral onions [$N_1=60p^2$, $N_2=60(p+1)^2$] [which correspond to the series $b=c=p$ in Eq. (1)] as a function of $N=N_1$. From the results of Table I it is clear that ΔE decreases monotonically with an increase in N_1 for the two-shell onions. The vdW energy E^{vdW} varies little, saturating slowly to about 0.0031 eV/atom. The crossover to onions occurs therefore when the ΔE vs N curve passes through this nearly constant value of E^{vdW}. This happens at $N\sim5800$ as indicated in Fig. 2 and supported by the explicit results of Table I. Calculations repeated with the vdW interaction of Ref. [24] yield very similar results, with a slightly lower vdW saturation energy (0.0028 eV/atom) and a slightly higher crossover size ($N\sim6200$). It can also be seen from Table I that the energy difference per atom $E^{\text{onion}}-E^{\text{cage}}=E^{\text{vdW}}-\Delta E$ is larger in onions with three or more shells than in those with two shells. Thus, with increasing clus-

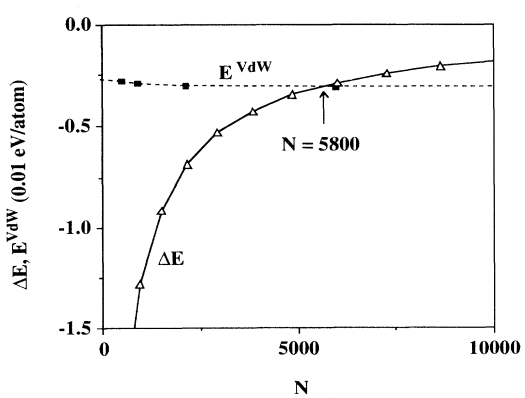

FIG. 2. Fragmentation energy ΔE and van der Waals energy E^{vdW} (defined in the text) for two-shell icosahedral onions as functions of the inner shell size. The crossover occurs near $N=5800$.

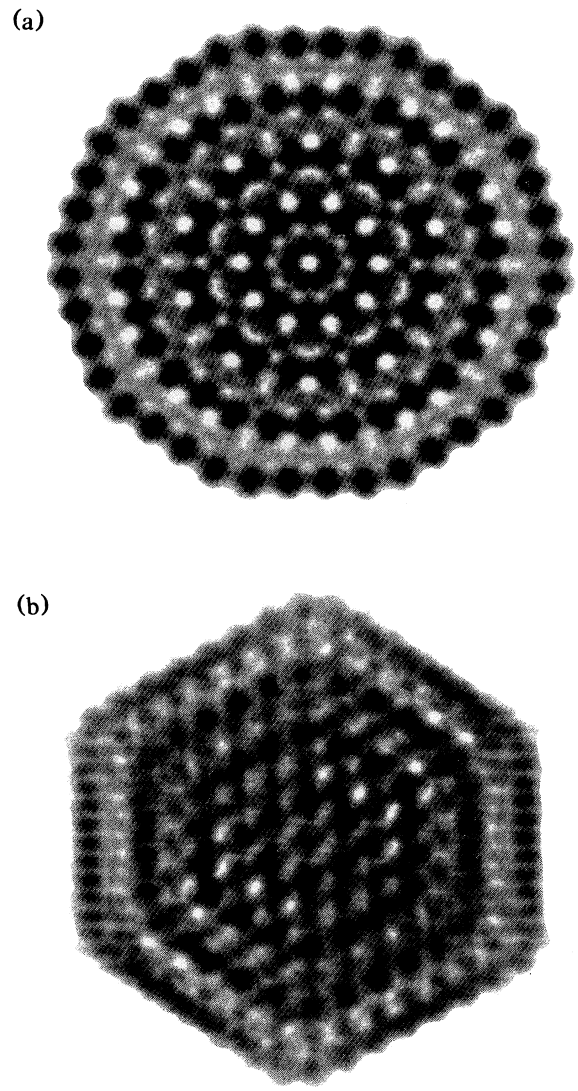

FIG. 3. Atomic density plot of the four-layer onion [60,240,540,960] projected onto a two-dimensional plane that is normal to (a) a fivefold symmetry axis and (b) a threefold symmetry axis. This plot is expected to simulate experimental TEM images.

ter size, one should expect a crossover first to two-shell onions, and then to the multishell ones. Onions with shells other than of icosahedral symmetry have also been examined for onion sizes smaller than 1000 atoms. The energetically most stable structure for an onion of a given size is difficult to obtain in this case because there is no clear rule to determine the sizes of the individual shells. However, our calculations on a large number of onions unequivocally establish the stability of single cages over onions in this size regime. This is also true for the experimentally observed [14] onions [50,230] and [70, 290,680].

