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Simulated annealing of carbon clusters

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A semiempirical many-body potential [J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988)] has been used to model carbon clusters (C_n) in the size range $50 \leq n \leq 72$. Ground-state geometries are identified by simulated annealing. Our results show that, for these sizes, all the structures of low energies are hollow spheres, with nearly graphitic atomic arrangement. The n dependence of the cohesive energy singles out $n=60$ and 70 as particularly stable structures. We investigate the effect of vibrations (zero-point energy) and temperature on the relative stability of different cluster sizes.

Carbon has unique properties among other elements, which makes it appealing from the point of view of pure and applied science. In the last few years a considerable interest has been focused on the physics and chemistry of very small carbon aggregates.[1] Carbon clusters have been recognized to be of great importance for catalysis and in combustion-related phenomena.[2] They are also responsible for some features in the absorption spectra of interstellar matter.[3]

Carbon clusters are produced in many ways. The generation of carbon aggregates by ablation of a solid target has been used for many decades.[4] The development of laser vaporization sources has made it possible to produce molecular beams of neutral and ionized cold aggregates over a wide mass range.[1]

The relative abundances in carbon-cluster mass spectra can be varied by adjusting production parameters. However, the process underlying the formation of the clusters is still poorly understood, and therefore no unambiguous information on stability and structure can be inferred from these data. Despite the variety of patterns connected to different experimental conditions, the persistency of some prominent features in the mass spectra strongly suggest that these reflect some intrinsic properties of the clusters, rather than being artifacts of the production technique. In the mass range of 1–100 atoms, two different behaviors are observed: For clusters smaller than 40 atoms, prominent mass peaks appear with periodicity $\Delta n=4$, starting from $n=11$. For larger sizes, odd numbers are very weak or absent and C_{60} appears to be the most abundant cluster. Less prominent, but also clearly distinguished, is the peak corresponding to C_{70}.[5]

From considerations of its unusual stability, the evidence of very low reactivity, and from photofragmentation patterns, Chesnovsky, Pettiette, and Smalley have postulated that C_{60} is a three-dimensional aromatic molecule with a truncated-icosahedron structure.[6] In this arrangement, the carbon atoms can saturate all their bonds and achieve a local coordination very similar to that of graphite, consisting of alternating fivefold and sixfold carbon rings. Generalizing this idea, Kroto[7] proposed a series of "magic numbers" in the range $24 \leq n \leq 70$.

Though very reasonable (and, for C_{60}, supported by the experiment), these conjectures do not provide a basis for a systematic understanding of the properties of carbon clusters. For this, it would be necessary to have a unique model, able to describe a range of different cluster sizes. Moreover, it is of great interest to theoretically study the vibrational spectrum and the thermal properties of these systems. This information can provide important clues to identify experimental geometries and would allow a comparison of stability at finite temperature.

For this purpose, we have applied the interatomic potential recently proposed by Tersoff[8] in order to model carbon clusters. This is a semiempirical many-body potential whose functional form was suggested by general considerations about the dependence of the bond strength on the local coordination.[9] Its free coefficients were fitted in order to reproduce the cohesive energies of several polytypes of carbon together with few selected properties of a diamond. Reference 8 reports a careful test of the ability of this potential to describe situations far outside the fitted data set. The usefulness of the model is enhanced by the short range of the interactions, making it computationally efficient.

Together with this list of positive features, some important notes of caution are in order. First of all, as testified by the variety of relevant polytypes, the Born-Oppenheimer (BO) surface for carbon is so complex to make very difficult its precise reproduction by an empirical potential. More importantly, the extension of the validity of this potential (fitted to homogeneous phases) down to very small sizes is clearly dangerous and, until now, untested. First-principles computations that can test the model in the size range of interest here ($n > 50$) are not yet available and would be very expensive to perform. The cluster sizes for which *ab initio* calculations do exist [up to about $n=10$ (Ref. 10)] are outside the range of validity of the model.[11]

