Molecular dynamics simulation of polymerization of the carbon under thermal decomposition of methane at constant volume

A V Kudinov¹, S A Gubin¹ and Yu A Bogdanova¹

¹National Research Nuclear University MEPhI (Moscow Engineering Physics Institute) Kashirskoye shosse 31, Moscow 115409, Russia

E-mail: bogdanova.youlia@bk.ru

Abstract. Thermal decomposition of methane was simulated at high temperature and pressure using the molecular dynamics method. The calculation was carried out employing ReaxFFlg potential. We show the dependence of the decomposition products on time and the results of methane polymerization at constant temperature. We also show the influence of gradual temperature decrease at the size of the polymers.

1. Introduction

The production of hydrogen during the thermal decomposition of methane became the reason of growing number of the studies of this process by many researchers [1, 2]. To study CH₄ decomposition shock tubes and experimental pyrolysis facilities were used [3–5]. The detailed mechanism of methane decomposition from 36 chemical reactions was proposed in [6]. The review of publications on the decomposition of methane is given in [7]. Condensed carbon is the second useful product of thermal decomposition of methane after hydrogen [1, 2]. MD simulation using the ReaxFFlg reaction field allows us to study the thermal decomposition of methane with the formation of condensed carbon and intermediate products that are difficult to observe in experiments. [8, 9]. The aim of this work was to attempt to study the formation of carbon nanoparticles with the structure of graphite during the decomposition of methane using MD simulation. In previous similar studies, only carbon polymerization was observed [8, 9]. Whereas in the experiments nanoparticles with the structure of graphite are formed [1, 2].

In this paper, we use MD simulations to study the polymerization of carbon at high temperatures (T = 3500 K) for a system with density of 0.05 g/cm³. To observe the polymerization the dissociation of methane molecules is necessary, which is possible with shock wave compression or thermal decomposition. In the present work, we have considered the process of thermal decomposition at constant volume.

2. Calculation details

Thermal decomposition was carried out using the LAMMPS program [10]. A cell containing 64 molecules of methane was used as a simulated system. The interaction between methane molecules and the other particles in the system was described by the ReaxFFlg force field [11]. The main feature
of this force field is the ability to describe chemical reactions in a system, which is executed by introducing a bond order between the particles of the system.

The time step during equilibration process was 0.05 fs. Equilibration was carried out via NPT ensemble at a temperature of 110 K and a pressure of 1000 atm for 10 ps. The boundary conditions on the cell walls are periodic, that is, molecules that experience a collision with the wall come out of the opposite boundary with conservation of energy and momentum. The cell obtained as a result of equilibration has a density of 0.475 g/cm$^3$. Thermal decomposition was carried out in the NVT ensemble at a temperature $T = 3500$ K and a density of 0.05 g/cm$^3$ ($P = 1600$ atm) using a time step of 0.1 fs.

To reduce the density from 0.475 g/cm$^3$ to 0.05 g/cm$^3$, the change_box command was used, with the help of which the cell volume was increased by $N^3$ times, where $N$ is the multiplier for each of the three directions, which provided the necessary density. When using this command, two options are possible: with changing the coordinates of the atoms or with conservation of the coordinates. In the first case, each atom will move to a new place, while the bond length in the molecule will change, and if the volume increase is too large, the molecule will. In the second case, the molecules remain in the same places (in the same volume), and empty space forms around them. In this work, the first option was used. In order to avoid breaking bonds in the molecules, the volume was increased stepwise, with relaxation in the NVT ensemble at a temperature of 300 K after each stage and recording of the final state in a new file, which was used for the subsequent volume increase. Ultimately, a cell with a density of 0.05 g/cm$^3$ was obtained and thermal decomposition was carried out over 100,000,000 steps (10 ns) for a density of 0.05 g/cm$^3$.

3. Results

At the first stage of CH$_4$ decomposition, hydrogen atoms and molecules and CH$_3$ radicals are formed, which is consistent with experimental studies [3, 4]. C$_2$ carbon dimers appear. Over time, heavier intermediate products of CH$_4$ decomposition (such as C$_n$H$_m$, $n>m$) appear. Starting from a certain time, carbon molecules begin to form filament-like structures shown in figures 1-2. At a time of 900 ps a C$_{10}$H$_2$ ring, a linear molecule of C$_{20}$H$_2$ and 110 hydrogen molecules H$_2$ are present in the system. Over time, the ring opens and after 70 ps at a time of 970 ps there are three large molecules in the system: C$_{18}$ - which is a carbon filament, C$_6$H$_2$, C$_{11}$H$_3$ and 115 hydrogen molecules H$_2$.

![Figure 1. Snapshot of the simulation cell at 900 ps. Bigger red particles – carbon atoms, smaller blue particles – hydrogen atoms ($\rho = 0.05$ g/cm$^3$, $T = 3500$ K)](image1)

![Figure 2. Snapshot of the simulation cell at 970 ps. Bigger red particles – carbon atoms, smaller blue particles – hydrogen atoms ($\rho = 0.05$ g/cm$^3$, $T = 3500$ K)](image2)
The authors [12] proposed the following criterion for determining the onset of polymerization: polymerization begins when 40% of carbon atoms are assembled in clusters with 5 or more atoms with a lifetime of more than 20 fs. The first condition determines the presence of polymers, and the second eliminates the transition to a plasma state. In their calculations the DFT-MD method was used to calculate shock-wave compression in the temperature range from 300 to 75,000 K. In this work, at $T = 3500$ K, the system is not in the plasma state, and the transition to the polymer state was determined when clusters of 5 and more carbon atoms were formed with 40% (25 carbon atoms) of total carbon atoms contained in these clusters. For a density of 0.05 g/cm$^3$, the transition of the system to the polymeric carbon state occurred at 452 ps, with the formation of $C_{11}H_3$, $C_{10}H_3$ and $C_8H_3$ molecules. Subsequently, long carbon filaments containing up to 60% of carbon atoms are formed in the system. Table 1 presents the largest molecules of the system having a filament-like structure and a lifetime of more than 1 ps.

