

MOLECULAR-DYNAMICS SIMULATIONS OF CARBON NANOCAGE STRUCTURES: NANOBALLS AND NANOTOROIDS

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The structural stability of carbon nanocages, fullerenes and toroids, have been investigated by performing molecular-dynamics computer simulations. The systems considered are C₁₂₀ and C₂₄₀ in ball and toroidal structures. Calculations have been realized by using an empirical many-body potential energy function for carbon. It has been found that C₁₂₀ ball is very unstable, and the other structures are relatively more strong against heat treatment.

Keywords: Molecular-Dynamics; Empirical Potential; Carbon Nanoball; Carbon Nanotoroid.

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1. Introduction

Carbon nanostructures have been paid attention in the last decade because of their potential applications in nanotechnology.¹ Carbon nanostructures may be classified into three groups such as nanoballs (fullerenes), nanotubes and nanotoroidal structures. Other possible nanostructures, such as fullerene anions, capsules, helical structures and schwarzite structures, are derivatives of the previous three groups.²

There are many theoretical and experimental studies on fullerenes and tubes in the literature.^{3,4} However, there is not any experimental work about toroidal structures giving detailed information and only a few theoretical study predicting possible structures of nanotoroids are available.^{2,5–8}

A wide range of potential applications has been discussed for both nanotubes and fullerenes. These include the construction of light materials with extraordinary strength, gas storage within the cage structure, nanoelectronics and lubricants. Also, their hollow structure enables them to collapse under compression and then restore volume; a property required for heavy-duty shock absorbers.^{1,3,4}

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The toroidal geometries of carbon are generated from the nanotube geometries,² and also possess the cage structure of fullerenes. Hence, it would be reasonable to expect that the toroidal forms carry some properties of the tubes and some properties of the fullerenes as well.

The toroidal geometry can be briefly described as a plane formed of hexagons being mapped on the surface of a torus. However, to reduce the torsion on the positively curved outer wall and negatively curved inner wall, pentagons and heptagons must be introduced, respectively, in place of hexagons.⁵

Structural stability of carbon nanotoroids has not yet been studied. We have investigated the structural stability of these structures considering one model for C₁₂₀ toroid and two models for C₂₄₀ toroids. We have compared the structural stability of carbon toroids with the same size (number of atoms) of carbon balls (fullerenes) C₁₂₀ and C₂₄₀ considering one model for each. We have simulated these systems by performing molecular-dynamics computer simulation technique, using an empirical potential energy function developed for carbon. We have investigated the stability of the carbon nanocage structures considered under heat treatment.

2. The PEF and the MD Simulation

The empirical many-body potential energy function (PEF) developed for carbon⁹ is used in the calculations. This PEF describes the structural properties and energetics of carbon relatively accurate. The total interaction energy of a system of particles is taken to be the sum of total two-body and total three-body contributions¹⁰:

$$\Phi = \phi_2 + \phi_3. \quad (1)$$

Total two-body and three-body energies are expressed, respectively, as:

$$\phi_2 = A \sum_{i < j}^N U_{ij}^{(1)}, \quad \phi_3 = -B \sum_{i < j}^N U_{ij}^{(2)} \left[1 + \beta^n \left(\sum_{k \neq i, j}^N W_{ijk} \right)^n \right]^{-1/2n}, \quad (2)$$

here, U_{ij} and W_{ijk} represent the two-body and three-body interactions, respectively.

$$\begin{aligned} U_{ij}^{(1)} &= f_c(r_{ij}) \exp(-\lambda_1 r_{ij}), \\ U_{ij}^{(2)} &= f_c(r_{ij}) \exp(-\lambda_2 r_{ij}), \\ W_{ijk} &= f_c(r_{ik}) g(\theta_{ijk}), \end{aligned} \quad (3)$$

where

$$g(\theta_{ijk}) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta_{ijk})^2}, \quad (4)$$

$$f_c(r) = \begin{cases} 1 & \text{for } r < R - D, \\ \frac{1}{2} - \frac{1}{2} \sin \left[\frac{\pi (r - R)}{2D} \right] & \text{for } R - D < r < R + D, \\ 0 & \text{for } r > R + D. \end{cases} \quad (5)$$

