

Molecular Dynamics Simulation of Carbon Structures Inside Small Diameter Carbon Nanotubes

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Motivated by recent experimental results of hydrocarbon formation in small diameter carbon nanotubes filled with ferrocene molecules, we present molecular dynamics simulations with a DFT-adjusted tight-binding method. We increase the number of carbon atoms from 60 to 150 by inserting carbon pentagon rings into a (14,0) nanotube. We find that the structures formed during the simulation depend on the temperature as well as on the density of the carbon atoms. At lower temperatures we obtain graphene ribbons, and at higher temperatures fullerenes or nanotubes are formed. For large enough density of the carbon atoms, the formation of nanotube like structure is preferred at both low and high temperatures.

1. Introduction

There is a growing interest in the research of chemical reactions inside carbon nanotubes serving as nanochambers.^[1–5] A well-known example is the annealing of C₆₀-filled single-walled carbon nanotubes (SWCNTs) with a diameter of about 14 Å, which results in the formation of an inner nanotube.^[6] Recently smaller organic molecules, like ferrocene (Fe(C₅)₂) have been used as filler materials. The exact outcome of such chemical reactions in the case of ferrocene-filled small diameter ($d \approx 10$ –13 Å) SWCNTs after a heat treatment at 800 °C is still an open question.^[7] After this annealing process, several new bands appeared in the Raman spectrum: three non-dispersive lines in the D-band region and a new line at 470 cm⁻¹.^[7–9]

Based on the analysis of these features of the Raman spectra, it seemed initially that an inner carbon nanotube comes into existence from the ferrocene molecules as the consequence of the heat treatment. Furthermore, we have found a possible explanation of the non-dispersive lines on the ground of the interlayer interaction between inner and outer carbon nanotubes.^[9] However, from further investigations, it turned out that the positions of the Raman bands in question are sensitive to deuteration of the ferrocene molecules which means that these

new lines belong to some hydrocarbon molecules. Based on the experimental data, we found that the most probable reaction products are members of the family of polyaromatic hydrocarbons (PAHs). Due to the constraint that these molecules are inside a small diameter SWCNT, they can be considered as narrow graphene nanoribbons (GNRs) with hydrogen atoms at their edges.

From a comparison of our density functional theory (DFT) calculations with experiments, based on molecular weight, excitation energy and Raman spectra (for both hydrogenated and deuterated forms) either quaterylene (dimer of perylene, C₄₀H₂₀) or the dimer of the 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA, C₄₄H₁₆O₆) seemed to be the most likely product of the heat treatment.^[10]

Our goal in the present work was to perform molecular dynamics calculation for the study of processes in nanochambers. In a past calculation^[11] mostly the fullerene-nanotube interaction was studied. In our work, we wanted to study the structure formation at elevated temperatures inside nanotubes. The study of such kind of processes is very timely and of general interest.^[1,5,7–10]

Motivated by the above-mentioned experimental results, we have performed molecular dynamics calculations for several number of C₅ carbon rings inside small diameter carbon nanotubes. Using this simplified model of the realistic experimental conditions, by replacing the ferrocene molecules by two C₅ carbon rings, we have obtained interesting insights into the carbon structure formation in nanochambers. Our results are in good agreements with the experimental findings that for relatively small diameter of tubes ($d \approx 10$ –13 Å) both graphene nanoribbons and inner tubes grow but the increase of tube diameter and/or temperature prefers formation of inner tubes.^[7]

2. Methods

In our molecular dynamics (MD) calculations, we inserted carbon atoms in a (14,0) carbon nanotube with 10.96 Å diameter and 25.578 Å length. This small diameter corresponds to the typical tube diameters of the experiments^[7] and as zig-zag tube it is convenient for the numerical calculations.

