

# Combustion-generated Particles Nucleation: Molecular Dynamics Approach

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## Abstract

Nucleation of combustion-generated particles remains the less understood process in particle formation in combustion and it is a challenge for both experimental and modelling sides. Despite of the efforts spent on the topic, a conclusive description of the process is not reached yet, particularly the formation of the first molecular clusters and their morphology.

Molecular dynamic (MD) approach allows to describe punctually the evolution of the particles and of their principal constituent, i.e., the polycyclic aromatic hydrocarbons (PAHs). In this paper, a study of the evolution of PAHs and their possibility to form cluster has been performed by using a commercial MD code (GROMACS v4.6). By molecular dynamics, it is possible to get a detailed description of molecule evolution, monitoring the internal coordinate over the time. Knowing the location of all atoms in space, it is possible to identify the formed clusters and to study their time evolution and their internal structure.

Simulations of homomolecular systems have been performed at a temperature of 500 K using the velocity Verlet algorithm coupled with a Nosè-Hoover thermostat. Two representative PAH molecules, pyrene (C<sub>16</sub>H<sub>10</sub>) and coronene (C<sub>24</sub>H<sub>12</sub>), have been selected as starting molecules in order to study the influence of the different extension of the aromatic island on particle inception, size and morphology.

In the investigated conditions, pyrene shows a small amount of formed clusters whereas coronene form large number of clusters with different sizes. Looking at the evolution of the cluster size distribution, it is evident in the coronene simulation the formation of clusters of size up to 50 molecules, although a large part of the cluster are mainly constituted by 2-4 molecules. Molecular dynamic approach also allowed to analyse the morphological arrangement of the coronene clusters, showing a peculiar pile-structure for clusters constituted by less than 10 molecules.

## Introduction

Nucleation of combustion-generated particles has been highlighted as the key step for controlling both particle total amount and size distribution in modern combustion devices. Despite of the large reduction of total amount of combustion-generated particles in commercial devices none of the modern combustion systems can be considered particles emission free. The main concern for the emission control has now been shifted toward the reduction of the number of particles rather

than the total amount. This has moved the focus of the research toward the understanding of the nucleation process. This latter is responsible for the formation of freshly nucleated combustion-generated particles, which are dominant in the emissions in terms of number concentration.

Unfortunately, nucleation process is hard to isolate in a real flame and thus systematically studied. Large efforts have been spent with increasing success to give insights of the chemico-physical nature of these freshly nucleated particles by means of state-of-the-art experimental techniques, such as laser induced emissions, scanning particles sizer, atomic force microscopy, liquid chromatography, mass spectrometry, HR-TEM [1-5].

From experimental findings it is possible to state that these particles are formed close to the flame front and grow, chemically, in the post-flame regions, reaching molecular masses of the order of 200-1,000u. Thereafter, incipient particles with sizes of few nanometers are formed on timescales of the order of milliseconds. Physical interactions among PAHs are significant and are responsible for particle inception via the clusterization of the PAH molecules [4-5]. These particles are characterized by the concurrent presence of well-organized and amorphous regions. On the other side, modelers have improved the mathematical description of this process. The evolution of the small particles is well captured and a size-dependent coagulation efficiency has been now accepted and widely implemented in several models. However, most of the models uses a nucleation rate based on semi-empirical considerations extrapolating from expressions used for larger structure or by means of tuning parameters, which diminish the general validity of the models themselves.

In this sense, molecular dynamic (MD) approach has been recently claimed to be a valid tool to explore the nature of the nucleation process. Far to be straight forward applied in a more complex model for the description of the whole combustion process, MD show the best application for the study of a single process [6-7]. Lately, MD codes have applied to study the evolution of PAHs in controlled temperature environment, starting from their reciprocal interactions, described as a potential [8-11]. Since PAHs have been universally accepted to be the constituents units of the combustion-generated particles, their evolution and eventually their capability to form three dimensional structures results of great interest.

