

Role of substrates in self-organized coalescence of 3D carbon nanostructures

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Abstract — In the present work we study how the existence of graphite substrates effect growing process of nanotubes from graphene nanoribbons. For this purpose a HPC (High Performance Computing) –oriented simulation method were implemented in our research lab. The new modeling and computation method allows us to obtain conditions for the chosen problem of material science tighter and more precise than ever before.

Keywords — molecular dynamics simulation, substrate, van der Waals force, graphite, carbon nanotube, graphene, Density Functional Tight Binding method, Lennard-Jones potential

I. INTRODUCTION

Regardless of the fact that the exceptionally good electric properties of carbon nanotubes has already been described in several publications [1], until now only very few electric devices were presented or realized [2-4]. This fact can be clarified by the absence of well controlled reliable technology for construction of either a standalone nanotube or a complex nanotube network. Constructing nanotubes from flat nanoribbons can be a promising possibility [5]. Nanoribbons can be produced with the help of nanolithography [6] and various chemical compounds [7].

For the time being the accuracy of nanoribbon cutting from graphene is about few nm, and only one order of magnitude is missing to real atomic accuracy. Approaching accurate physical feasibility, it is particularly appreciated to design and execute simulations. It was demonstrated in molecular dynamics simulations that graphene patterns of atomic accuracy can develop in a self organizing way to the predetermined fullerenes or nanotubes [5, 9-11].

There are studies for the instabilities at nanoribbon edges and nanotubes are obtained in molecular dynamics simulations from two nanoribbons [8]. 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 [9].

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Coalescence of nanotube from nanoribbons is a very complex process (even in simulation) although the idea has already been published [8, 12].

In our previous work we made Density Functional based Tight-Binding (DFTB) Molecular Dynamics (MD) simulations. The constant temperature simulations were controlled by the aid of Nosé-Hoover thermostat. We used two superposed parallel nanoribbons of different size, shape and position in our simulation model. We obtained following topological and energetical conditions [13] for growing straight nanotube self-assembling from two nanoribbons [5]: For armchair nanotubes the critical ribbon width is 9.23 Å (chirality 5,5) corresponding to the critical curvature energy of 0.18eV. For zigzag nanotubes we obtained the critical ribbon width of 15.99 Å (chirality 14,0) and the corresponding critical curvature energy of 0.1eV. These values concern models without any substrate, so we have a way to take them lower, as discussed later.

In the present work we study how the presence of a substrate changes these experiences. Interaction between the graphene model itself and its substrate were determined by van der Waals forces [14].

The two nanoribbons are placed between two blocks of graphite substrates. This new type of theoretical experimental setup is closer to practical realization than previous models. Thus, the new experiences gained with the improved model are more valuable. In this work we summarize our experiences with the new model, and determine lower diameter nanotubes can be constructed.

II. THE METHOD

The method we used is based on our previous models but has some improvements which ensure more accuracy and helps our model approaching reality [15]. Molecular dynamics computations generally think of the model as alone entity without interaction with its environment. It is usually assumed in basic methodology that the model hovers in empty space. This simple approach can be useful in most cases, but we wanted to get closer to reality. Whenever a graphene nanoribbon will be produced using in some way it is assumed that it will be created from a graphene sheet placed on an appropriately chosen substrate or between substrates.

The interatomic interaction (between the atoms of the model) was calculated with the help of Density Functional Tight Binding method [16]. The nanoribbons were cut out from a graphene sheet of interatomic equilibrium distance

$r=1.42 \text{ \AA}$ at which atoms prefer to stay. The two nanoribbons are placed facing each other in parallel position. During the molecular dynamics calculation constant environmental temperature was provided [17-18]. Verlet algorithm [19] was used to calculate velocity. The initial atomic displacements during the simulation time step of $\Delta t = 0.7 \text{ fs}$ were sorted randomly and they gave the initial velocities by appropriate scaling. In this scaling we supposed an initial kinetic temperature T_{init} . This initial temperature was chosen from the range of $T_{\text{init}} = 1000\text{K}$ 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 T_{init} . 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 [17-18, 20-21] 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_{init} temperature and the temperature of the Nosé-Hoover thermostat (the environment temperature).

