

On the stable forms of carbon clusters produced in low pressure sputtering discharge

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Abstract: Molecular Dynamics (MD) simulation was used to identify the stable structures of carbon clusters C_n ($10 \leq n \leq 60$). The adopted a simulated annealing procedure randomly distributed in the phase-space and submitted to a thermal cycle involving a heating ramp, a relaxation period and cooling phase. We found that for neutral carbon cluster size $n < 20$, the most stable structure of the cluster is linear or monocyclic. For cluster size $n \geq 20$, graphene and fullerene structures are obtained to be the most stable structures involved in dusty plasmas.

Keywords: Dusty plasma, carbon clusters, Simulated Annealing Molecular Dynamics (SA-MD), REBO potential, LAMMPS

1. Introduction

Dusty plasma is an ionized gas that contains solid particles with sizes ranging from few nanometers to several hundred microns. They are often generated by the molecular growth of a precursor and a subsequent nucleation of solid nuclei that grows and evolve through aerosol dynamic processes. Particles formed in the plasma often acquire a negative electric charge that fluctuates due to the discrete character of the charging process. The kinetics of the processes involved in the aerosol dynamics strongly depend on the particle charge and its fluctuation. Conversely, the charged particle cloud can affect the plasma equilibrium, which results in a strong coupling between the particle and the plasma characteristics [1]. In particular, this coupling strongly affects the size distribution and structural characteristics of the nanoparticles. The use of dusty plasmas as tools to produce advanced functional nanoparticles requires the understanding of this coupling and especially how the plasma affects the particle structure especially during the first stage of their formation. These are however difficult to fully investigate experimentally and numerical simulation can help in shedding light on several aspects.

Several modeling approaches were developed to understand the phenomena leading to the formation of solid carbon particles in plasma. Fluid codes was used by A. Michau *et al.* [1] to study the formation of carbon clusters produced by sputtering a graphite cathode in a DC discharge. These models require the knowledge of basic data on the properties of clusters (geometry, enthalpy of formation and characteristic size of clusters

for example). These basic data are given by ab-initio and DFT calculations for small carbon clusters and by molecular dynamics methods for large clusters. Using ab initio calculations K. Raghavachari and J.S. Binkley [2] studied the structures and energies of small carbon clusters C_n ($n=2-10$). A.C. Ngandjong *et al.* [3] used a Density Functional calculations DFT to analyse the energetics of many neutral and anionic carbon clusters C_n ($n < 10$). Cai *et al.* [4] used a Genetic Algorithm (GA) with Brenner potential for carbon in order to obtain the lowest potential energies of carbon clusters from C_2 to C_{71} . These authors were interested in fullerene-like structures. Kosimov *et al.* [5, 6] employed an energy minimization method with a modified Brenner potential to study the most stable structure of neutral carbon clusters from C_2 to C_{55} . For $n > 18$, they studied graphene sheet-like structures.

The Classical Molecular Dynamics may offer a description at the molecular scale of the reaction route [7]. The implementation of molecular dynamics simulations requires the choice of an interaction potential between atoms that depend on the nature of the simulated material. To account for both the physicochemical properties of the entities studied and the chemical reactivity between these entities, the use of a reactive potential such as Tersoff [8], REBO [9], AIREBO [10] or ReaxFF [11] potentials is necessary. In this study, a simulated annealing molecular dynamics (SA-MD) simulations [12] using the reactive empirical bond-order (REBO) [9] potential is performed to study the energetics and conformations of carbon clusters C_n ($10 \leq n \leq 60$). These simulations were carried out using the LAMMPS software [13].

This paper is organized as follows. In sec. 2, a description of the interatomic potential used in Molecular Dynamic simulation is given and the details of SA-MD simulations are presented. A statistical study enabling the determination of the abundance of the different cluster isomers is discussed in sec. 3 in the case of C_{36} . Comparison of the stable geometries and energetics of large carbon clusters predicted in this study with available theoretical and numerical data published in the literature is presented in sec. 4 and a brief conclusion is given in sec. 5.