The parameters of the PEF for carbon are as follows⁹: $A = 1393.6$ eV, $B = 346.74$ eV, $\lambda_1 = 3.4879 \text{ \AA}^{-1}$, $\lambda_2 = 2.2119 \text{ \AA}^{-1}$, $\beta = 1.5724 \times 10^{-7}$, $n = 0.72751$, $c = 38049$, $d = 4.3484$, $h = -0.57058$, $R = 1.95 \text{ \AA}$ and $D = 0.15 \text{ \AA}$.

The equations of motion of the particles are solved by considering the Verlet algorithm.¹¹ The canonical ensemble molecular-dynamics NVT¹¹ is proceeded. The temperature scaling is taken into account at every MD step and the temperature of the system is kept constant at a given temperature. One time step is taken as 10^{-16} s. The initial velocities of the particles are determined from the Maxwell distribution at the given temperature.

The simulations are carried out starting at low temperature (1 K) and the temperature of the system is increased by a predetermined step (100 K) until the system considered disintegrates. Each system was disintegrated at different temperature. At every temperature rise, the system is relaxed for 40 000 time steps. This much steps were enough to reach equilibrium at every temperature rise. We should point out that the simulations are performed for isolated systems, hence, no periodic boundary condition was applied.

In the present simulations, carbon nanocages in various sizes have been investigated. We have considered two different carbon nanoballs with number of atoms 120 and 240, and three different carbon nanotoroids with number of atoms 120, 240 and 240. Two isomers of C_{240} have been considered. We have generated C_{120} ball considering the icosahedral symmetry. The coordinates of C_{240} ball are taken from Ref. 12 and the coordinates of C_{240} toroid (model-1) are taken from Ref. 13. The coordinates of C_{120} toroid and C_{240} toroid model-2 are obtained using the generating coordinates proposed in Refs. 5 and 2, respectively.

3. Results and Discussion

The starting structures and the relaxed structures at various temperatures for the systems considered are shown in Figs. 1–5. The C_{120} ball considered in this study consists of many squares and octagons. For this reason, its structure is not stable against heat treatment. The spherical form started to distort at about 100 K and its bonds started to break at 200 K. On the other hand, the toroidal structure with 120 atoms is much more stronger against heat treatment compared to its spherical isomer; it started to distort at about 4500 K and its bonds started to break at about 4600 K. The reason for the toroidal structure of C_{120} being more stable is probably due to the majority of hexagons in its structure.

C_{240} ball has a highly symmetric structure similar to C_{60} . It consists of only hexagons and pentagons. This system is also strong against heat treatment. It

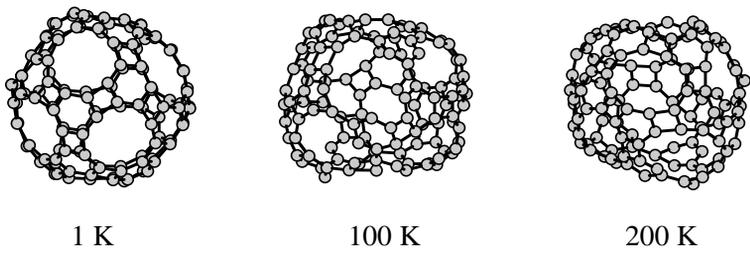


Fig. 1. The relaxed structures of C_{120} ball at various temperatures.

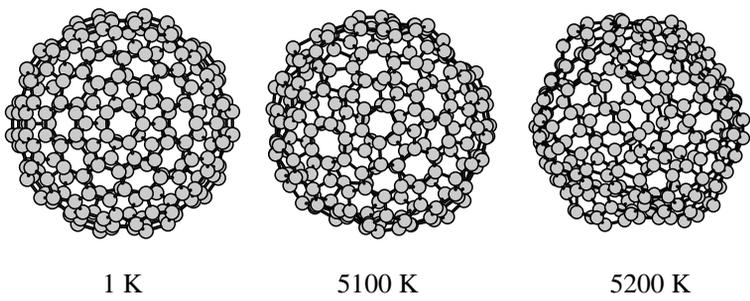


Fig. 2. Same as Fig. 1, but for C_{240} ball.

