Molecular dynamics simulations for lithographic production of carbon nanotube structures from graphene

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Abstract — In the present work we shall study the topological and energetical conditions for the growing of perfect nanotubes and their Y-junctions. For this purpose Density Functional based Tight-Binding (DFTB) Molecular Dynamics (MD) simulations were performed for producing carbon nanotubes and their Y-junction from graphene nanoribbons.

Keywords — molecular dynamics simulation, Density Functional Tight Binding method, graphene, carbon nanotube

I. INTRODUCTION

Although the exceptional electric properties of carbon nanotubes has already been proved in several publications [1], until now only very few electric devises were presented or realized [2-4]. This fact can be explained by the lack of well controlled reliable technology for nanotube or nanotube network construction. Nanotube construction from nanoribbons is a promising possibility. Nanoribbons can be produced with the help of nanolithography [5] and various chemical compounds [6]. Various ribbon structures as the L [7], the T [8] and the Z [9] structures were suggested for various nano-electric building blocks. Experimental and simulational methods are used for the study of nano electric networks [10] and functional units [11].

For the time being the accuracy of nanoribbon cutting from graphene is about few nm, and only one order of magnitude is missing to the atomic accuracy. There are studies for the instabilities at nanoribbon edges and nanotubes are obtained in molecular dynamics simulations from two nanoribbons [12]. It was demonstrated in molecular dynamics simulations that graphene patterns with atomic accuracy can develop in a self organizing way to the predetermined fullerenes or nanotubes [13-15].

The importance of nanotube production from two nanoribbons comes from the fact, that in this way open ended carbon nanotubes are developed but the one pattern nanotubes are always closed at one end [13]. Nanotube growing from nanoribbons is not a trivial tusk although the idea has already been published [12, 16].

In the present work we shall study the topological and energetical conditions for the growing of perfect nanotubes and their Y-junctions. For this purpose Density Functional based Tight-Binding (DFTB) Molecular Dynamics (MD) simulations were performed for producing carbon nanotubes and their Y-junction from graphene nanoribbons. The constant temperature simulations were controlled with the help of Nosé-Hoover thermostat. In our systematic study we obtained critical curvature energies and determined topological conditions for nanotube productions from one over the other put two parallel graphene nanoribbons.

II. THE METHOD

The interatomic interaction was calculated with the help of Density Functional Tight Binding method [17]. The nanoribbons were cut out from a graphene sheet of interatomic distance r=1.42 Å. After putting the two nanoribbons one over the other with parallel position, the nanotube formation was simulated in a molecular dynamics calculation with constant environmental temperature [18-19]. The time step was Δt = 0.7fs and the Verlet algorithm [20] gave the velocity. The initial atomic displacements during the time step of Δt = 0.7fs were sorted randomly and they gave the initial velocities by appropriate scaling. In this scaling we supposed an initial kinetic temperature Tinit. This initial temperature was chosen from the range of Tinit =1000K and 1100 K. We have found that the final structure was depending more strongly on the direction of the initial velocities than the actual value of Tinit. That is by scaling of the initial temperature in the above mentioned range the final structure was not strongly changing. As the formation of new bonds decreased the potential energy and increased the kinetic energy we had to keep the temperature constant. In a constant energy calculation the kinetic energy obtained by forming new bonds destroyed other bonds of the structure. We used Nosé-Hoover thermostat [18-19, 21-22] for the constant temperature simulation. It is evident that in the Nosé-Hoover thermostat there is an oscillation of the temperature but it cannot destroy the
structure formation. In the following the temperature of the
calculation will mean the temperature of the thermostat. If the
constant temperature were realized with the help of random
scaling of the kinetic energy we could not distinguish the
temperature of the environment and the structure. This is why
we can speak about the $T_{\text{init}}$ temperature and the temperature
of the Nosé-Hoover thermostat (the environment temperature).

### III. RESULTS

We were studying armchair and zigzag nanotubes. The initial
structure contained two congruence graphene nanoribbons put
one over the other at a distance of 3.4 Å (Figure 1). We
calculated the interatomic forces between the carbon atoms
and we were waiting new bond formations at the edges of the
ribbons. We wanted to obtain the predefined nanotube in a self
organizing process. According to our simulations the
formation conditions were depending on the type of the
nanotube.

In the cases of straight nanotubes we found topological and
energetic conditions for the perfect growing of the
nanoribbons.

The basic problem of armchair nanotube formation can be
seen on Figure 1. The simulation process of two congruence
and parallel nanoribbons was performed at 1000 K
temperature. We observed the initial growing together at both
side of the ribbons but the process stopped at the established
structure of the figure. At one side there is a tendency to form
a graphene sheet. According to our computations there is a
critical curvature energy over which the heat energy of the
environment cannot produce the energy sufficient for overtake
energy barrier of the bond formation. By increasing the
temperature the structure could overtake this barrier but it
could destroy the other bonds as well. The correct formation of
nanotube can happen only if the corresponding curvature
energy is less than a critical curvature energy of 0.18 eV. This
critical curvature energy corresponds to the nanotube (5,5) of
radius 3.3 Å which is obtained from the ribbons of widths 9.23
Å as we can see in Figure 2.

![Figure 2](image2.png)

In the case of zigzag nanotubes the critical curvature energy is
less, the critical ribbon width is greater than the same value at
the armchair nanotubes. In Figure 3 the width of the two
parallel ribbons of the initial model is 9.23 Å. We can see the
structures after the simulation times of 1.7 ps and 2.8 ps. There
is a tendency of constructing a flat structure here, as well.

![Figure 3](image3.png)
The critical ribbon width of zigzag nanotubes is larger than it was in the case of the armchair nanotubes: The critical width of 15.99 Å corresponds to the nanotube (14,0) and the critical curvature energy of 0.1 eV. This case is shown in Figure 4: at 0.4 ps we observed an initial nanotube formation and at 2.8 ps we obtained a perfect zigzag nanotube.

Building from parallel graphene nanoribbons can give chances for controlled reliable technology in the case of more complicated carbon nanostructures, according to molecular dynamics simulations. The most important unit of the nanoelectronic networks, the carbon nanotube Y-junction can grow from parallel ribbons by self-assembled way. The example of an armchair Y-junction is shown in the followings.

In Figure 5 several initial models of the simulation can be seen:
- In Figure 5.a. the width of the ribbons is less than the critical width.
- In Figure 5.b. the width of the ribbons equals to the critical width.
- In Figure 5.c. the width of the ribbons is larger than the critical width.

The correct Y-junction structure cannot grow up from nanoribbons having width less than the critical width. During the simulation flat graphene parts appear in the structure even if some parts start to grow in tube form, as it can be seen in Figure 6.

The correct Y-junction structure can grow up from nanoribbons having width same or larger than the critical width, as it can be seen in Figure 7-8.
From our molecular dynamics simulations we obtained the following conditions for straight nanotube formation from two parallel nanoribbons put one over the other:

- For armchair nanotubes the critical ribbon width is 9.23 Å corresponding to the critical curvature energy of 0.18eV.
- For zigzag nanotubes we obtained the critical ribbon width of 15.99 Å and the corresponding critical curvature energy of 0.1eV.

In the case of more complicated carbon nanostructures there is possibility for the self-assembly growing from graphene nanoribbons, which was shown on the example of an armchair carbon nanotube Y-junction.

REFERENCES