Doctoral school of Physics - Eötvös Loránd University (ELTE)

Third Semester report

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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 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. Annealing of peapods which to the formation of inner double-walled carbon nanotubes.

Another examples are Ferrocene [3] and Coronene [4].

Motivated by recent experimental results of hydrocarbon formation in small diameter carbon nanotubes, I. László et al. [5] presented molecular dynamics simulations with a DFT-adjusted

tight-binding method. Their research is one of the main references in our project. They increased the number of carbon atoms from 60 to 150 by inserting carbon pentagon rings into a (14,0) nanotube. As a result, they found that the structures formed during the simulation depend on the temperature as well as on the density of the carbon atoms. In other words, at lower temperatures graphene ribbons are obtained, 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. Although this method is accurate and there is a good agreement with experimental results, there are some limitations: only carbon atoms were presented and the number of atoms are restricted. Their calculation is also time consuming. Figure 1 illustrates their results. According to Figure 1, the carbon rings encapsulated SWCNT at high temperature (2000 or 3000 K) form different carbon structures such as an inner tube, fullerene-like, chain-like, and ribbon-like structures. Among all possible structures, the ribbon-like is the most favorite structure and our goal is to achive same results by using LAMMPS as a simulation environment.

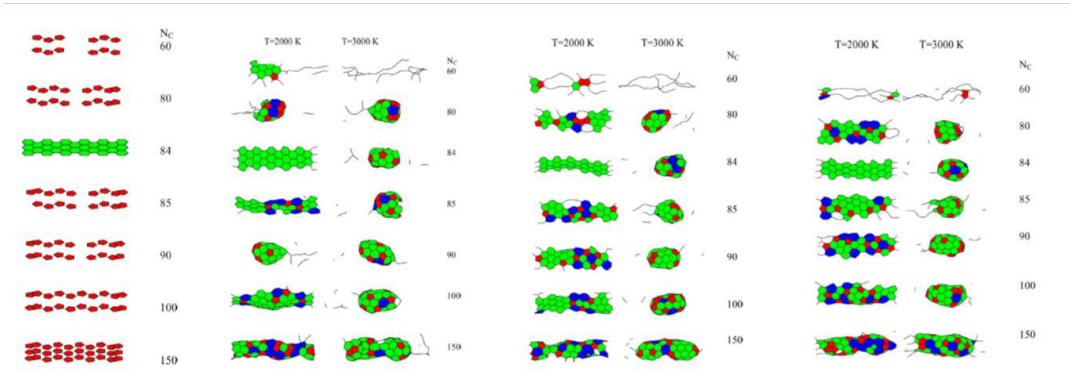
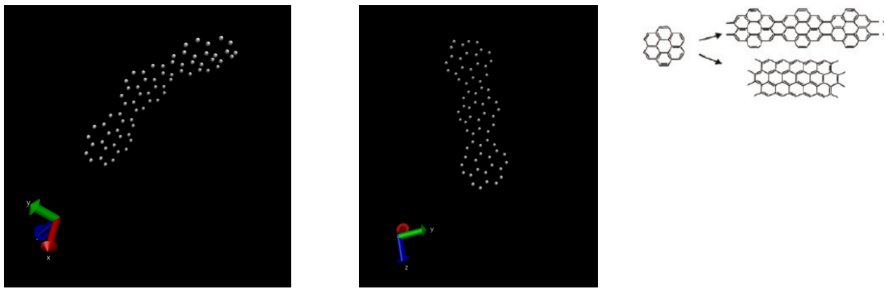


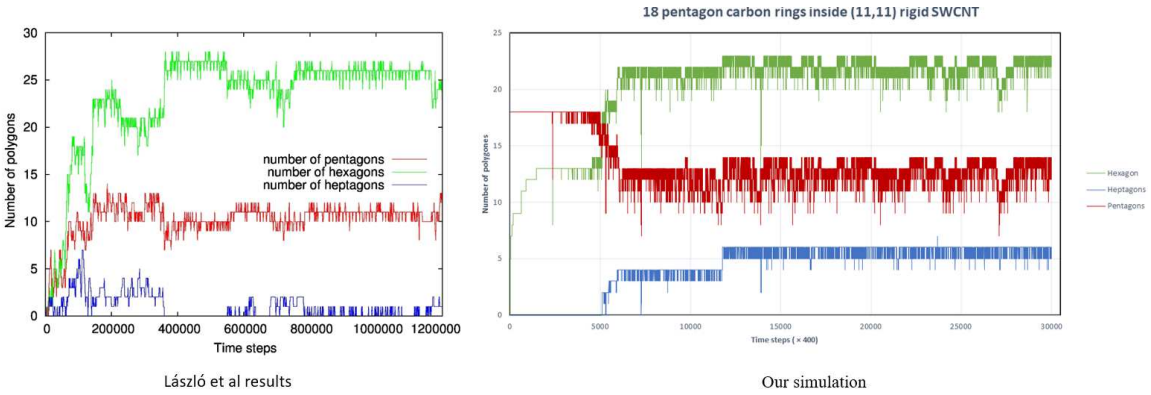

*Figure 1. the initial and final structures at different tempreture with different number of atoms [5]. From left to right, initial structures, final structures by different random initial velocity of atoms.*

Experimentally, annealing of Coronene was performed for 1-24 h at temperature range starting from just above the melting point of Coronene (711 K) up to the temperatures at which bulk Coronene fusion reactions were observed previously (803 K). In our simulation, we used , Tersoff and lcbop pair potentials. As shown in Figure 2, the results agree with the experimental one. Figure 3 compares the number of polygones in László's simulation [5] and in our simulation. In this case, eighteen pentagon carbon rings are located inside (11,11) rigid SWCNT.