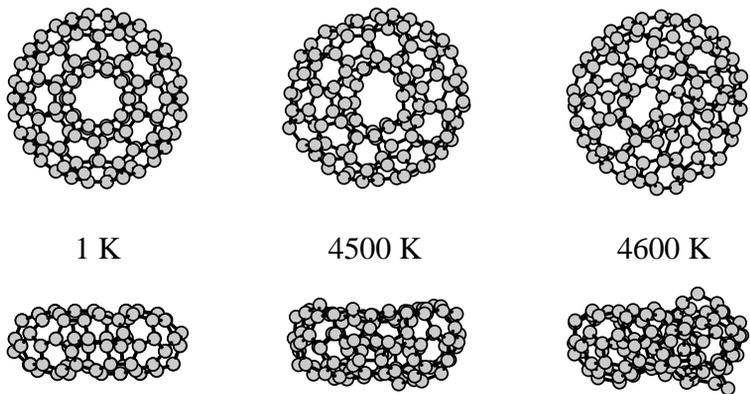


Fig. 3. Top and side views of the relaxed structures of C_{120} toroid at various temperatures.

started to distort at about 5100 K, and its bonds started to break at 5200 K. The isomers of C_{240} in toroidal structures, model-1 and model-2, show different characteristics against heat treatment. The model-1, which has a rounder geometry, the heptagons in the inner wall are adjacent to each other. However, model-2 has more flat regions, and furthermore, there are hexagons in between the heptagons in the inner wall. This structural difference shows a drastic stability difference between these two toroidal models. Model-1 is relatively unstable with respect to model-2

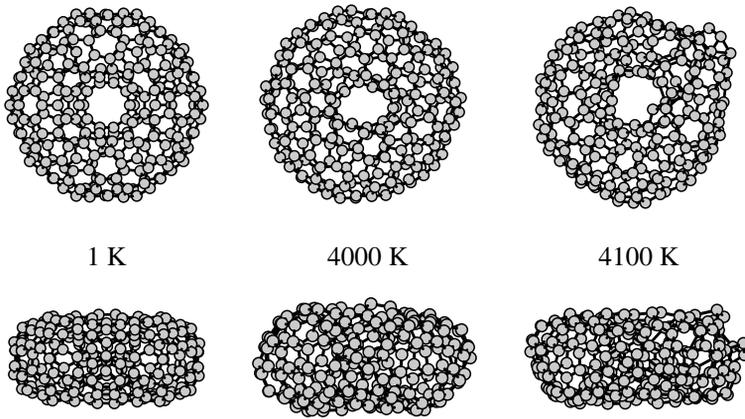


Fig. 4. Same as Fig. 3, but for C_{240} toroid model-1.

against heat treatment. Model-1 started to distort at about 4000 K, and its bonds started to break at about 4100 K. On the other hand, model-2 started to distort at about 5300 K and its bonds started to break at 5400 K. An interesting feature appears in C_{240} toroidal structures is that model-1 starts to disintegrate gradually, however, model-2 sustains its form for a longer time, but then suddenly disintegrates; this could be due to the fact that model-2 has relatively larger curvature in specific regions, where disintegration starts at these points (see Fig. 5). The general feature, which appears in toroidal structures is that when they are heated, they expand slightly along the axis of symmetry; this expansion is remarkable in C_{240} toroid model-2.

It is obvious that the structural change will affect the energetics of the system. The total energy versus temperature of the systems considered, are shown in Fig. 6.