Finally, it is interesting to consider the shapes of onions in their ground states. Figures 3(a) and 3(b) display two-dimensional projections of the atomic density for the four-shell onion [60,240,540,960], viewed from two orthogonal directions. In Fig. 3(a) the atomic density is projected onto a plane normal to a *fivefold* symmetry axis, while Fig. 3(b) corresponds to the projection normal to a *threefold* symmetry axis. These pictures are very similar to the recently simulated TEM images of icosahedra [29]. While the onion looks quite circular when viewed from the fivefold axis, much like the experimental TEM images of Ref. [13], it appears polyhedral when viewed from a more general direction.

In summary, carbon onions are energetically favorable over single fullerene cages only above a certain critical size $N \sim 6000$. The existence of onions smaller than this critical size [14] should be due to specific nucleation mechanisms prevalent during the experiment. The ground state structures of large single cages as well as onions ($N > 200$) are always *polyhedral,* consisting of pentagons and hexagons only. However, the TEM image of moderately large onions (outer-shell size < 2000) might consist of concentric circular rings if viewed from certain high symmetry directions. The most stable single cage fullerenes are found to be of icosahedral symmetry, although large cages of lower symmetry are only slightly less stable and should thus be observable.

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[1] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).
[2] H. W. Kroto, Nature (London) **359**, 670 (1992).
[3] Q. L. Zhang, S. C. O'Brien, J. R. Heath, Y. Liu, R. F. Curl, H. W. Kroto, and R. E. Smalley, J. Phys. Chem. **90**, 525 (1986).
[4] D. H. Robertson, D. W. Brenner, and C. T. White, J. Phys. Chem. **96**, 6133 (1992).
[5] R. Ettl, I. Chao, F. Diederich, and R. L. Whetten, Nature (London) **353**, 149 (1991).
[6] F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani, and A. Koch, Science **252**, 548 (1991).
[7] K. Kikuchi, N. Nakahara, T. Wakabyashi, S. Suzuki, H. Shimomaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, Nature (London) **357**, 142 (1992).
[8] S. Iijima, Nature (London) **354**, 56 (1991).
[9] T. W. Ebbesen and P. M. Ajayan, Nature (London) **358**, 220 (1992).
[10] S. Iijima, P. M. Ajayan, and T. Ichihashi, Phys. Rev. Lett. **69**, 3100 (1992).
[11] X. Liu, D. J. Klein, T. G. Schmalz, and W. A. Seitz, J. Comput. Chem. **12**, 1252 (1991), and references therein; P. W. Fowler, J. E. Cremona, and J. I. Steer, Theoret. Chim. Acta **73**, 1 (1988); Q. Zhang, J.-Y. Yi, and J. Bernholc, Phys. Rev. Lett. **66**, 2633 (1991); D. E. Manolopoulos, J. C. May, and S. E. Down, Chem. Phys. Lett. **181**, 105 (1991); B. L. Zhang, C. Z. Wang, K. M. Ho, C. H. Xu, and C. T. Chan (to be published).
[12] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992); N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992); M. S. Dresselhaus, G. Dresselhaus, and R. Saito, Phys. Rev. B **45**, 6234 (1992); M. Fujita, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **45**, 13834 (1992); B. I. Dunlap, Phys. Rev. B **46**, 1933 (1992); D. H. Robertson, D. W. Brenner, and J. W. Mintmire, Phys. Rev. B **45**, 12592 (1992); J.-Y. Yi and J. Bernholc, Phys. Rev. B **47**, 1708 (1993).
[13] D. Ugarte, Nature (London) **359**, 707 (1992).
[14] D. Ugarte (to be published).
[15] J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986); **61**, 2879 (1988); Phys. Rev. B **37**, 6991 (1988).
[16] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).
[17] P. Ballone and P. Milani, Phys. Rev. B **42**, 3201 (1990).
[18] J. R. Chelikowsky, Phys. Rev. Lett. **67**, 2970 (1991).
[19] J. Y. Yi and J. Bernholc, J. Phys. Chem. **96**, 8634 (1992).
[20] B. L. Zhang, C. Z. Wang, and K. M. Ho, Chem. Phys. Lett. **193**, 225 (1992).
[21] H. S. M. Coxeter, in *A Spectrum of Mathematics* (Oxford Univ. Press, Oxford, 1972), p. 98.
[22] T. Tarnai, Comput. Math. Appl. **17**, 639 (1989).
[23] H. A. Rafizadeh, Physica (Utrecht) **74**, 135 (1974); A. A. Ahmadieh and H. A. Rafizadeh, Phys. Rev. B **7**, 4527 (1973).
[24] J. T. Sprague and N. L. Allinger, J. Comput. Chem. **1**, 257 (1980).
[25] A. Maiti and L. M. Falicov, Phys. Rev. A **44**, 4442 (1991).
[26] M. Goldberg, Tôhoku Math. J. **43**, 104 (1937).
[27] T. G. Schmalz, W. A. Seitz, D. J. Klein, and G. E. Hite, J. Am. Chem. Soc. **110**, 1113 (1988); R. E. Haufler, Y. Chai, L. P. F. Chibante, J. Conceicao, C. Jin, L. S. Wang, S. Maruyama, and R. E. Smalley, Mater. Res. Soc. Symp. Proc. **206**, 627 (1991).
[28] G. E. Scuseria, in *Buckminsterfullernes,* edited by W. E. Billups and M. A. Ciufolini (VCH Publishers, New York, 1992).
[29] K. G. McKay and H. W. Kroto, J. Chem. Soc. Faraday Trans. **88**, 2815 (1992).