We used periodic boundary condition, and the number of carbon atoms (N_C) of the initial structures were 60, 80, 84, 85, 90, 100, and 150. By the number of carbon atoms, we changed the

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density of carbon atoms inside the tube. According to the experiments the final structure depends on the nanotube diameter, but before studying the diameter effect, the dependency on the carbon density must be studied. The structure of the 84 carbon atoms was a polyhex carbon ribbon and the other structures contained multiples of carbon pentagon rings C_5 (Figure 1).

The carbon–carbon interactions between the atoms inside nanotube were calculated with a DFT adjusted tight-binding method.^[12] In this version of TB method, one *s* orbital and three *p* orbitals belong to each carbon atom. At each time step the solution of the eigenvalue problem provides the forces. The code was developed in our laboratory and was successfully applied for various nanostructures.^[13,14]

The interaction with the nanotube was described with a Girifalco potential.^[13] The position of the nanotube atoms was not changing during the simulation. The time step of the MD calculations was 0.7 fs and the environmental temperature *T* was controlled by Nosé–Hoover thermostat.^[13]

In each simulation except those of $N_C = 150$ carbon atoms, the total number of time steps were 1 200 000. It corresponds to 0.84 ns. For $N_C = 150$ we used about 700 000 time steps. The initial random velocities of the carbon atoms corresponded to a kinetic energy of $T = 600$ K. For each initial geometric structure, we made three different calculations (Run 1, Run 2, and Run 3) using various random numbers for the initial velocities

generation. That is, we generated $3N_C$ random numbers uniformly in the interval $(-0.5, 0.5)$ and added them to the atomic coordinates of N_C atoms. The initial temperature was adjusted by scaling of this displacement vector. Here we remark that at the beginning of each simulation the initial distribution of the carbon atoms transformed to a chain-like structure.

3. Results and Discussion

We performed simulations at two environmental temperatures $T = 2000$ K and $T = 3000$ K. Figures 2–4 show our final structures obtained for Run 1, 2, and 3, respectively.

Let us see the final structures at various Runs. The final structure of $N_C = 60$ both at $T = 2000$ K and $T = 3000$ K is a chain like one. At 2000 K, there are some pentagons and hexagons but the structure looks mostly chain like. For $N_C = 80$ atoms the final structures at 3000 K are fullerene like in each Runs. At 2000 K in Runs 2 and 3 we obtained ribbon like structures and Run 1 gave fullerene-like structure.

In the case of $N_C = 84$ carbon atom we tested the stability of the ribbon structure. During a simulation time of 0.84 ns the polyhex ribbon structure turned to be a stable one at $T = 2000$ K. At 3000 K, it was transformed to a fullerene-like structure. The