We chose solid graphite as the material of substrate. Its layered, planar structure, and its hexagonal (honeycomb) lattice with the same atomic distances ($r=1.42 \text{ \AA}$) made it easy to add to the simulation. Graphite is very stable in standard conditions, and highly resistant to chemical attack even in high temperatures we use in our simulations. Its bond energy between layers is quite weak, so layers of graphite layers can be easily separated or slid past each other, but in our simulation layout (Figure 1) the layers are perpendicular to the resultant forces so it has no effect on the simulation.

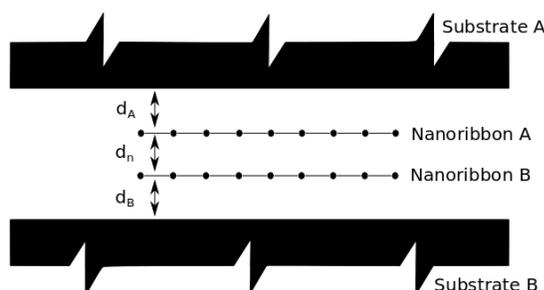


Figure 1. Two graphene layers of initial model placed between two blocks of graphite substrates.

The graphene nanoribbons are placed between two blocks of graphite substrates as we can see on Figure 1. This improvement was inspired by possible production technology

and aims to achieve better control of growing perfect nanotubes. Our models contain two parallel nanoribbons of d_n distance. The distance of the model is d_A from Substrate A and d_B from Substrate B. Usually

$$d_A = d_B = d_n = 3.35 \text{ \AA} \quad (1)$$

which equals to the interlayer graphite distance. The long-range van der Waals interaction between the substrates and the ribbons is characterized by Lennard-Jones (LJ) term [22]. The LJ 6-12 potential is as follows:

$$U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

The parameters were calculated as $\sigma = 2.9845 \text{ \AA}$ and $\epsilon = 0.002 \text{ eV}$. Parameter r is the distance of the given model atom and the substrate atom. With these parameters the atom distance (r) corresponding to the minimum value of the LJ 6-12 potential function is 3.3499 \AA which is considered exactly the same value as of the distance of the layers of the model and the distance of the model and the substrates (Figure 1, 3).

On Figure 2 the Van der Waals force between atoms can be seen as a function of atomic distance. Our simulation computations clearly show the well-known feature of Van der Waals forces: the force become insignificant at greater distances while going through strong repulsion below the equilibrium distance.

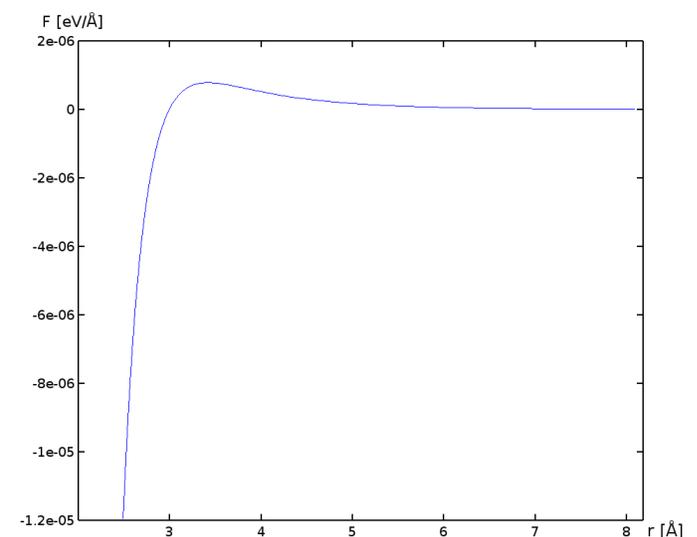


Figure 2. Van der Waals force versus atomic distance (r). When the slope of the function is negative, it means repellent effect. In case of positive slope attractive force will present in a very narrow range of distance. In higher distances attractive forces goes to zero.

