Nucleation of carbon nanostructures: Molecular dynamics with reactive potentials

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Abstract. In this paper, we present our first results in the study of the details of nucleation in the homogeneous carbon gas phase using computer calculations with molecular dynamics methods. Direct and controlled molecular-dynamics approaches are used and two reactive potentials (ReaxFF and AIREBO) are compared. The calculations have shown that the nucleation process in the AIREBO model is going more actively than in the ReaxFF one.

1. Introduction

Due to their extraordinary properties, nanotubes, nanofibers, fullerenes, graphenes and other carbon nanostructures attract much attention. However, their applicability is currently limited because of its high cost. A deeper understanding compounds' growth mechanisms can help to overcome this obstacle. The motivation to this work was the interest in theoretical study of the nucleation process. We use molecular dynamics (MD) methods [1] with different interatomic potentials. The work is dedicated to investigation of reactive force field's impact on simulation results. This paper is the first step in the development of such computational methods.

The relatively cheap way to obtain nanostructures is the chemical vapor deposition (CVD). There are experimental studies [2] of the temperature influence on carbon particle formation of benzene and benzene–ethanol mixtures in shock wave pyrolysis [3], the temperature values vary from 1650 to 2600 K. Catalysts significantly accelerate the nucleation process and another experimental work [4] is devoted to the study of synthesis of carbon nanotubes in the presence of catalysts using a direct current with plasma torch.

Different experimental studies motivated us to explore the nucleation of carbon nanostructures using molecular simulation tools. Molecular dynamics is a prolific method for studying nucleation phenomena. The initiation of the critical nucleus is a process that requires atomistic level of description. The papers below are dedicated to study nucleation mechanism in the three phase states of matter using MD modeling. The paper [5] was aimed to investigate the homogeneous-nucleation process (formation of nuclei) in a superheated crystal by MD-methods. An approach to study cavitation in liquid metals under negative pressures via MD simulation was presented in the article [6]. The work [7] was devoted to the development of a model of fracture of liquid on the base of MD simulations. In the study [8] simulations of crystal nucleation in an overcooled melt were carried out using analysis of statistics on macroscopically identical MD trajectories.

The studies of a homogeneous nucleation of vapor phase with molecular dynamics methods were started from work [9]. Recent papers use large-scale MD–approaches with billion atoms and huge simulation times (56 million time steps) [10] or investigate the condensation of supersaturated water vapor in the presence and absence of ions [11]. Formation of carbon nanostructures can be considered in the framework of thermodynamics [12,13]. But these works do not study the nucleation process on the atomic level. Only several works [14–16] are dedicated to modeling of carbon compounds (nanotubes, graphene) formation by catalytic chemical vapor deposition (CVD) and plasma-enhanced CVD [17].

In the paper [18], quantum molecular dynamics (QMD) based simulations of carbon nano-structures formation were conducted under nonequilibrium conditions on the nanosecond time scale. But QMD modeling cannot be practical for systems with more that $\sim 10^2$ atoms because of the huge computational requirements [19].

The modeling of the nucleation process in carbon vapor requires an accurate model for atomic interaction suitable for MD simulations that can capture bond formation and decay processes as well as different variants of hybridization (sp^1, sp^2, sp^3). Our work is aimed at comparison of the two complicated reactive potentials AIREBO and ReaxFF that are among the most widely used for reactive MD studies.

2. Methods and parameters of calculations

As was mentioned above CVD modeling at the atomic level can be carried out using ab initio and MD approaches. Quantum approaches are expensive, so at this stage we use manybody reactive potentials, which have shown good agreement with density functional theory (DFT) on a wide range of compounds, including carbon [20]. Simulations were conducted with reactive potentials ReaxFF (Reactive Force Field) [21, 22] and AIREBO [23]. The main advantage of these potentials is the ability to describe chemical reactions. Works [24,25] describe the graphite melting with reactive potential AIREBO and calculations gave explanations to the experimental results.