However, carbon does not seem to show the close competition between metallic and covalent bonding that makes the description of silicon microclusters so challenging.[12,13] Instead, it presents a general tendency toward a $(\sigma(sp^k)+\pi, (k=1,2))$ type of bonding,[14] with the transition from linear $(\sigma(sp)+\pi)$ to graphitic bonding $(\sigma(sp^2)+\pi)$ expected to occur already around $n=20$–40.[5]

Our attitude is that the present model is a reasonable candidate for the description of carbon clusters of intermediate size. In the last section of the paper we shall return to this point for a justification of our approach on the basis of the results. In doing this we arbitrarily set $n=50$ as the lower limit for our investigation and concentrate on the qualitative picture given by the model, while we shall not emphasize the small quantitative details.

The first problem we address is the determination of the ground-state (g.s.) geometries. For n larger than a few atoms, this is known to be an intrinsically difficult problem.[15] To overcome this limitation and to treat all the cluster sizes on the same footing, we applied the simulated-annealing (SA) strategy.[16] However, even in the framework of an empirical-potential model, this remains a formidable task, especially for carbon. The complexity of the BO surface for this element, together with the strength of the cohesion makes a satisfactory sampling of the relevant configuration space very problematic.

In particular, the stiffness of the bonds makes the molecular-dynamics (MD) algorithm impractical. For this reason we resort to the (otherwise less efficient) Monte Carlo (MC) method.

Clearly, the SA is not meant to simulate the formation process. As already mentioned, the latter is only poorly characterized. Moreover, the formation is a nonequilibrium process and, at least in the first high-temperature phase, may involve excited electronic states. Instead, SA is used as a recipe to search for low-energy structures. As such, we found it useful to supplement the SA with constraints which minimize the probability of being trapped in a metastable minima of high energy.

The schedule of the basic annealing cycle was as follows: Starting from 10^4 K, we decreased the temperature to 4×10^3 K while keeping the atoms on the surface of a sphere. The radius of the sphere was an additional dynamical variable updated according to the MC rules. The cooling from 10^4 to 6×10^3 K was mainly used to randomize the system, and the cooling rate was 10^{-3} K per MC step (K/MCS). For temperatures lower than 6×10^4 K, the cooling rate was reduced to 5×10^{-4} K/MCS. At 4×10^3 K, we removed the constraint of a spherical shape and cooled the system to $\sim$ 20 K. This cycle was repeated several times for each cluster size. The resulting structures were annealed at $T\sim1600$ K for about 5×10^4 MC steps per atom in order to remove residual defects. The temperature ranges for the different phases of the SA have been chosen on the basis of the atomic mean-square displacement.

The SA is not a deterministic process, and there is no proof that, at any finite cooling rate, it must end up in the g.s. geometry. However, if the cooling is sufficiently slow, it is reasonable to expect that the SA will drive the system in a region of the configuration space not very different (for the cohesive energy E_c, the local coordination, etc.) from that of the true ground state.[16] For the structures of lowest energy found in our study, this conclusion is supported by the following arguments: (i) Repeated SA, following the basic cycle described above, gave very similar results, with a spread in the final cohesive energies per atom $e_c(n)=E_c(n)/n$ of the order of 50 K. (ii) For each n, the structure of lowest energy proposed as a g.s. is the result of an extensive sampling of the configuration space, involving at least 6×10^5 MC steps per atom. (iii) The strong local stability of these structures has been tested via MD by equilibrating the clusters at 1500 K and then annealing them for 10^5 MD steps (the time step was 3.5×10^{-14} sec). Despite the short simulation time, this test is significant because in the configuration space MD follows a path very different from that of a MC, that moves the atoms one at a time. (iv) In the case of C_{60}, SA arrived at a structure that is a slightly distorted version of the geometry proposed by Smalley, with an energy only marginally higher than the ideal one ($\Delta e_c<0.01$ eV/atom or 77 K).

We verified that relaxed crystal fragments, derived both from diamond or graphite lattices, were always significantly higher in energy.

