Nanostructures nucleation in carbon–metal gaseous phase: A molecular dynamics study

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Abstract. We perform nonequilibrium molecular dynamics simulation of carbon nanoclusters nucleation and early stages of growth from the gaseous phase. We analyze the catalytic effect of iron atoms on the nucleation kinetics and structure of the resultant nanoparticles. Reactive Force Field (ReaxFF) is used in the simulations for the description of bond formation and dissociation during the nucleation process at the nanoscale. The catalytic effect of iron reveals itself even on nanosecond simulation times: iron atoms accelerate the process of clustering but result in less graphitized carbon structures.

1. Introduction

The nucleation in chemically reactive compounds sparks a great interest because of applicability in the industry processes. For the past few decades the necessity in a simple fabrication of the carbon compounds increases with high rates. The most common and relatively cheap way of synthesis of carbon nanotubes, fullerenes, nanofibers and graphenes is the chemical vapor deposition (CVD). There are a few of experimental works in which carbon nanostructures are receiving using CVD or plasma-enhanced CVD [1–6].

In papers [7–12] theoretical study of the relaxation, melting and nucleation in vapor or liquid states was conducted. The works [13–15] describe nucleation of carbon nanotubes, single- and multilayer graphene. Using MD methods in this kind of research is crucial because the formation of the critical nucleus is a process that requires atomistic level of description.

Several works used MD calculations to consider carbon nucleation in the presence of catalyst. In the papers [15–17] the graphene and carbon nanotubes (CNT) growth on Ni(111) surface was studied. The initial stage of graphene growth was investigated by the ab initio MD methods on the nickel(111) [18] and copper [19] surfaces. In the paper [20] the single-walled CNT (SWCNT) growth in the presence of 55 atom nickel cluster (Ni\textsubscript{55}) was described using DFT (density functional theory) methods.

In the work [21] authors report the results of ab initio calculations on the early stages of SWCNT growth on Fe and Au catalysts. They established that SWCNT grows on the iron cluster (55 atoms, 1 nm) and does not grow on the gold cluster. They also emphasized the importance of nanocatalysts size.

In our previous work [22] the homogeneous nucleation of carbon nanostructures from the gas phase was simulated with ReaxFF (Reactive Force Field) [23] and AIREBO (adaptive...
intermolecular reactive empirical bond order) \cite{24} reactive potentials. Our results have shown
that nucleation in the AIREBO model has a higher rates than in the ReaxFF one. In \cite{22}
we argued that AIREBO provides more accurate description of condensed carbon. We use the new
parametrization of ReaxFF \cite{25} that is in good agreement with the AIREBO model.

2. Reactive force field (ReaxFF)
Current computer capabilities do not allow to study the nucleation process by ab-initio
calculations on the nanosecond scale \cite{26}. For this reason simulations are carried out with
classical methods of molecular dynamics by numerical solving of the Newton’s equations.
Modeling of the nucleation process in carbon vapor requires an accurate model for atomic
interaction suitable for molecular dynamics (MD) \cite{27} simulations that can capture bond
formation and dissociation processes as well as different variants of hybridization (sp, sp\textsuperscript{2}, sp\textsuperscript{3}).
The reactive force field ReaxFF was chosen in the work because this model can describe the
chemical reactions in the system and provide the accuracy level comparable with quantum
description. In the papers \cite{28, 29} the calculations with ReaxFF model have shown good
agreement with experimental studies. Unfortunately, the model demands large computational
resources: for example, in the present work the calculations of a trajectory of 1 ns with the
density 0.12 g/cm\textsuperscript{3} and \( N = 2304 \) atoms require from 4 to 10 days depends on chosen
parametrization on single 14-core Intel Xeon Processor E5-2697V3.

We use the ReaxFF\textsubscript{FeOCH} \cite{30} parametrization for studying of nucleation process in carbon–
metal gas. We treat to the FeOCH parameterization of ReaxFF potential carefully because in
the work \cite{22} we have shown that this parameterization has the problem of high energy barriers
in the carbon–carbon interaction. In the C-2013 parametrization of ReaxFF \cite{25} the problem
of high energy barriers was fixed but this model is capable of describing the processes only in
carbon systems. While there is no such a combined approach, where the carbon–iron and iron–
iron interactions are described by the ReaxFF\textsubscript{FeOCH} parametrization and the carbon–carbon
interactions are described by the ReaxFF\textsubscript{C-2013} parameterization, we use the ReaxFF\textsubscript{FeOCH}
parametrization in this work.