ReaxFF is a general bond-order-dependent potential in which the van der Waals and Coulomb forces are included to describe nonbonded interactions between atoms. Similar to empirical nonreactive force fields, the reactive force field divides the system energy into various partial energy contributions. The energy parts (except van der Waals and Coulomb) additionally depend on bond order. Van der Waals and Coulomb interactions depend on distance and parametrized constants. A fundamental ReaxFF assumption is that the bond order between a pair of atoms can be obtained directly from the distances between neighboring atoms. The AIREBO potential bases on the reactive empirical bond-order potential of Brenner [26–28] but includes torsion and nonbonded interactions. Reactive nature of potentials takes into account the breaking and the formation of bonds and calculations are close to quantum mechanical precision without requiring such computational resources as ab initio ones.

In this work computations are performed in the periodic boundary conditions (the simulation cell volume is 85*85*85 $Å^3$, density is 0.008 g/cm^3) with the program package LAMMPS [29]. The simulations are conducted from 1 ps to 200 ps with timestep 0.2 fs in the Nose-Hoover thermostat. Coordination number is determined on the basis of considerations that the two atoms are neighbors if their bond length is less than or equal to 1.75 Å. To obtain the carbon structures in the gas phase cooling are carried out from 3000 K to 1500 K with cooling rate 10^{10}–10^{11} K/s.

3. Results and discussions

The calculations with atomic carbon have not resulted in sp^2 or sp^3 structures neither with ReaxFF, nor with AIREBO potentials during cooling of the gas phase. Addition and increasing
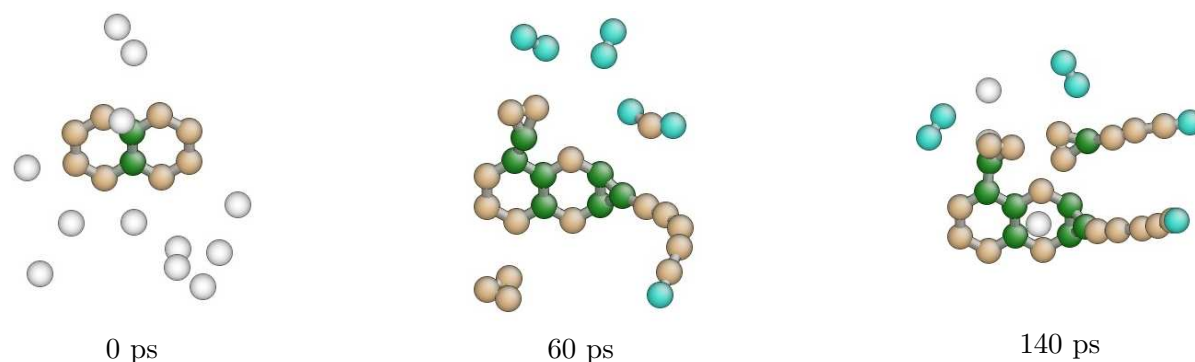
Figure 1. Direct MD-simulations with a double ring seed with ReaxFF model.
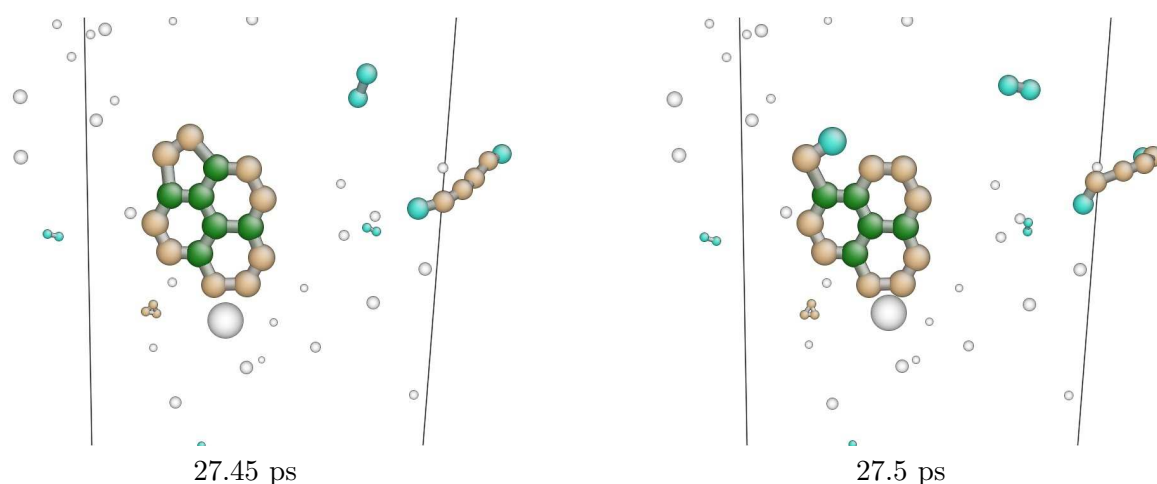

Figure 2. The case of a transient 4-ring formation and decay in the direct MD-simulations with a triple ring seed in ReaxFF model.

of the carbon seeds raises the possibility of nucleation. Here we present the results for the single and double carbon rings (6 and 10 atoms respectively).