| $t$ (ns) | Polymer  | $t_{\text{life}}$ (ps) |
|---------|----------|----------------------|
| 0-1     | $C_{24}H_3$ | 2,1                   |
| 1-2     | $C_{32}H_4$ | 3,4                   |
| 2-3     | $C_{36}H_6$ | 6                     |
| 3-4     | $C_{38}H_7$ | 4,7                   |
| 4-5     | $C_{39}H_5$ | 9,3                   |
| 5-6     | $C_{29}H_3$ | 5,3                   |
| 6-7     | $C_{28}H_5$ | 4,3                   |
| 7-8     | $C_{29}H_6$ | 9,5                   |
| 8-9     | $C_{28}H_7$ | 3,5                   |
| 9-10    | $C_{34}H_5$ | 1,1                   |

From Table 1 it is seen that the lifetime of the filament-like structures lies in the range from 1 to 9 ps, after which these structures decompose into their component parts. This is explained by the fact that smaller molecules that possess sufficient kinetic energy to break bonds in the filament structure are present in the system. To test this hypothesis, a further study of the polymer system was carried out. In previous calculations, it was shown that at $T = 2500$ K and at variable scales of the order of 1 ns, methane decomposition does not occur. Therefore within 1 ns the temperature in the system decreased linearly from $T = 3500$ K to $T = 1500$ K. Then an additional calculation at $T = 1500$ K for 1 ns was performed. The pressure $P$ in the system was 800 atm. At the beginning of the calculation, the system contained polymers of the form: $C_5H_2$, $C_{10}H_5$, $C_{10}H_5$, $C_{10}H_5$, see Figure 3. At time $t = 10.56$ ns, when $T$ decreases to 2400 K, the $C_5H_6$ molecule is formed from $C_{17}H_5$ and $C_{14}H_6$ molecules. After 5.6 ps, it decomposes into $C_{27}H_4$ and $C_{28}H_2$. After $t = 369.3$ ps, $C_{27}H_4$ captures the acetylene molecule ($T = 1500$ K) and the resulting filament structure of $C_{39}H_6$ remains in the system for 1062 ps. Thus, we can conclude that when the temperature decreases to the level of the onset of methane dissociation ($T = 2500$ K), large filamentary structures stop decomposing and form a stable molecule, see Figure 4. In addition to the polymer structures ($C_{29}H_6$, $C_{34}H_3$, $C_{14}H_3$) in the system also contains molecules $H_2$, $C_2H$, $C_2H$, $C_2H$, $C_2H$. The number of hydrogen atoms in this case is $N_{H2} = 117$, that is, 91.4% of the hydrogen atoms of the system are in molecular form. In this case, most of the hydrogen molecules are formed during thermal decomposition ($T = 3500$ K), and not as a result of cooling the system.
similar result was obtained by the authors of [12] for calculating methane dissociation under compression in a shock wave up to $T = 4000$ K using the DFT-MD method.

Figure 3. Simulation cell before cooling. Bigger red particles – carbon atoms, smaller blue particles – hydrogen atoms ($T = 3500$ K, $P = 1600$ atm)

Figure 4. Simulation cell after cooling. Bigger red particles – carbon atoms, smaller blue particles – hydrogen atoms ($T = 1500$ K, $P = 800$ atm)

In addition to the polymer structures ($C_{29}H_6$, $C_8H_3$, $C_{13}H_3$), $H_2$, $C_4H_3$, $C_2H$, $C_2H_2$, and $C_4H_2$ molecules are also present in the system. The number of hydrogen atoms in this case is $N_{H2} = 117$, that is, 91.4% of the hydrogen atoms of the system are in molecular form. In this case, most of the hydrogen molecules are formed during thermal decomposition ($T = 3500$ K), and not as a result of cooling the system.

4. Discussion

In this work we investigated the mechanism of methane thermal decomposition. At high temperature (3500 K) and low density (0.05 g/cm$^3$), methane decomposes to hydrogen atoms and molecules, CH$_3$ radicals, and light hydrocarbons. Their concentrations reach a maximum and then decrease over time. Simultaneously carbon dimers are formed. After that unstable hydrocarbons of the form $C_nH_m$ are formed, where the number of carbon atoms significantly exceeds the number of hydrogen atoms. In fact, these molecules are carbon polymers with several hydrogen atoms. Formed carbon filaments and rings eventually decompose into their constituent parts and form again throughout the whole simulation (10 ns). Thus, our attempts to obtain a nanoparticle with a graphite structure, using ReaxFFlg potential, by increasing the calculation time were unsuccessful.

Then the system was cooled to 1500 K over 1 ns and held at this temperature for another 1 ns. At high temperatures, large filament-like molecules have lifetimes of 1 - 9 ps. As the temperature decreases to 2500 K, the $C_{29}H_6$ carbon polymer is formed, containing 45% of the system’s carbon atoms, with a lifetime of 1062 ps.

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