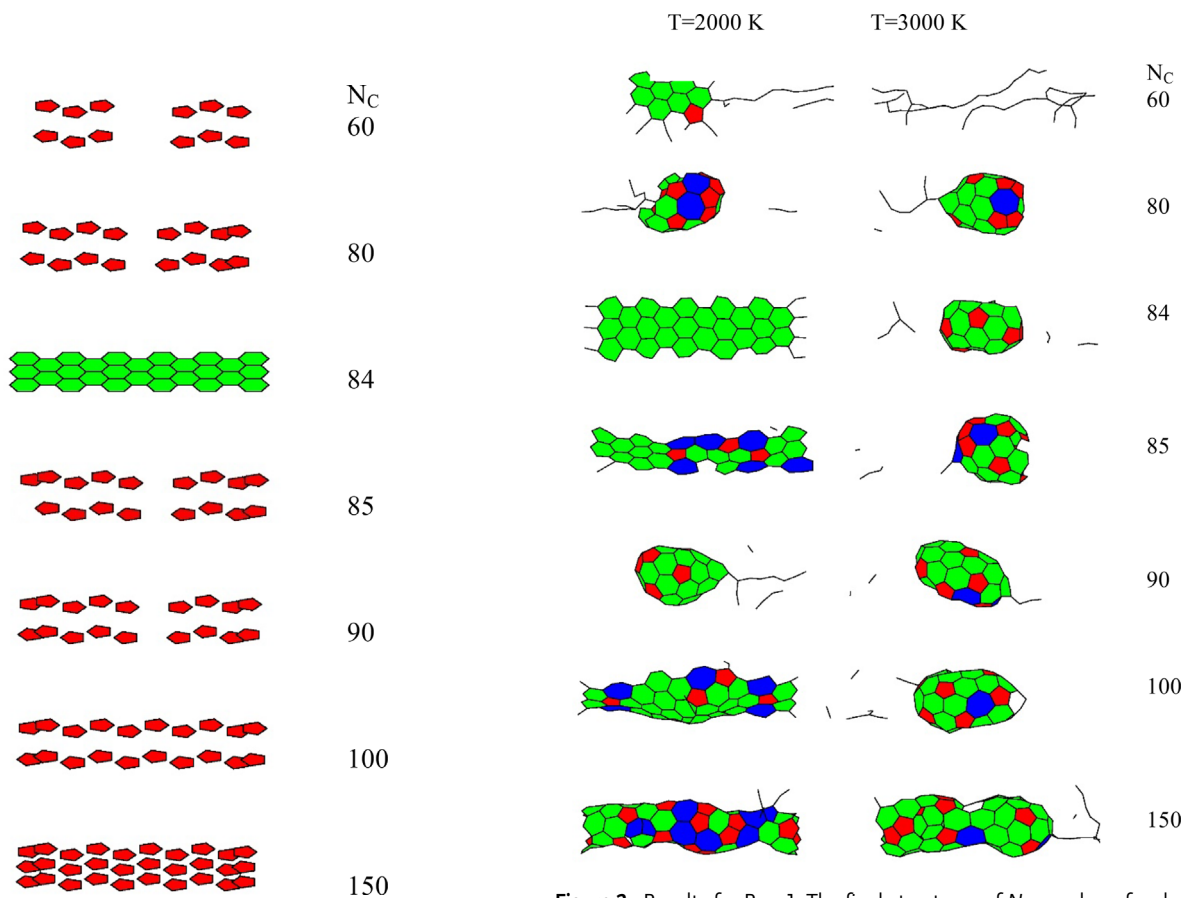


Figure 1. The initial structures of N_C number of carbon atoms.

Figure 2. Results for Run 1. The final structures of N_C number of carbon atoms.

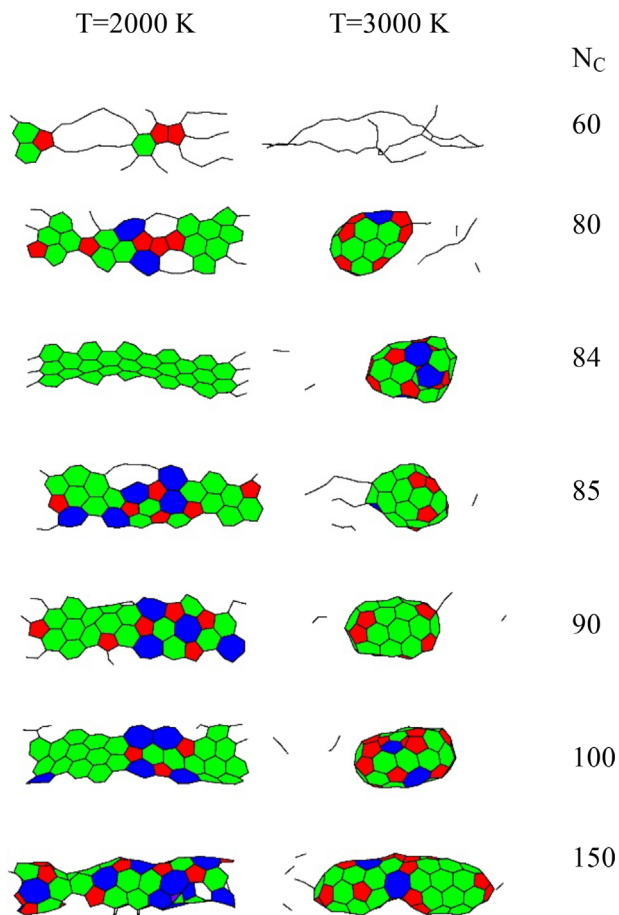


Figure 3. Results for Run 2. The final structures of N_C number of carbon atoms.