In Fig. 1(a) we plot the cohesive energy per atom e_c as a function of cluster size. The general trend of this curve is well reproduced by $e_c(n)=e_c(\infty)-a/n$, where $e_c(\infty)$ is the experimental cohesive energy of graphite and a (determined by a least-squares fit) is 39.3 eV. To this smooth behavior are superimposed a strong even-odd alternation and two steps at $n=60$ and 70. The special properties of these two cluster sizes are clearly evident in the plot of $\Delta_2E_c(n)=2E_c(n)-E_c(n+1)-E_c(n-1)$ [Fig. 1(b)], that gives a measure of the relative strength of the competing processes of growth and evaporation. In this plot all the even numbers appear as local maxima, with the peaks corresponding to C_{60} and C_{70} dominating the others by more than 2 eV.

All the geometries of lowest energy found by the SA

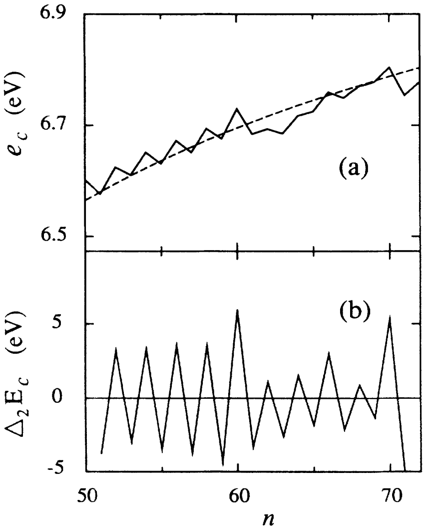

FIG. 1. (a) Cohesive energy per particle e_c as a function of size. The dashed line is the result of the interpolation $e_c(n)=e_c(\infty)-a/n$ described in the text. (b) Second-order difference $\Delta_2E_c(n)=2E_c(n)-E_c(n+1)-E_c(n-1)$ of the cohesive energy $E_c(n)$.

process can be described as slightly distorted hollow spheres, with a local atomic coordination very similar to that of graphite. We stress that the nearly spherical shape is not an artifact of the constraint introduced in the cooling from 10^4 to 4×10^3 K. Around 4×10^3 K, the mobility of the carbon atoms is such that they could have broken this configuration. This is, in fact, observed in some SA cycles. However, all these cases resulted in structures of significantly higher energy than the spherical ones ($\Delta e_c \sim 0.1$ eV/atom). Similar results were obtained in test runs performed without any spherical constraint at high T. The resulting geometries were quite similar to those produced by the constrained annealing, with, however, many defects, important deviations from the spherical shape, and an energy per atom typically 0.1 eV higher.

A closer analysis of the ground-state structures reveals an important size evolution. For $50 \le n \le 60$ the g.s. geometries appear to belong to a highly homogeneous family of structures. For even n's all the atoms are threefold coordinated and the surface of the cluster is composed only by five- and six-membered rings. For odd n's this pattern is perturbed by localized defects, characterized by twofold-coordinated atoms. In accordance with the geodesic rules stated by Jones[17] and Kroto,[7] there is a strong regularity in the number of five-membered rings (FMR) composing the surface of the clusters. In this size interval, the even n's have exactly 12 FMR, while the odd n's have 10 FMR. Again in accordance with the rules mentioned above, C_{60} is characterized by having all the FMR surrounded only by hexagonal rings.

In contrast with this high regularity, the region $60 < n < 66$ is characterized by lower relative stability and less predictable structures. The number of FMR changes from 9 to 13 without a recognizable scheme, and some of these clusters present a seven-membered ring.

The regular behavior of the interval $50 \le n \le 60$ is then recovered for $n > 65$.

This general picture may be an important factor for the enhanced yield of C_{60}. The extended region of reduced stability beyond $n = 60$ may inhibit further growth of C_{60} even if the building blocks are not single atoms, but units of two or four carbon atoms.

The structural characteristics discussed above are reflected in the ground-state vibrational spectra. In fact, it is possible to establish a correlation between the relative stability of different sizes and the amplitude of their vibrational density of states (VDOS). The VDOS for n's corresponding to local maxima of cohesive energy is structureless and fills the interval (0, 0.24) eV. Instead, for all the n's corresponding to local minima, we observe, in addition to the broad distribution, few modes at significantly higher energy, up to about 0.3 eV.