Figure 1 shows that the double ring seed has not grown to any sp^2 structures in the ReaxFF model at the simulation time 140 ps. The same double ring system has grown to triple ring at simulation time 60 ps and to the highly defective graphene layer at 140 ps in the AIREBO model (figure 3). Different colors represent different coordination numbers (white–0, blue–1, brown–2, green–3).

There are no events of the forming of stable graphene layers from the seeds in the set of MD-computations with simulation times from 1 ps to 200 ps in the ReaxFF model. Even if the formation of the 4-th ring from the triple ring seed has happened (as in figure 2a), no stable structure has been formed and just after 0.05 ps this structure has decayed (figure 2b). The calculations with the AIREBO potential have shown the growth of the stable structure at the considered simulation times.

We have taken a notice that the nucleation of carbon structures in the direct MD-calculations with ReaxFF and with AIREBO potentials are significantly different in nature. To analyze the obtained results we have decided to apply methods of controlled molecular dynamics. We use the simple systems to compare the influence of the interatomic potentials on the bonds formation. And since analytical method does not allow to compare potentials informatively because of their complexity we use graphical illustrations to elucidate action mechanism of the two potentials.
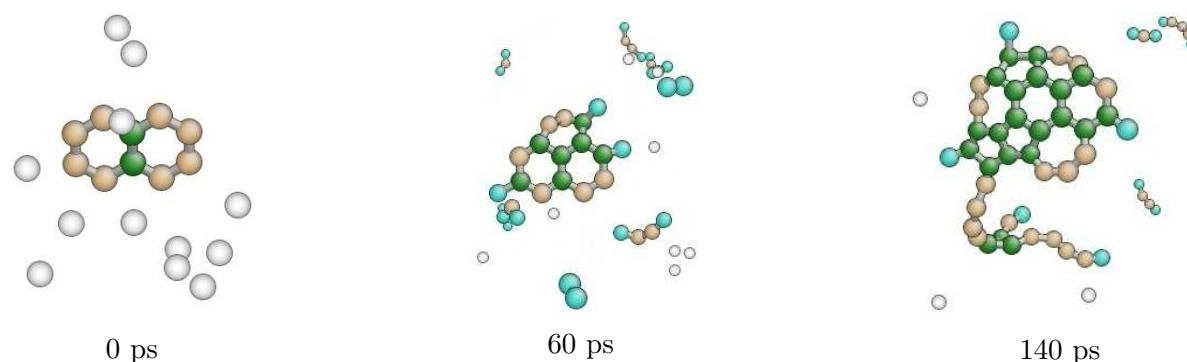
0 ps   60 ps   140 ps

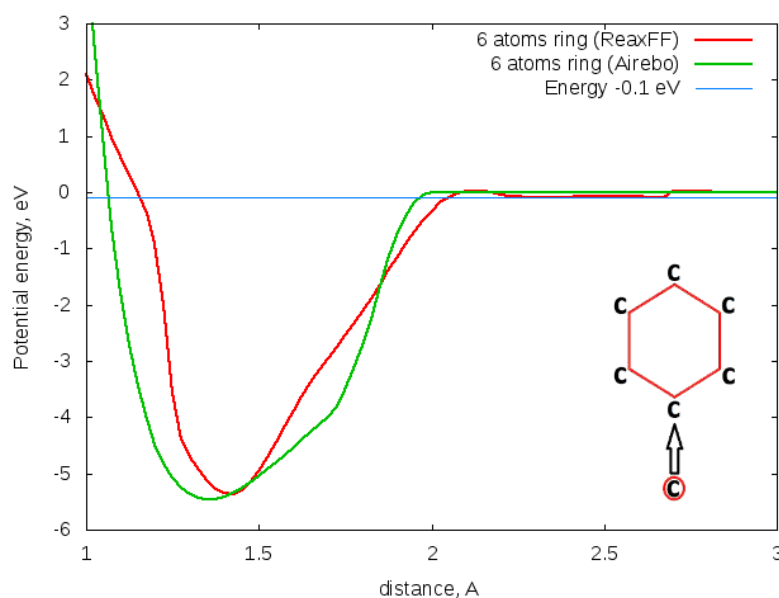**Figure 3.** Highly defective graphene layer nucleation in the AIREBO model.

