Doctoral School of Physics - Eötvös Loránd University (ELTE)

Fourth semester report

By Somayeh Eskandari (Eskandari.somaye@gmail.com)

Ph.D. program: Statistical Physics, Biological Physics, and Physics of Quantum Systems (Stipendium Hungaricum)

Supervisor: Prof. Kürti Jenő

Ph.D. Thesis title: **Modifying and parameterization of Brenner potential and its implementation in molecular dynamics simulation (LAMMPS)**

I) Research work

*a. **Introduction***

One of the most important aims of theoretical studies of chemical reactions is to develop, understand and apply new methodologies to study the reaction pathways and thus the outcome of chemical reactions. Historically, a variety of methods have been developed to achieve this through the understanding and careful control of temperature, pressure, concentration, charge transfer and other variables and hence our capacity to manipulate chemical transformations is ever improving [1]. One such tool, which is adopted more recently, is the confinement of a guest species within a nanoscale host so called nanoreactor [1]. Therefore, a nanoreactor can be defined as any nanoscale structure capable of hosting a chemical reaction. In this project, we focus exclusively on the chemical reactions confined within carbon nanotubes (CNTs).

b. Molecular Dynamics and LAMMPS

Conceptually, nanoscale confinement can influence the pathways of reactions by various pairwise interactions between the host nanostructure and either the reactant, transition state or product of a reaction [1, 2]. The annealing of C_{60}-filled single-walled carbon nanotubes (SWCNTs) with a diameter of about 14 Å is an important example. Encapsulation of C_{60} fullerenes inside SWCNTs were discovered by Smith, Monthioux, and Luzzi at the University of Pennsylvania using high resolution transmission electron microscopy [2]. This discovery soon led to the birth of a vivid new field within the nanotube research, the field of the peapods, as the structure was baptized. It was shown that annealing of peapods under appropriate conditions led to the formation of an inner tube (double-walled carbon nanotubes) [3].

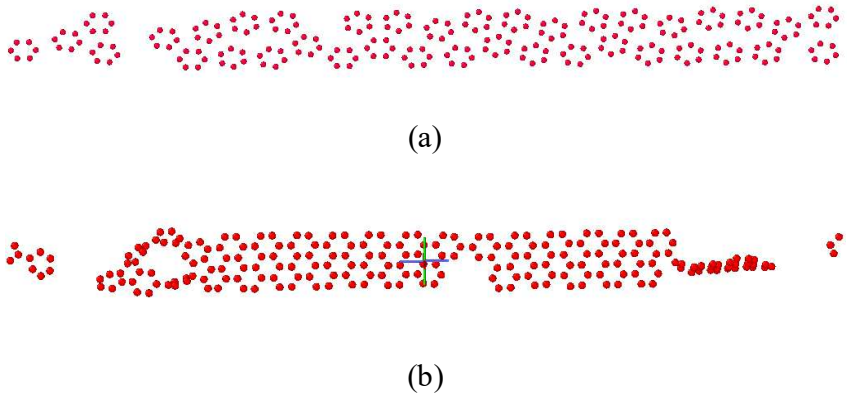
Another examples are filling SWCNT with ferrocene [4] or coronene [5].

Our work in the first three semester was reproduction and continuation of the molecular dynamics simulation with a DFT-adjusted tight-binding method by I. László et al. [6]. Their research is one of the main references in our project. These results show that Tersoff potential is an appropriate candidate in our simulation with LAMMPS. On the other hand, we aim to simulate ribbon-like structures. To this end, the interaction between carbon structure and SWCNT plays a significant role which distinguish chemical reaction in free-space and confined-space. In our studies, we used Lennard-Jones (LJ) pair potential for interaction between wall and atoms inside the tube. The most common expression of the LJ potential are

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

Where ϵ is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, r is the distance between the particles, and r_m is the distance at which the potential reaches its minimum. These parameters can be fitted to reproduce experimental data or accurate calculations [7].