On Figure 3 the Lennard-Jones potential can be seen as a function of the atomic distance.

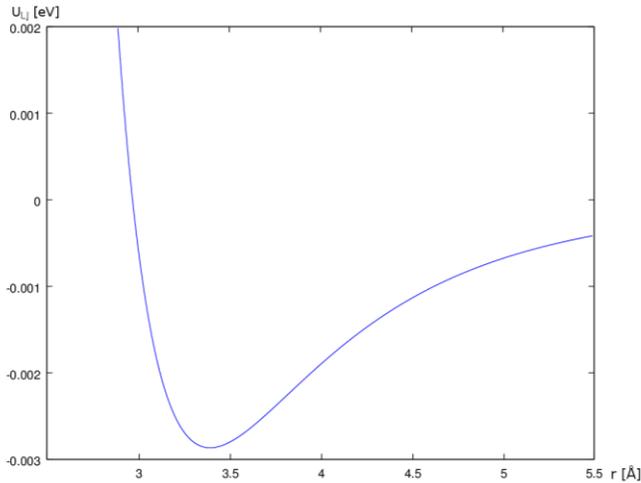


Figure 3. Van der Waals Lennard-Jones Potential (U_{LJ}) versus atomic distance (r). When the slope of the function is negative, it means repellent effect. In case of positive slope attractive force will present.

Both Figure 2 and 3 clearly shows that self organizing simulations can be successful in a quite narrow range of distances between the substrates and the model itself. If the model is too far from the substrates, there will be no effect on the outcome of simulation. If the model is closer than the zero-force equilibrium distance, force attractive decreases fast and turns into repulsion.

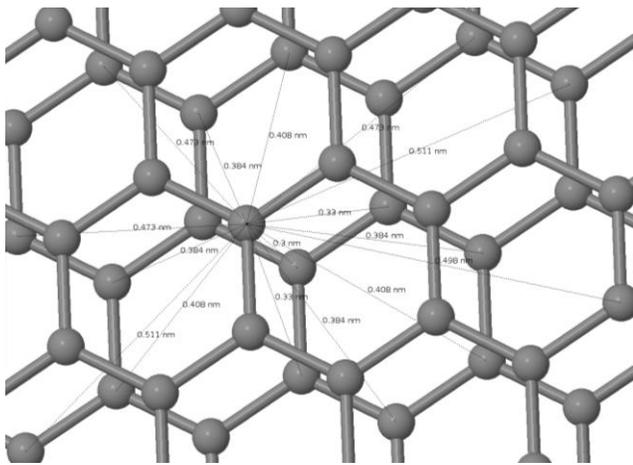


Figure 4. Van der Waals forces are taken into consideration. Figure shows a selected atom and some of its “neighbours” from another graphite layer. As Van der Waals forces are of long-distance type, resultant force of each atom is counted from many other atomic interactions.

Our basic molecular dynamics simulation has already a high demand of computational power, but IT demand strongly increases to compute long-distance interactions between all the atoms of the model and each atom of the substrate blocks

(Figure 4). In addition, substrates have one or two order of magnitude more atoms, as they contains several parallel graphite layers and their extent is significantly higher than the model to ensure the same interacting forces at each part of the model.

We can discover many similarities when we are looking for patterns in the set of force vectors, though. Model atoms being in the same distance from a given substrate subject to the same forces if the atoms are in a suitable chosen initial position.

A mathematical model was created to calculate and estimate the resultant Van der Waals force of each atom in the model:

$$F_{vdw}(i) = \sum_j F_{vdwij} \quad (3)$$

$F_{vdw}(i)$ is resultant Van der Waals force of atom number i , while F_{vdwij} is the force between model atom number i and substrate atom number j . Depending on the positions between model and the layers of graphite substrate the resultant force vector is perpendicular to the plane of substrate layers. If not, it can be shown that the resultant of all the resultant vectors goes perpendicular as the model would be slipped between the substrates into a perpendicular force vector position.