initial structure of 85 carbon atoms gave ribbon-like structures at 2000 K and fullerene-like structures at $T = 3000$ K. At $N_C = 90$ atoms, we obtained once more fullerene-like structure at 2000 K in Run 1 but the other Runs gave the same structure tendency as the previous ones. For 100 carbon atoms at the lower temperature came the ribbon-like structure and at the higher temperature came the fullerene-like structure. The increased number of carbon atoms ($N_C = 150$) gave fullerene-like structures at both temperature. These fullerenes are, however, elongated thus it is better to call them nanotube-like structure instead fullerene like.

Thus, if the number of carbon atoms N_C is in the range from 80 to 100 the final structure at $T = 3000$ K is fullerene like and if the temperature is 2000 K the final structure is ribbon like. We have two exceptions in Run 1. It is since at such a small number of atoms the fluctuation of the transition temperature is large. To obtain the final structures with a relative small number of time steps, we were using the possibly highest temperatures in the simulations. As a test calculation, we performed simulations at significantly lower temperature, $T = 743$ K for $N_C = 85$, and we obtained the ribbon-like structure after a simulation time of 6.72 ns. This result agrees with the experimental finding, that growth of extended carbon

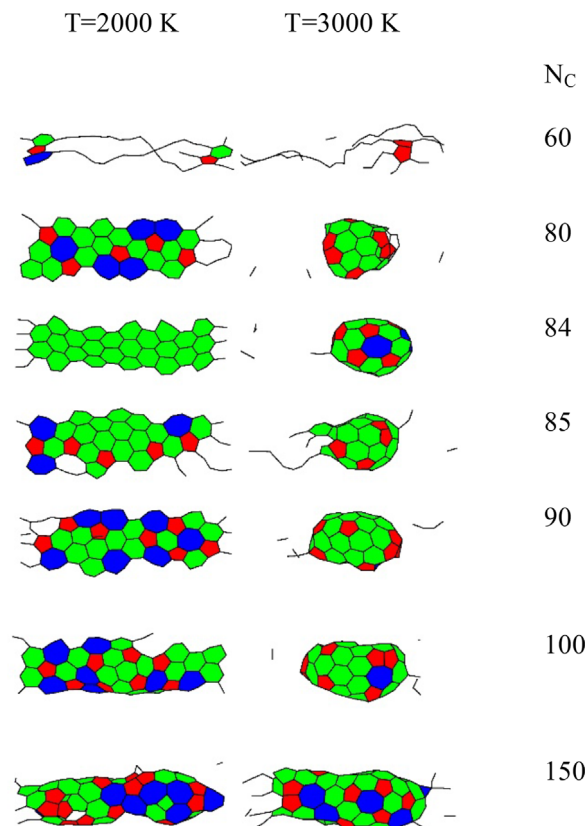


Figure 4. Results for Run 3. The final structures of N_C number of carbon atoms.

nanophases from ferrocene was observed to start from temperatures as low as 470°C .^[7]

In **Figures 5 and 6**, we can see the number of pentagons hexagons and heptagons as a function of the number of time

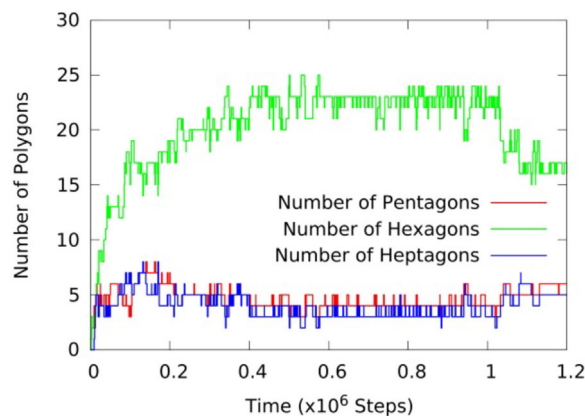


Figure 5. The number of pentagons (red line), the number of hexagons (green line), and the number of heptagons (blue line) as a function of the time steps. $N_C = 90$, Run 2, $T = 2000$ K.