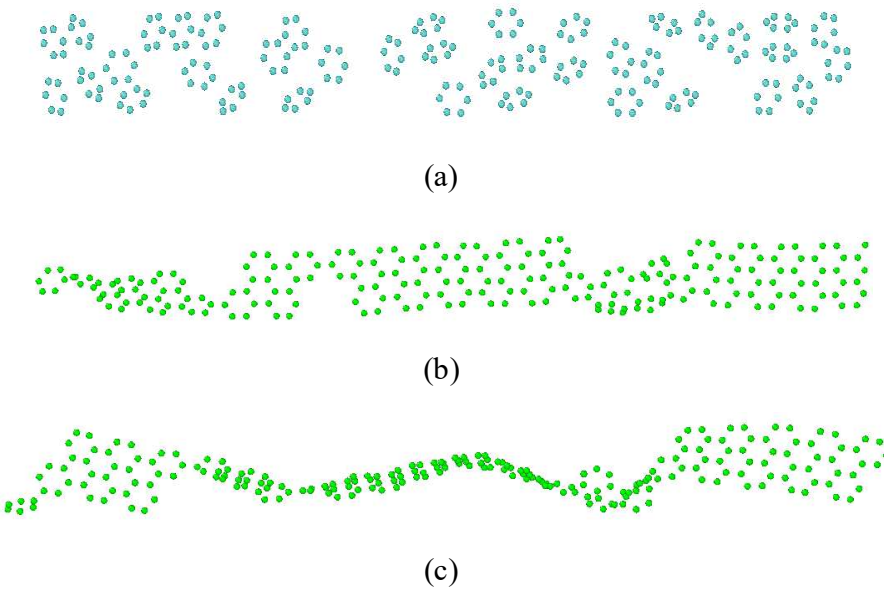
Then we arranged the hexagon carbon rings inside a (18,0) SWCNT with $10\ nm$ in length. The SWCNT is long enough to avoid boundary effects. Now one should find the appropriate parameters such that ribbon structure is created along the SWCNT. This is the most important part of this section. Therefore, by changing LJ parameters and study the results of simulation we find out effective parameters. Figure 1 and Figure 1 illustate the initial and final arrangement of thirty-eight hexagon rings located inside SWCNT in $50\ ps$ at $600 - 800\ K$. the initial arrangement in Figure 1-a is regular configuration while the initial rings in Figure 1-a are located randomly. In both cases, 6-graphene nanoribbon (6-GNR) is created where there is a good agreement with experimental result [7]. (6 is the number of carbon atoms perpendicular to the length of the ribbon.)



(a)

(b)

Figure 1. thirty-eight hexagon rings are located inside (18,0) SWCNT. a) initial configuration. b) final configuration



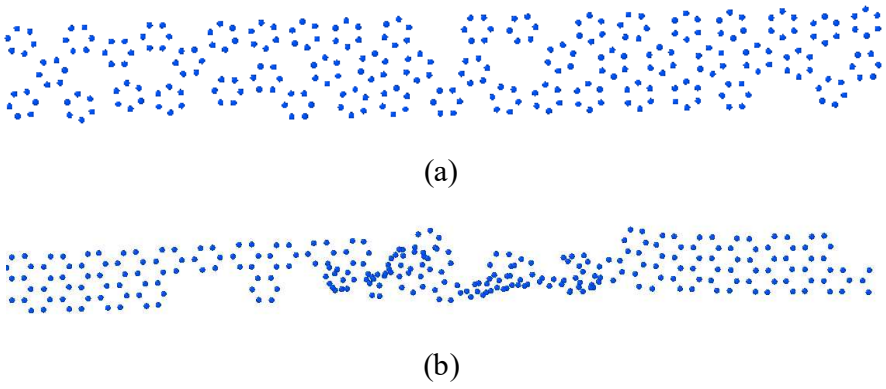
(a)

(b)

(c)

Figure 1. thirty-eight hexagon rings are located inside (18,0) SWCNT. a) initial configuration. b, c) final configuration.

To investigate the effect of density of the atoms inside SWCNT, we increased the number of the hexagon rings. As shown in Figure 2, the 6-GNR is created. However, 8-GNR is also created.



(a)

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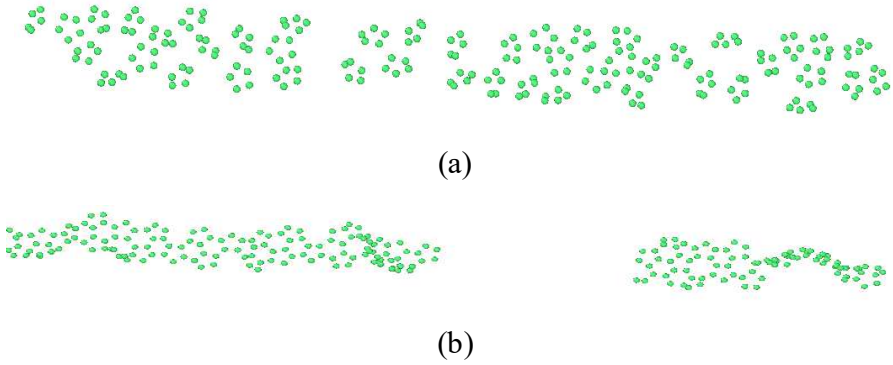
Figure 2. increasing the number of hexagon rings to forty-eight. a) initial structure. b) final results

We also implement the simulation with initial pentagon rings configuration with the same parameters as for hexagon rings. However, the result in Figure 3 shows the ribbon-like structure where pentagon rings remain stable. In other words, the bonds are not broken even in high temperature. In this case, wee need to modify the potentials. Since there is a ribbon-like structure, and the interaction between wall and carbon-rings are set correctly it is necessary to modify tersoff potential between carbon atoms inside the tube.