2. Computational method

A. Molecular dynamics simulation

Molecular Dynamic simulation (MDs) is a powerful technique for studying the time evolution of systems of atoms in a variety of states. It consists of solving the classical Newton equations of motion:

$$\sum_i \vec{F}_i = m_i \vec{a}_i = m_i \frac{\partial^2 \vec{r}_i}{\partial t^2} \quad (1)$$

$$\vec{F}_i = - \frac{\partial V_{ij}(\vec{r}_1(t), \vec{r}_i(t), \dots, \vec{r}_j(t))}{\partial \vec{r}_i} \quad (2)$$

Where $\vec{r}_i(t)$ is the position of atom i at time t with mass m_i , and V_{ij} is the interaction potential between all j involved species. The velocity Verlet algorithm is adopted to integrate the equation of motion. The carbon-carbon interactions are expressed by the REBO potential whereas the total potential energy of the system is expressed as [9]:

$$V_{ij}^{\text{REBO}} = \sum_i \sum_{j(j>i)} f_c(r_{ij}) [V_r(r_{ij}) - B_{ij} V_a(r_{ij})] \quad (3)$$

Here, $V_r(r_{ij})$ and $V_a(r_{ij})$ are respectively the repulsive and attractive force terms that take the Morse-type form with a certain cut-off function $f_c(r_{ij})$. B_{ij} represents the effect of the bonding order parameters [9]. It depends on the local coordination and bond angles for atoms i, j respectively which appears in $b_{ij}^{\sigma-\pi}$ and $b_{ji}^{\sigma-\pi}$ terms [9]. The b_{ij}^π function is further written as a sum of two terms, the first term π_{ij}^{RC} depends on whether a bond between atoms i and j has a radical character and is part of a conjugated system. The value of b_{ij}^{DH} depends on the dihedral angle for carbon-carbon double bonds [9].

$$V_r(r) = (1 + \frac{Q}{r}) A e^{-\alpha r} \quad (4)$$

$$V_a(r) = \sum_{n=1,3} B_n e^{-\beta r} \quad (5)$$

$$f_c(r_{ij}) = \begin{cases} 1 & r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2} \cos\left(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right) & R_{ij} < r_{ij} < S_{ij} \\ 0 & r_{ij} > S_{ij} \end{cases} \quad (6)$$

$$B_{ij} = \frac{1}{2} [b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}] + b_{ij}^\pi \quad (7)$$

$$b_{ij}^\pi = \pi_{ij}^{RC} + b_{ij}^{DH} \quad (8)$$

B. Method : Simulated Annealing Molecular Dynamics (SA-MD)

The SA-MD consists of heating an initially disordered carbon mass and then quenching the structure rapidly to 0 K. The main task of SA-MD is to explore the different locally stable conformation for a given cluster size. For this propose the cluster is submitted to slow heating rate allows scanning the different conformation in the phase space.

Fig. 1 shows the different steps involved in the simulation procedure and the parameters used. A number N of carbon atoms close to 0K are placed in the gas phase with random positions and velocities in a $10 \text{ nm} \times 10 \text{ nm} \times 10 \text{ nm}$ simulation box. The system is heated up to 3000 K with a rate of $3 \times 10^{10} \text{ K/s}$ during 100 ns. Then a constant temperature waiting phase of 0.1 ns is operated before proceeding to a cooling phase down to 0 K for 100 ns with the same rate used for heating phase. The temperature is controlled using Berendsen thermostat with a thermal relaxation time of 1 fs. The simulation is performed in the micro canonical ensemble NVE, and the time step used for all simulations is 0.1 fs. The periodic boundary conditions are applied to the simulation cell.

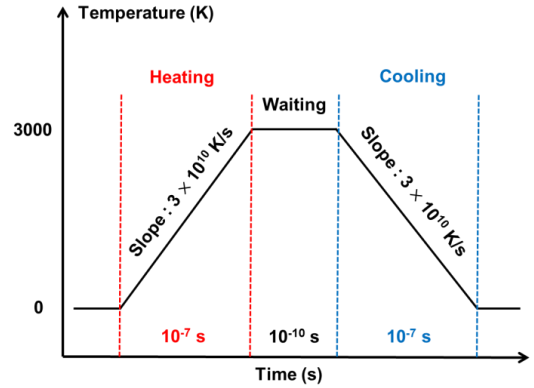


Fig. 1: Diagram representing the steps of the SA-MD molecular dynamics.

Fig. 2 shows the evolution of the structure and the energy as a function of time of carbon C_{36} . In the beginning of the simulation, and during the heating phase, the large decrease in energy indicates the transition from a random structure to a compact one. This structure evolves over time to give a stable shape at the end of the heating process. A small waiting phase allows the structure to relax and find a well-defined state. When the cooling phase starts, only small changes are observed in the topology of the cluster. These indicate that the system evolved around an equilibrium state and a stable structure is identified at the end of cooling.

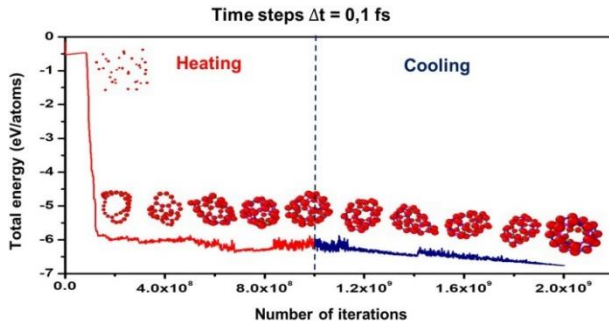


Fig. 2: The evolution of structure and energy as a function of time of carbon.