III. RESULTS

We were studying armchair and zigzag nanotubes. We examined all the cases of different orientations and nanotube diameters to know, how the existence of the substrates influences the self-organized growing of nanotubes. The initial structure contained two parallel (coincident or similar size) graphene nanoribbons $d_n=3.35 \text{ \AA}$ from each other. We also set the initial distance of the nanoribbons and the substrates the same value: $d_A=d_B=3.35 \text{ \AA}$. We calculated the interatomic forces between the carbon atoms considering repulsive and attractive van der Waals forces of the substrates.

It was expected that larger models would show similar behavior so we started creating nanotubes due to diameter of critical size and above. Figure 5 shows such a large model. Figure 5.a shows initial model and Figure 5.b shows the developed structure after 2 ps. It can be seen easily that the structure fits compressed is the two substrates. Then we started to pull apart the two substrates so the structure reached its final shape as seen on Figure 5.c. The speed of pulling apart was calculated with the typical speed of piezo movers. For better understanding Figure 5.d shows initial and the flattened model between the substrates. Note that on the figure only one graphite layer can be seen instead of each block of graphite substrates.

On Figure 6 two narrow nanoribbons and the well-formed nanotube can be seen. The width of 7.1 \AA of the ribbons would be below critical width if we did not use substrates. Using the two graphite substrates in the described setup, perfect nanotubes can be grown as seen on the figure.

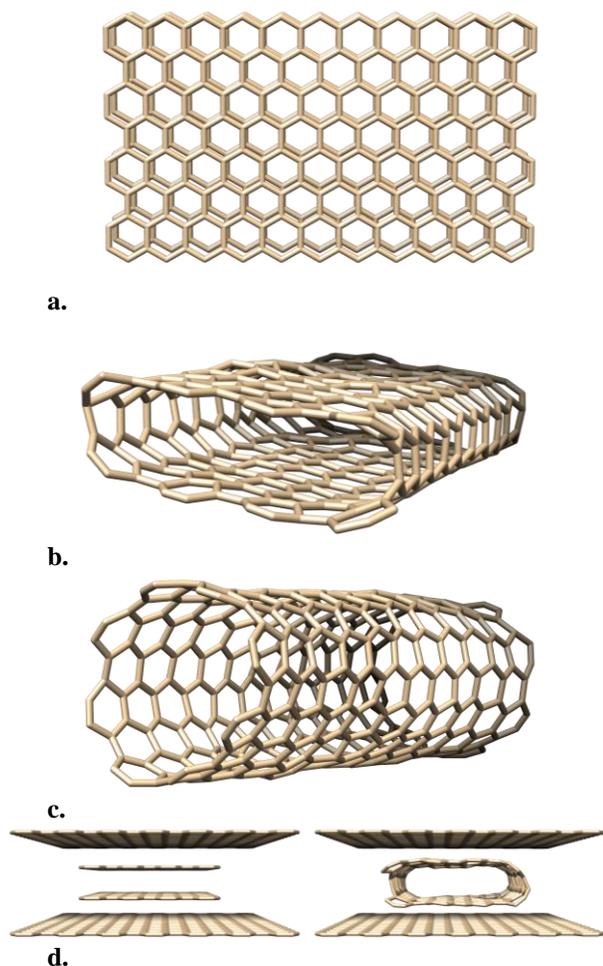


Figure 5. Simulation of armchair nanotube.
a. The initial model
b. The flattened shape model at 2 ps. (Flattening caused by the two substrates)
c. The final shape of the model after the substrates were removed
d. The initial and the flattened model between the substrates (note only one graphite layer of each substrate block is shown)

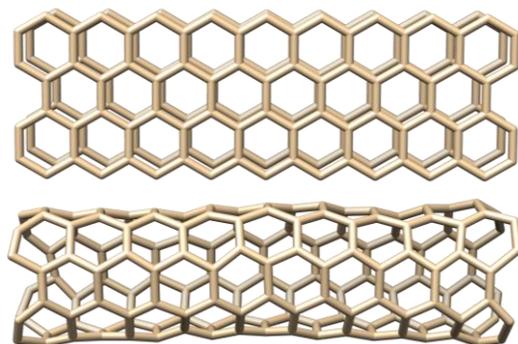


Figure 6. Simulation of armchair nanotube. The initial (upper) and the final (lower) structures. The simulation parameters are the following: 1000K simulation temperature, 22.14 Å of length and 7.10 Å of width for the parallel nanoribbons.