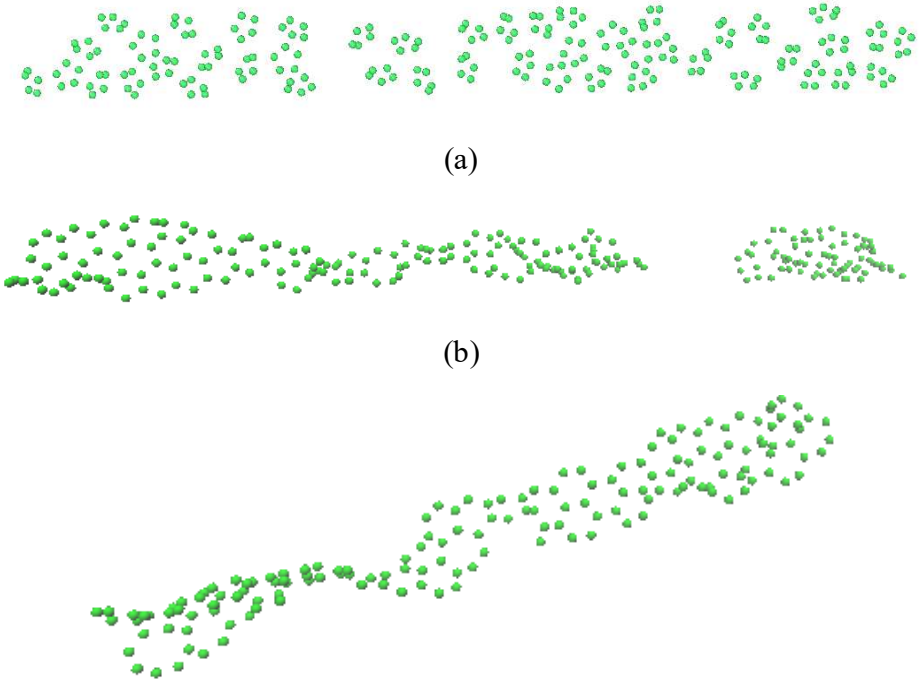
Figure 4 illustrates the result of simulation with modified Tersoff potential. The number of hexagons increase significantly. The ribbon 8-GNRs is observed.



(a)

(b)

Figure 3. pentagon rings without modifying the parameters of the Tersoff potential. a) initial structure. b) final results



(a)

(b)

(c)

Figure 4. pentagon rings and ribbon structure after modifying the parameters of the Tersoff potential. a) initial structure. b,c) final results

In summary, we found that among the built in potentials in LAMMPS, Tersoff and LJ can be good candidates to apply them in MD simulations of forming carbon nanostructures inside carbon

nanotube. In addition to the appropriate potential, careful adjustment of various parameters of the potential is needed.

By optimizing the parameters of the potentials, we obtained the graphene nanoribbon (GNR) structure, in agreement with experiments. Based on this, we used the potentials, modified parameters and nanotube size to study different initial configurations. Using 38 hexagons of carbon rings as the initial structure we obtained 6-GNRs at 800K. Current results shows that we are in a correct path in the simulation. However, in order to reach hydro-carbon structures we need to add H atoms and find appropriate parameters in the simulation. Therefore, the next step is adding hydrogen atoms into the initial structures. So it is necessary to define appropriate interatomic potential between hydrogen atoms and between hydrogen and carbon atoms. According to the experimental results [4, 5], hydrogen atoms should be located at the edge of GNR structure formed inside carbon nanotube.

II) Studies in the current semester

Technology of Materials (FIZ/1/031E)

Prof. Groma István,

Physical materials science I. (FIZ/1/015E)

Prof. Groma István

III) Conference

This study and the results were presented at a conference in Visegrád, Hungary (Conference of the ELTE Excellence Program in Materials Science, Visegrád, January 20-22, 2020). In this conference, I presented the simulation results and supplementary animations that confirm our results. I made a comparison between these results and those of László et al and presented new achivements.

References

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