The ReaxFF potential includes the Coulomb force and van der Waals forces and depends
upon the bond order. Its parameterization is based on quantum-mechanical calculations. In this
model, the formalism of central forces is saved, all pairs of atoms have a long-range interactions,
but local adjustment for covalent, valence, torsion and other energy terms are added for a more
accurate description of complex molecules. The total potential energy of the system ReaxFF is
divided into several energy contributions as follows:

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{over}} + E_{\text{under}} + E_{\text{pen}} + E_{\text{conj}},
\]

where as in any classical force field \( E_{\text{bond}} \) describes the bond energy between atoms, \( E_{\text{val}} \)
describes the interaction of atoms through valence angles, \( E_{\text{tors}} \) is the energy of torsion (four-
particle) interactions, \( E_{\text{vdW}} \) and \( E_{\text{Coulomb}} \) are the energies which represent the long-range
interactions. The other contributions have not previously been taken into account in traditional
classical models. The energies \( E_{\text{over}} \) and \( E_{\text{under}} \) are included in the force field to handle the
change in the coordination number when the distance between atoms is varied. \( E_{\text{pen}} \) term
ensures the stability of systems where atom may have two double bonds. \( E_{\text{conj}} \) takes into
account the conjugation of bonds because the alternation of single and double bonds increases
the thermodynamic stability of the compounds.

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,

\[
BO'_{ij} = \exp \left[ p_{bo,1} \left( \frac{r_{ij}}{r_\sigma} \right)^{p_{bo,2}} \right] + \exp \left[ p_{bo,3} \left( \frac{r_{ij}}{r_\sigma} \right)^{p_{bo,4}} \right] + \exp \left[ p_{bo,5} \left( \frac{r_{ij}}{r_\sigma} \right)^{p_{bo,6}} \right],
\]

(2)
where $BO'_{ij}$ is uncorrected bond order which consists of three exponential terms: the $\sigma$-bond, the first $\pi$-bond and the second $\pi$-bond.

A fundamental ReaxFF assumption is that the bond order between a pair of atoms can be obtained directly from the distances $r_{ij}$ between neighboring atoms as shown in equation (2).

The final bond order in molecule is obtained by multiplying $BO'_{ij}$ on adjustment coefficients which depend on different parameters and the $BO'_{ij}$ as described below:

$$BO_{ij} = BO'_{ij} f_1(\Delta'_i, \Delta'_j) f_4(\Delta'_i, BO'_{ij}) f_5(\Delta'_j, BO'_{ij}),$$

where $\Delta'_i$ is parameter which represents the quantity of deviation of the sum of uncorrected bond orders near the atomic center ($N_{\text{bond}}$ is the number of bonds around the atomic center) from its valence (the Val$_i$ parameter):

$$\Delta'_i = \sum_{j=1}^{N_{\text{bond}}} BO'_{ij} - \text{Val}_i.$$  \hspace{1cm} (4)

Correction functions $f_1(\Delta'_i, \Delta'_j), f_4(\Delta'_i, BO'_{ij}), f_5(\Delta'_j, BO'_{ij})$ and parameters $p_{\text{bo},i}$ where $i = 1, \ldots, 6$ from equations (2) and (3) were represented in paper [23] in detail.

Originally the ReaxFF model was developed and parameterized only for hydrocarbon compounds but it can be parameterized also for many other systems of different classes of compounds [31]. The atomic charges are determined by electron equilibration method (EEM) approach [32].