We made several experiments with even smaller width nanoribbons. We can discover the tendency to form the two

separate ribbons into a flat graphene sheet. Even with using substrates self organized growing of perfect nanotubes of such a small diameter could not be done (Figure 7 and 8).

Figure 7 shows a tube where some bonds already formed but the tube is not perfectly grown in its full length. We can see that the open end remains to be as flat as possible next to the well-formed part of the tube. On Figure 8 an unexpected problem can be seen which clearly shows that further size reduction is impossible even with using substrates. For narrow nanoribbons we faced to a behavior which was observed in many cases before without using substrates [13]: the two ribbons join together and creates a single surface. On Figure 8.a such a narrow initial model and the substrates are shown. For the purpose of visualization, only one graphite layer can be seen instead of each block of graphite substrates. On Figure 8.b one side is already perfectly connected, while the atoms on the other edge are moved apart. In this situation curvature energy goes minimal if the radius of the surface increases [13]. For this reason the model swivels and slips between the substrates thus complies with the flattening force (Figure 8.c and 8.d).

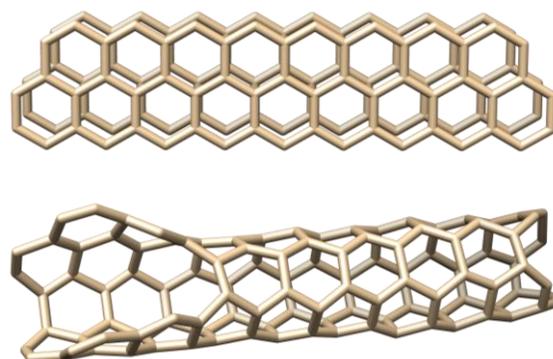


Figure 7. Simulation of armchair nanotube. Initial (upper) and final (lower) structures. Initial nanoribbons are 4.97 Å wide.

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. Zigzag simulations were performed again with using substrates. In Figure 9 a wide model is shown. The initial structure would be above critical size if substrates were not used and with the substrates perfect nanotube structure has been developed.

We experienced that behavior of models wider than or equal to the model shown in Figure 9 show the same behavior. We wanted to know how the structures with smaller width behave when substrates are in use. In Figure 10 a narrower model (initial width: 13.53 Å) is shown. Although this model cannot coalesce to nanotube without substrates, it develops well with proper setup, as can be seen in Figure 10.b. When the self-organized growing of the nanotube has finished after 0.4 ps, we gradually pulled off the two substrates to allow the nanotube forming a perfect round shape. This can be seen on the bottom (Figure 10.c).