Tersoff lcbop Experimental results

*Figure 2. comparing the simulation results of Coronene with different pair potentials and experimental result [4].*




László et al results Our simulation

*Figure 3. compare the number of polygones. Left: László et al. [5] right: simulation by LAMMPS.*

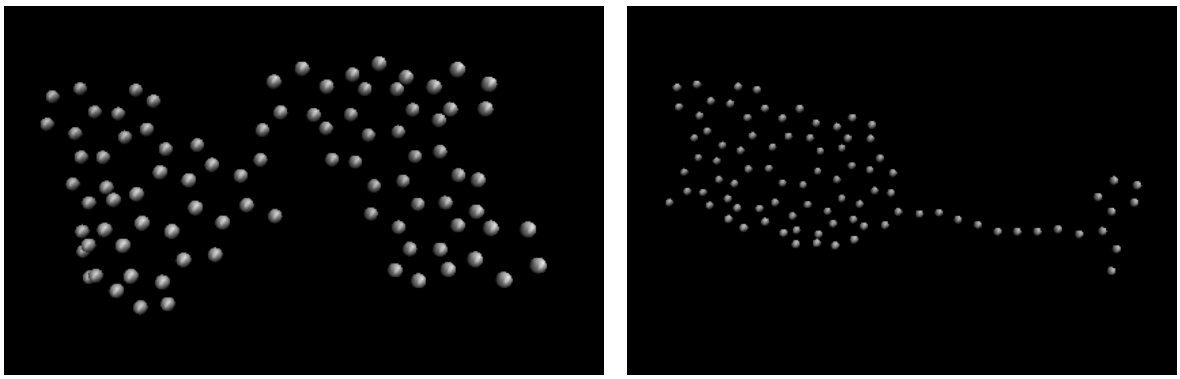


*Figure 4. simulation results of pentagon rings inside SWCNT at 1000K. Left:Tresoff potential. Right: lcbop potential.*

In summary, we found that among the built in potentials in LAMMPS, Tersoff and lcbop 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.

In the case of coronene, we obtained the graphene nanoribbon (GNR) structure, in agreement with experiments. Based on this, we used the same potentials, parameters and nanotube size in the case of ferrocenes. Using 18 pentagons of carbon atoms as the initial structure we obtained ribbon-like structure at lower temperature (1000K) whereas at higher temperature (2000K) various kind of curved structures (fullerene or initiative of an inner tube) were observed. Current results shows that we are in a correct path in the simulation. However, in order to reach the experimental results in the case of ferrocene we have to do the simulation for larger number of time steps.

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 [3, 4], hydrogen atoms should be located at the edge of GNR structure formed inside carbon nanotube.

*II) Studies in the current semester*

*Macromolecules* (FIZ/03/016E)

Prof. Kürti Jenő

*Data Mining and Machine Learning* (FIZ/03/084)

Prof. Csabai István

*Data Science Computer Laboratory* (FIZ/3/087)

Prof. Csabai István, Dr. Visontai Dávid

## References


[1] S. A. Miners, G. A. Rance and A. N. Khlobystov, "Chemical reactions confined within carbon nanotubes," *Chem Soc Rev,* vol. 45, no. 17, pp. 4727-4746, 2016.

[2] S.Bandow, K.Hirahara, M.Yudasaka and S.Iijima, "Raman scattering study of double-wall carbon nanotubes derived from the chains of fullerenes in single-wall carbon nanotubes," *Chemical Physics Letters,* vol. 337, no. 1-3, pp. 48-54, 2001.

[3] H. Kuzmany, L. Shi, J. Kürti, J. Koltai, A. Chuvilin, T. Saito and T. Pichler, "The growth of new extended carbon nanophases from ferrocene inside single-walled carbon nanotubes," *Phys. Status Solidi RRL,* vol. 11, no. 8, 2017.

[4] A. V. Talyzin, I. V. Anoshkin, A. V. Krasheninnikov, R. M. Nieminen, A. G. Nasibulin, H. Jiang and E. I. Kauppinen, "Synthesis of Graphene Nanoribbons Encapsulated in Single-Walled Carbon Nanotubes," *Nano Letters,* vol. 11, no. 10, pp. 4352-4356, 2011.

[5] I. László, B. Gyimesi, J. Koltai and J. Kürti, "Molecular Dynamics Simulation of Carbon Structures Inside Small Diameter Carbon Nanotubes," *Phys. Status Solidi B ,* 2017.