These stiff modes, related to the localized defects of the less favorable structures, are responsible for an increased zero-point energy of the odd-numbered clusters. This effect is apparent from Fig. 2, where we display the average energy per vibrational mode e_v as a function of size. Here we see again the regular even-odd alternation for $50 \le n \le 60$ and $n > 65$. The range $61 \le n \le 65$ is marked by large oscillations and presents an anomalous peak for $n = 61$.

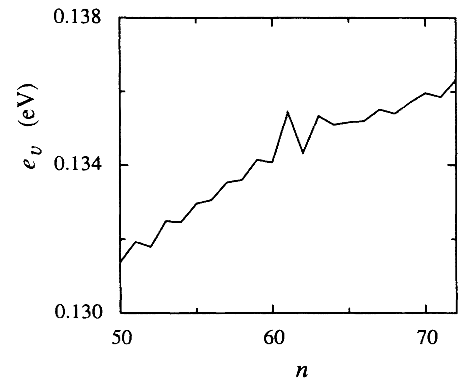

FIG. 2. Average energy per vibrational mode e_v as a function of cluster size.

The inclusion of e_v in the ground-state energy has the effect of enhancing the alternation in cluster stability already observed in Fig. 1(b). The quantitative importance of this zero-point contribution, however, is very small, since the magnitude of e_v represents, on average, only a few per cent of that of e_c. Nevertheless, the size dependence of e_v has an interesting effect, that may be relevant to the understanding of the experimental spectra. Starting from the g.s. structures described above, we computed the free energy per atom f_n as a function of temperature in the range $T < 2000$ K. Up to $T_0 = 800$ K we applied the quantum harmonic approximation. Beyond T_0 we integrated numerically the expression

$$\frac{f_n(T)}{k_B T} = \frac{f_n(T_0)}{k_B T_0} + \int_{1/(k_B T_0)}^{1/(k_B T)} [e_c(T') + \tfrac{3}{2} k_B T'] d\left(\frac{1}{k_B T'}\right),$$

where k_B is Boltzmann's constant and $e_c(T)$ was computed in a classical MC simulation. Our T_0 is higher than the Debye temperature for bulk graphite. However, the vibrational spectrum of carbon clusters appears to be stiffer than that of graphite and 800 K seems to provide a reasonable compromise between the necessity of describing quantum features at low T and anharmonic effects at higher T.

Mainly, as a consequence of the n dependence of the VDOS, we observe that over a wide range, increased temperature does not blur the differences in relative stability

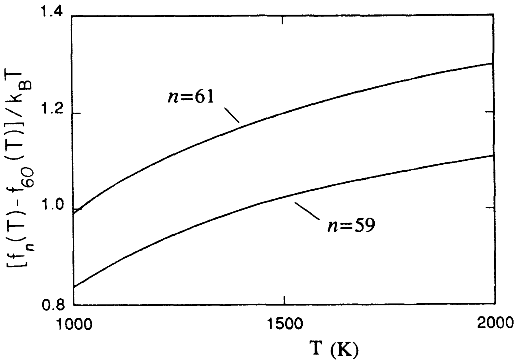

FIG. 3. Temperature dependence of the free-energy difference $[f_n(T) - f_{60}(T)]$ for $n = 59$ and 61 in units of $k_B T$.

computed at $T=0$ K. Indeed, it may even reinforce them, as shown in Fig. 3, where we plot the behavior of f_n as a function of T for $n=59$, 60, and 61.

In conclusion, we have presented a systematic study of carbon clusters in the range $50 \leq n \leq 72$, based on the interatomic potential proposed by Tersoff. The model provides a simple and coherent description of the properties of these clusters, with qualitative features strongly reminiscent of the experimental findings. For C_{60}, simulated annealing found a geometry practically equivalent (although slightly higher in energy) to the "buckminsterfullerene" structure proposed by Smalley and collaborators. These results enhance our confidence in the validity of the model down to the very small sizes considered here, thus allowing to use its predictions for a microscopic understanding of these systems.

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