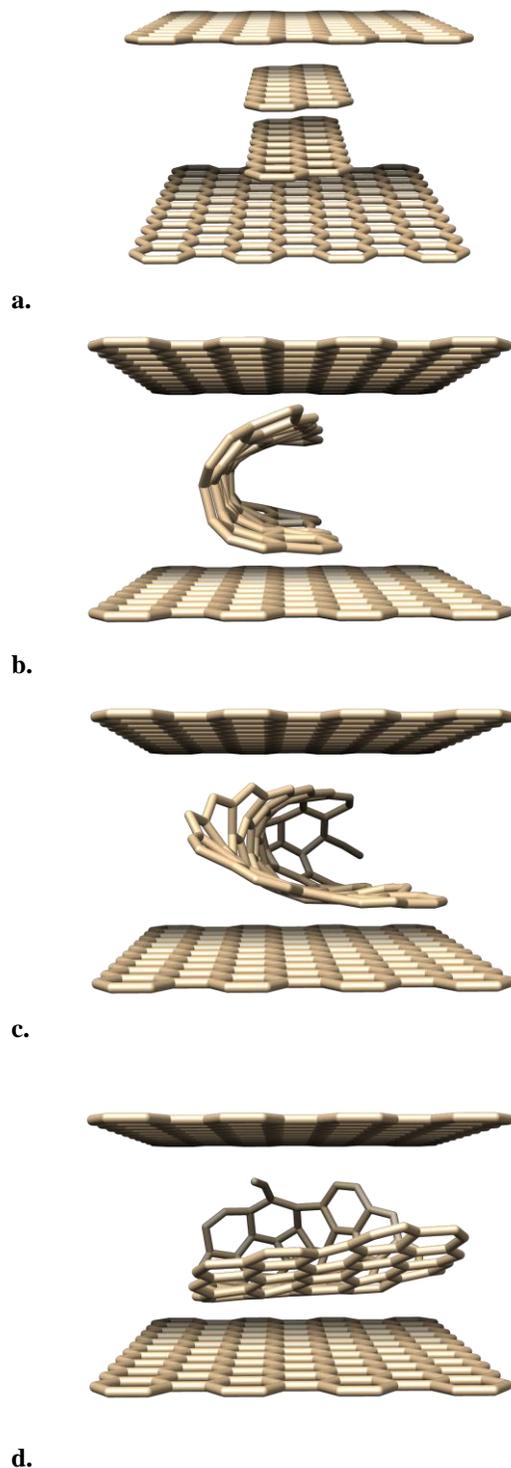


Figure 8. Failed formation of nanotube (note only one graphite layer of each substrate block is shown)

- The initial model of two ribbons
- The ribbons have bonds on one edge pair, have no bonds on the other side
- The model starts turning and slips among the substrates
- The model became more or less flat

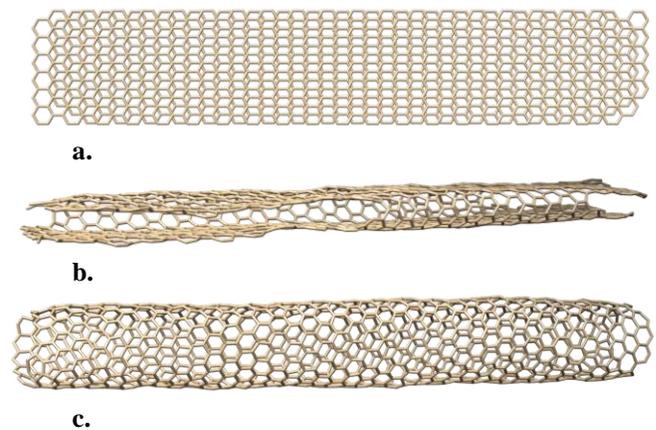


Figure 9. Simulation of zigzag nanotube.

- The initial model
- The flattened structure after a simulation time of 0.8 ps (Not all the bonds are formed yet)

c. The final shape of the model at 3.6 ps. After all the bonds are formed, the substrates were removed.

The simulation parameters are the followings: 1000 K simulation temperature 85.91 Å of length and 15.99 Å of width for the parallel nanoribbons.

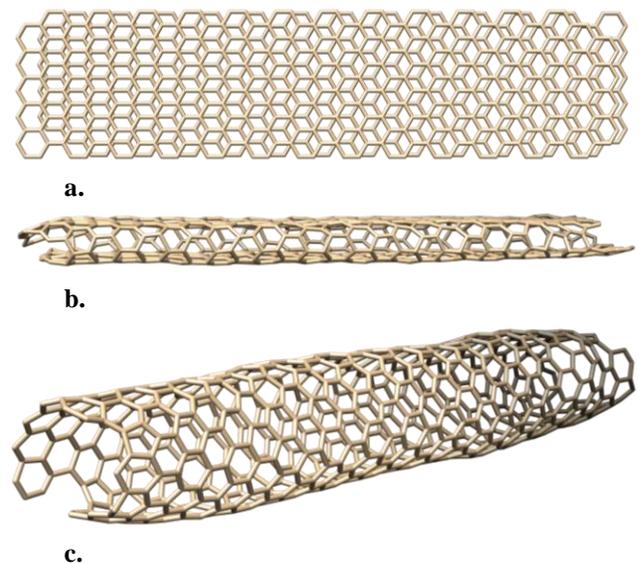


Figure 10. Simulation of zigzag nanotube.