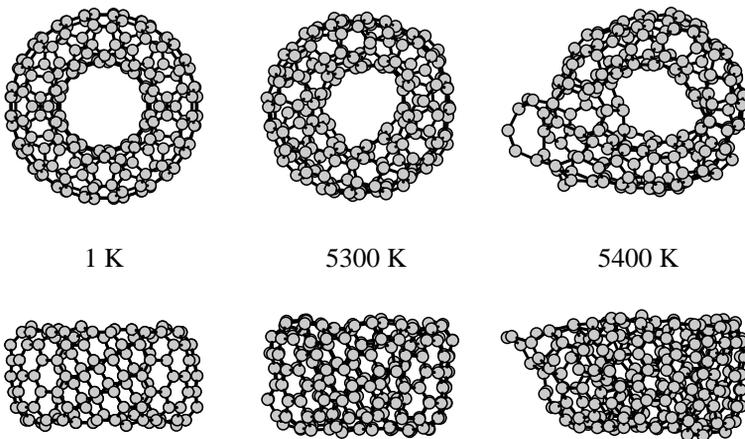


Fig. 5. Same as Fig. 3, but for C_{240} toroid model-2.

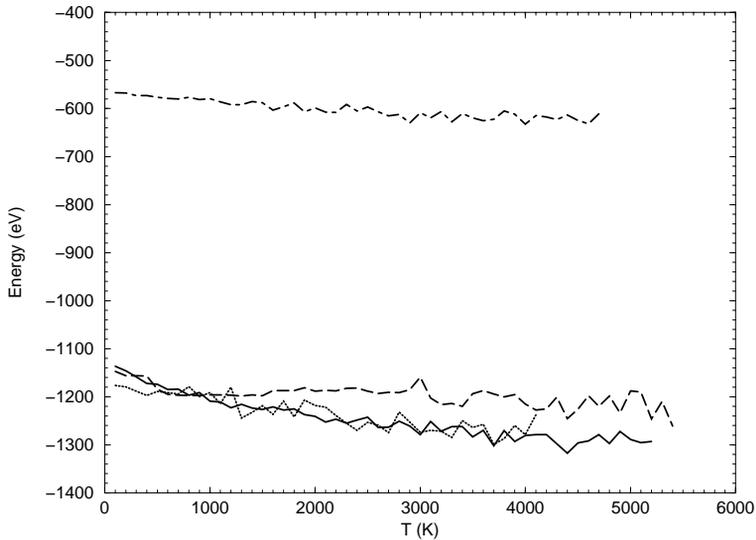


Fig. 6. Total energy versus temperature of carbon nanocage structures. Dash-dot line in for C_{120} toroid; solid line is for C_{240} ball; dotted line is for C_{240} toroid model-1; dashed line is for C_{240} toroid model-2.

These data show the snapshot values at the last MD step, at the corresponding temperatures. We should point out that the stability of carbon nanocage structures depends strongly on the geometry; stability varies drastically even between isomers.

References

1. M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, 1996).
2. S. Itoh and S. Ihara, *Phys. Rev. B* **48**, 8323 (1993).
3. H. Kuzmani, J. Fink, M. Mehring, and S. Roth (eds.), *Electronic Properties of Fullerenes, Springer Series in Solid State Sciences*, Vol. 117 (Springer-Verlag, Berlin, 1993).
4. R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, 1998).
5. S. Ihara, S. Itoh, and J. Kitakami, *Phys. Rev. B* **47**, 12908 (1993).
6. S. Ihara, S. Itoh, and J. Kitakami, *Phys. Rev. B* **48**, 5643 (1993).
7. S. Itoh and S. Ihara, *Phys. Rev. B* **49**, 13970 (1994).
8. J. K. Johnson, B. N. Davidson, M. R. Pederson, and J. Q. Broughton, *Phys. Rev. B* **50**, 17575 (1994).
9. J. Tersoff, *Phys. Rev. Lett.* **61**, 2879 (1988).
10. J. Tersoff, *Phys. Rev. B* **38**, 9902 (1988).
11. D. W. Heermann, *Computer Simulation Methods in Theoretical Physics* (Springer-Verlag, 1990).
12. <http://shachi.cochem2.tutkie.tut.ac.jp/Fuller/fsl/Goldberg/c240.inp>.
13. <http://physics.technion.ac.il/avron/tori.coor>.