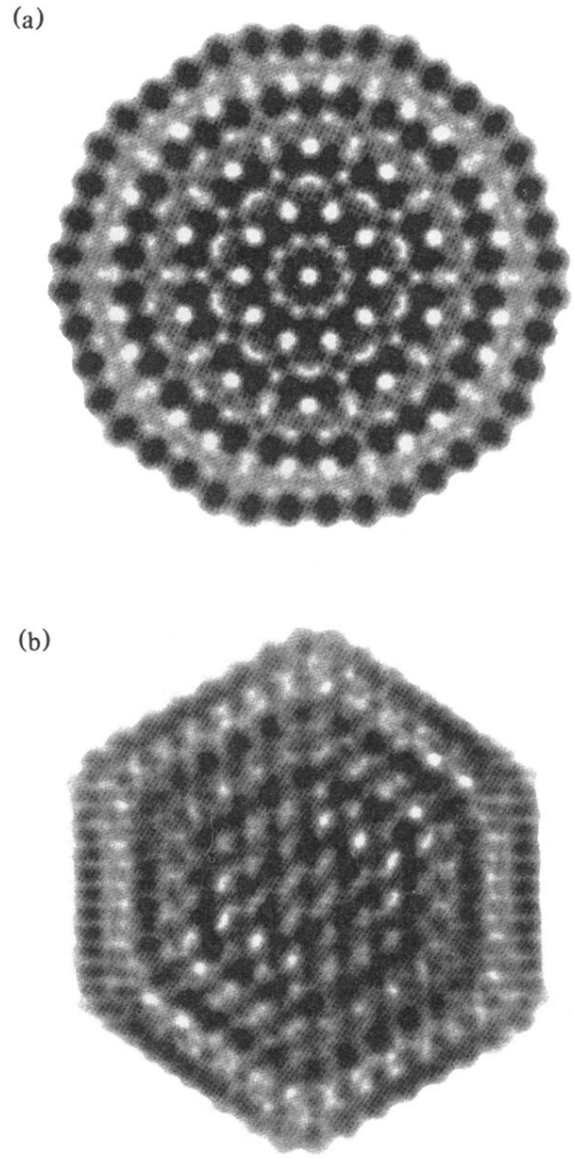

FIG. 3. Atomic density plot of the four-layer onion [60,240,540,960] projected onto a two-dimensional plane that is normal to (a) a fivefold symmetry axis and (b) a threefold symmetry axis. This plot is expected to simulate experimental TEM images.