Figure 4. Dependence of potential energy on distance when the probe atom moves to the 6 atoms ring in the specified direction.

We move the probe carbon atom in a specified direction and watch the differences between ReaxFF and AIREBO models.

As we can see, the figure 4 does not show any fundamental differences between two reactive potentials in this direction. But a 2-dimensional ordinary plot can not fully describe the mechanism of nucleation in space. We make the computations where probe atom are moved in 3D space around benzene with the step 0.2 Å. Potential energy has been calculated in each point. For visualization we build the map of the potential energy surface that can demonstrate the complicated picture of potential barriers and wells in space.

At figure 5 the blue surface represents the moment when the system falls to the edge of the potential well (–0.1 eV), the orange is the potential barrier (0.2 eV). The picture shows that in the ReaxFF case atoms have to overcome a more extended barrier to slide in the potential well. This complicates the attaching atoms and nucleation of carbon nanostructures. Conversely, the carbon ring in the AIREBO model has almost no barriers. This map can explain why seeds do not grow to the graphene layers in the ReaxFF model and do grow in the AIREBO one at simulation times 1 ps–200 ps. The analysis for a double ring seed shows the similar dependency.
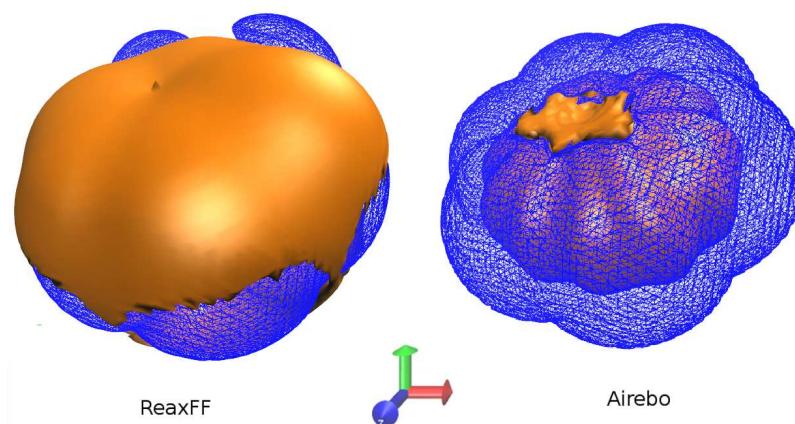
Figure 5. Equipotential surfaces of interatomic interactions for the 6 atoms ring: the blue surface shows the energy–0.1 eV and the orange surface corresponds to 0.2 eV.

4. Conclusion

In our work we have analyzed the influence of the interatomic potential on the nucleation of carbon nanostructures in the gas phase on the basis of different seeds. Our results have shown that nucleation of the carbon structures depends on the model in which the calculations are performed. The various approaches for studying carbon compounds formation are applied for the ReaxFF and AIREBO force fields: direct and controlled molecular dynamics (MD) methods.

Also 2D and 3D plots of potential energy analysis are presented. And they have shown that the barriers in the AIREBO model are smaller and can be overcome by incident atoms. This can explain why the nucleation is going more actively and the resulted nanostructures are more stable in the AIREBO model than in the ReaxFF one.

Furthermore, the bond formation depends on orientation of atoms relatively to each other. And the 3D maps show that carbon structures in the AIREBO model are more likely to grow to the sp^2 or sp^3 carbon nanostructures. But some directions in the ReaxFF case let the structures grow on the base of seeds.

The actual picture of the nucleation mechanism has not known and we cannot say yet which of the considered reactive potential describes this process better. Quantum-mechanical calculations of the electronic structure should be deployed as a benchmark. We are going to perform such simulations in the future.

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