3. Statistical studies for carbon C_{36}

Preliminary studies showed that the final cluster structure depends on the initial state (positions and velocities) of the carbon atoms. We therefore performed a several simulations in order to determine the statistical abundance of the different stable carbon clusters. For each simulation, the initial position and velocities were assigned randomly to carbon atoms using uniform distribution. The simulation conditions, e.g., maximum temperature, box size, heating dynamics, time steps are set constant. C_{36} was particularly examined using 23 simulations. The occurrence frequency of isomers at the end of the simulation is used as a measure of its abundance. The most stable topology is defined as the one that shows the minimum energy and this corresponds to the one that has the largest occurrence frequency. In the case of C_{36} carbon, fullerene-like isomers are the most stable. A graphene-like sheet is the second stable isomer of C_{36} . Other isomers with unstable structures (3D polycyclic, open cage...) appear with a small percentage, see Fig. 3.

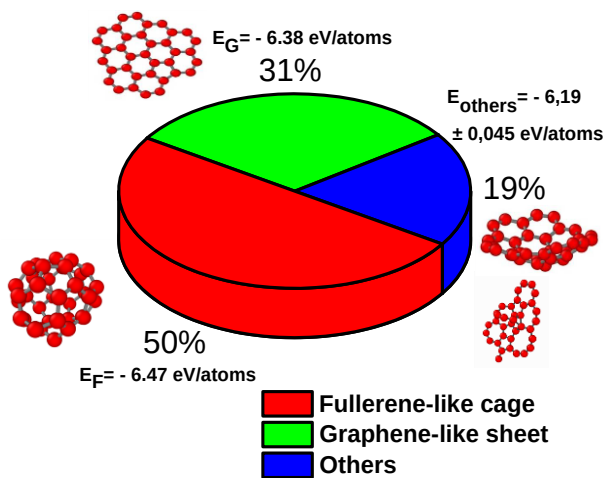


Fig. 3: Diagram showing percentages of appearance and energy of carbon isomers C_{36} .

4. Configurations and energies of carbon clusters

The SA-MD is then applied to a wide range of carbon clusters C_n ($n= 6- 60$). The stable geometries and energies for some clusters C_n are shown in Fig. 4. For these first results at least 4 cases have been performed.

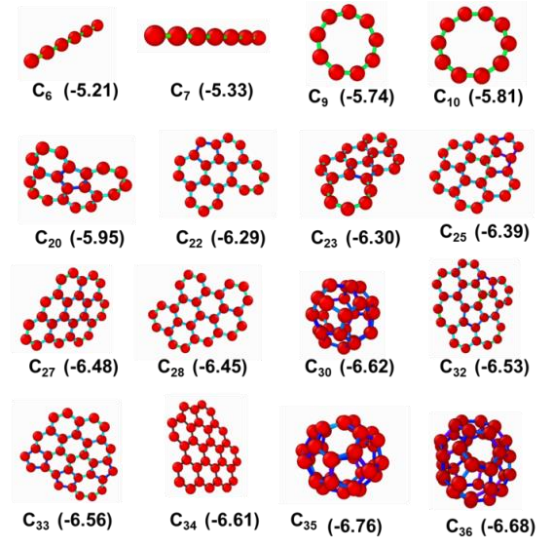


Fig. 4: The stables configurations for C_n clusters. The numbers in parentheses are the total energies per atoms (eV/atoms).

The most stable planar structure for small clusters ($n \leq 10$) is linear or monocyclic being in good agreement with several previous theoretical calculations [3, 5]. For a cluster size between 20 and 36 atoms, graphene-like sheet and fullerene-like cage are obtained in agreement with the results of the literature [4,6].

5. Conclusions

Simulated Annealing Molecular Dynamic simulation is used with the REBO potential to study neutral carbon clusters C_n ($n= 6-60$). In the present work we are interested in the study of the most stable clusters starting from gas phase carbon atoms. Our results show that C_n is linear or single ring for $n \leq 10$. We found that fullerene-like cage and graphene-like sheet can be formed as ground state for $n \geq 20$. The SA-MD method can be applied later to study the stable forms of hydrocarbon clusters with other interatomic potentials. Also, this method can be adapted to the real kinetics: study of the sticking between clusters.

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7. References

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See also <https://lammps.sandia.gov/index.html>