3. Results and discussions

In this work computations are performed in the periodic boundary conditions (the simulation cell volume is $80 \times 80 \times 80$ Å$^3$, density is 0.12 g/cm$^3$) with the program package LAMMPS [34]. The simulations are conducted from 1 ps to 1 ns with timestep 0.2 fs in the Nose–Hoover thermostat [35, 36]. Coordination number is determined on the basis of considerations that the two atoms are neighbors if their bond length is less or equal to 1.73 Å. To obtain the carbon structures in the gas phase super-fast cooling was applied from 6000 to 2500 K with cooling rate $0.35 \times 10^{13}$ K/s. Iron atoms were added in the ratio of 1 : 8 with the carbon atoms.

Figure 1. The curve of carbon vapor pressure from the JANAF tables [33]. The red point shows the system at the start of simulations. The arrow displays the direction of system trajectory in our calculations.
Figure 2. The system of 2304 atoms at 20 ps where the system consists of (a) carbon, (b) carbon and iron (concentration ratio 8 : 1); $T = 5757$ K, cooling rate $0.35 \times 10^{13}$ K/s. Blue color—carbon atoms; red color—iron atoms. Simulation box size is $80 \times 80 \times 80$ Å$^3$.

Figure 3. The system of 2304 atoms at 1 ns where the system consists of (a) carbon, (b) carbon and iron (concentration ratio 8 : 1); $T = 5757$ K, cooling rate $0.35 \times 10^{13}$ K/s. Blue color—carbon atoms; red color—iron atoms.

Figure 1 shows the curve of equilibrium vapor pressure of carbon from the Janaf tables [33]. The red point represents our results at the beginning of simulations. From figure 1 we can see that start point lies in the vicinity of the vapor–liquid curve. The system is a dense supercooled vapor in a metastable state at the beginning of the nucleation process. Accurate measurement and determination of phase diagram of carbon require particular research [37–39]. We assume that the system trajectory in our calculations is similar to the direction of the arrow from figure 1.

The difference between the nucleation process in the presence of iron atoms and the same calculation without metal particles become apparent at small simulation times (20 ps). In the
homogeneous system only chains succeed to form at the early beginning of the simulation when the temperature is still sufficiently high, figure 2(a). Whereas in the carbon–iron system the condensed-phase nuclei formed throughout the cell volume. It is interesting to note that iron atoms are inside the carbon nanoclusters, figure 2(b). This moment also was detected at the experiments. For example, the work [40] shows that the carbon nanostructures grew radially from Ni nanoparticles and the maximum benefits are obtained when catalyst size was a few of tens of nm.

The calculations at 1 ns simulation time show that the both systems resulted in some carbon soot (figure 3). However, in the homogeneous system the nanostructures consist of long chains and large rings. The carbon–metal compound has more ordered structure. To analyze the obtained nanoparticles the graphs of $N$-membered carbon rings formation are built (figure 4). In these compounds we do not observe ideal 6-membered rings which are typical for graphene-like structures, including CNT and fullerenes. The iron particles have catalytic effect though because the rings of 5, 6 and 7 members form from the beginning of the simulation. While the system without metal atoms starts to form these rings only at $\approx 0.8$ ns.

It is interesting to note that the nanoclusters form and explode during the simulations in carbon–metal gaseous phase (figure 5). We suppose the cause of that process is the repulsive potential barriers in the ReaxFF$_{FeOCH}$ parametrization which were discussed in the paper [22].
4. Conclusions
Molecular dynamics study of the initial stage of condensed phase nucleation in gaseous carbon was conducted using ReaxFF potential with the ReaxFF$_{FeOCH}$ parametrization. Nucleation was held in a super-fast cooling of the gas phase (cooling rate of $0.35 \times 10^{13}$ K/s) in the Nose–Hoover thermostat from 6000 to 2500 K.

The presence of iron atoms accelerates the nucleation process even at the beginning of the simulation at $T > 5500$ K. Metal particles locate inside the carbon nuclei at the beginning and stay inside the carbon clusters. Meanwhile the carbon nuclei without metal particles formed from the gas phase only at $\approx 0.8$ ns (3200 K). It shows that the iron catalysts will have a cumulative effect at longer simulation times which allows to accelerate the process of nucleation of the carbon nanostructures. The resulting structures are far from sp$^2$-hybridized graphene-like materials and look more like soot. This work is the first step towards quantitative modelling of the initial stage of nucleation of carbon nanostructures with catalytic agents.

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