- The initial model
- The flattened shape model at 0.4 ps
- The final round shape model at 0.67 ps. After 0.4 ps the substrates were pulled off gradually to give enough space for perfect round nanotube.

The simulation parameters are the followings: 1050 K simulation temperature, 56.10 Å of length and 13.53 Å of width for the parallel nanoribbons.

Our experience with the observed flattening force can be explained with curvature energy of the surface:

$$E_c = E_{\text{tube}} - E_{\text{graphene}} \quad (4)$$

where E_{tube} and E_{graphene} are the formation energies of nanotube

and graphene. These energies are normalized to atoms. The directly proportional (linear) connection between curvature energy and the square of surface curvature is already published [13] which explains that nanotubes of larger diameters are grown easier without external influences.

On Figure 11 curvature energies of both armchair and zigzag are shown. The two sets of values are practically on the same curve but there are significant differences in the critical curvature energies. The higher horizontal line represents the critical energy (0.3 eV) of armchair tubes of critical size with using substrates. Then follows the armchair tube without substrates (0.18 eV). The third line belongs to zigzag tube with substrates (0.13 eV). The lowest line is critical energy of standalone zigzag tubes (0.1 eV).

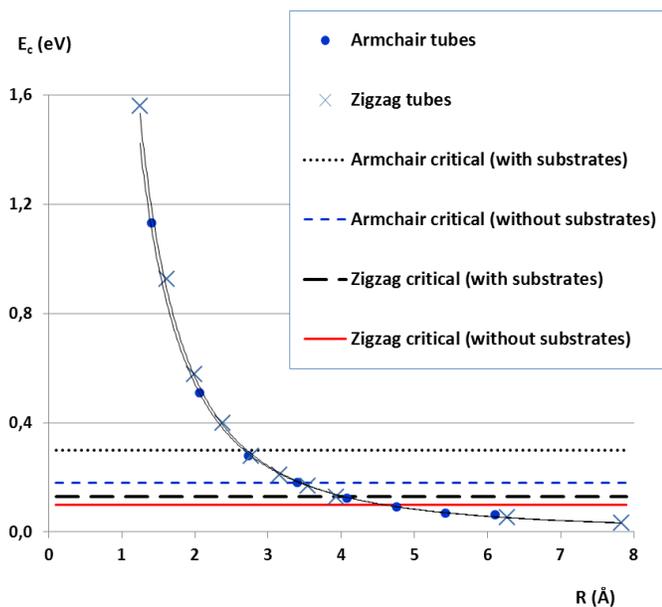


Figure 11. The curvature energy (E_c) of armchair and zigzag nanotubes in the function of the nanotube radius (R). The four horizontal lines correspond to the critical formation energies the tubes with and without using substrates.

IV. CONCLUSION

With our new simulation model self-organizing formation of different 3D nanostructures can be predicted more accurately.

From our molecular dynamics simulations we obtained the following conditions for straight nanotube formation from two parallel nanoribbons placed between two graphite substrate blocks:

- For armchair nanotubes the critical ribbon width is 7.10 \AA .
- For zigzag nanotubes we obtained the critical ribbon width of 13.53 \AA .

We also computed critical energies which belong to these critical physical dimensions. These quite different energy levels explain the different behavior of various crystal orientations.

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.

Both critical widths are significantly narrower than critical widths without using substrates. Further conditions will be researched to find even lower values as critical width for self-organized building nanotubes.

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