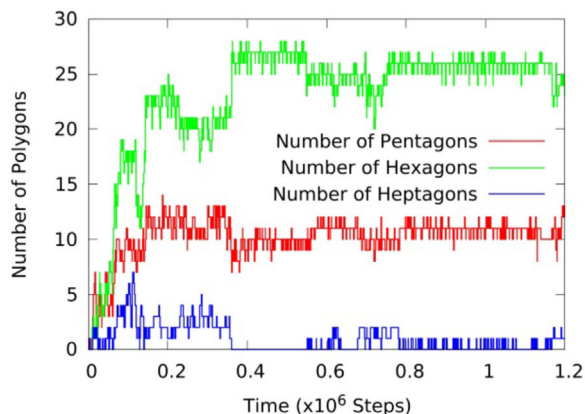


Figure 6. The number of pentagons (red line), the number of hexagons (green line), and the number of heptagons (blue line) as a function of the time step. $N_C = 90$, Run 2, $T = 3000$ K.

steps. These are the results of Run 2 for $N_C = 90$ with $T = 2000$ K (Figure 5) and $T = 3000$ K (Figure 6). In Figure 5 the number of pentagons and heptagons are nearly the same. They oscillate about 5. This is also an index of the carbon ribbon formation. We can see also the larger number of hexagons. In Figure 6 the number of pentagons and heptagons are significantly different. The number of heptagons oscillate about 1 and the oscillation of the number of pentagons is near 12. This is the indication of the fullerene-like structure formation.

Figure 7 shows the number of pentagons hexagons and heptagons for $N_C = 84$ in Run 1 at $T = 3000$ K. This is the case when the initial nanoribbon transforms to a fullerene-like structure. Initially there are only hexagons but when the number of time steps reaches the range from 39 000 to 49 000, the number of polygons decreases significantly and a chain-like structure is formed. This chain-like structure will transform to the fullerene-like structure. That is there are

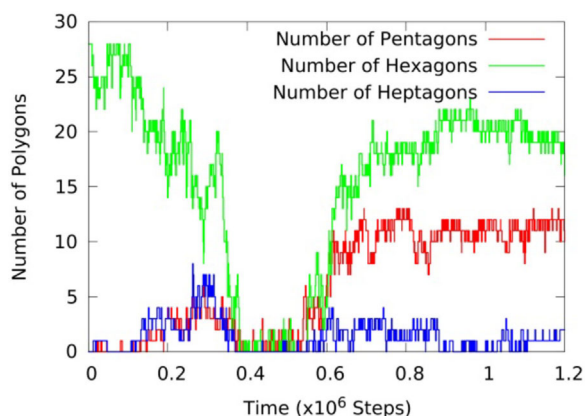


Figure 7. The number of pentagons (red line), the number of hexagons (green line), and the number of heptagons (blue line) as a function of the time step. $N_C = 84$, Run 1, $T = 3000$ K.

not hexagons which survive the transformation. This complete destruction of the ribbon structure was observed in each Runs.

4. Conclusion

We presented molecular dynamics simulations of carbon-filled SWCNTs. Our results suggest that in agreement with the experimental results,^[7] the character of carbon structures formed inside the nanotube depends on both the temperature and the initial density of the filling carbon atoms. At lower temperatures, we obtained ribbon-like structures and at higher temperatures the final structures were fullerene like. In the low filling limit, the final compounds were mostly chain-like structures. In the case of higher initial carbon density, there is a clear tendency of inner fullerene or nanotube formation. Furthermore, we observed that the initially hexagonal ribbon structure is stable at lower temperature, and at higher temperatures it is destroyed before the formation of a fullerene-like complex.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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