In this paper, a commercial MD code - GROMACS v4.6 [12] - has been applied for the study of the evolution of two gas phase PAHs, namely pyrene and coronene, in a low temperature environment. The MD simulations have been performed over long simulation time to study not only the first nucleation step but also the stabilization of the new PAH cluster into larger ones.

### **Molecular Dynamics Code**

All simulations were performed using a commercial MD code (GROMACS v4.6) [12]. Homomolecular systems of two representative PAH molecules were simulated at a temperature of 500 K using the canonical NVT (Number, Volume

and Temperature) ensemble that ensures a constant temperature during the simulations. Velocities and positions of all atoms in the system were obtained solving Newton's equation of motion. The simulations were performed using the velocity Verlet algorithm [13] as integration method, with an integration time step of 1 fs, coupled with a Nosè-Hoover thermostat [14] with a time constant of 0.05 ps. Pyrene and coronene were selected as starting molecules in order to observe the molecule size dependence on the clustering.

In each simulation, 1000 molecules were initially casually located in a cubical box at a concentration of  $2 \cdot 10^{18}$  PAHs/cm<sup>3</sup>, a concentration higher than the usually hydrocarbon rich real flames one. With these initial conditions, each nanosecond of simulation corresponds to 4 ms for a concentration of  $1 \cdot 10^{15}$  PAHs/cm<sup>3</sup>, typical of a flame [9-10]. Simulations were run for 6 ns to explore both the cluster formation and their successive evolution. The initial velocities were generated from a Maxwell-Boltzmann distribution at the reference T.

The non-bonded interaction of the interaction potential contain a repulsion and dispersion terms expressed as Lennard-Jones (LJ) potential form. The electrostatic term is neglected. The parameters used for the LJ potential are reported in Table 1. For the intramolecular interactions, the OPLS-AA force field parameters for bonds, angles and dihedrals were used [15].

**Table 1.** LJ potential parameters.

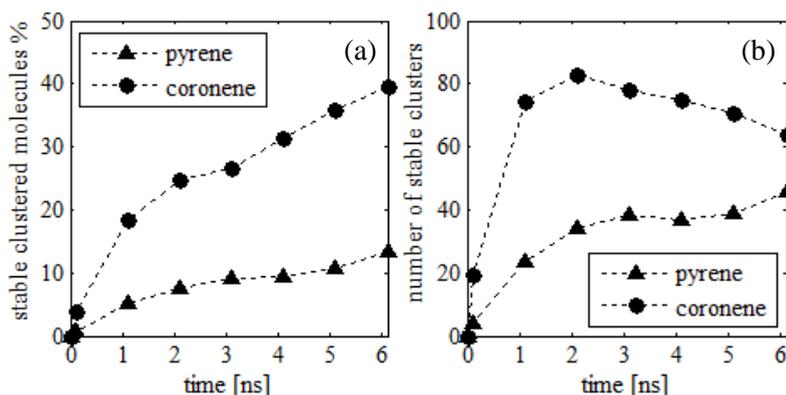
parameters	C-C	H-H	C-H
$\sigma_{ij}$ [nm]	0.3512	0.3011	0.3008
$\epsilon_{ij}$ [kJ mol <sup>-1</sup> ]	0.2571	0.08002	0.2362

Five trajectories for each PAH system were run and the clustering data were averaged over these runs. For identifying a cluster, it was necessary to define a distance cut-off ( $r_{crit}$ ) measured between molecule centers of mass and a critical period of time ( $t_{crit}$ ). Two molecules were considered in the same cluster if the distance of their centers of mass is lower than  $r_{crit}$  for a period of time bigger than  $t_{crit}$  [11]. Once the spatial location of all atoms was known from trajectories, stable clusters were identified by using  $r_{crit}=1.2$  nm and  $t_{crit}=16$  ps.

## Results and Discussion

The output of the simulations is a trajectory up to 6 ns, that represent the time evolution of molecules locations and velocities. Once the spatial location of all atoms is known, stable clusters can be identified according to the definition reported in the previous section.

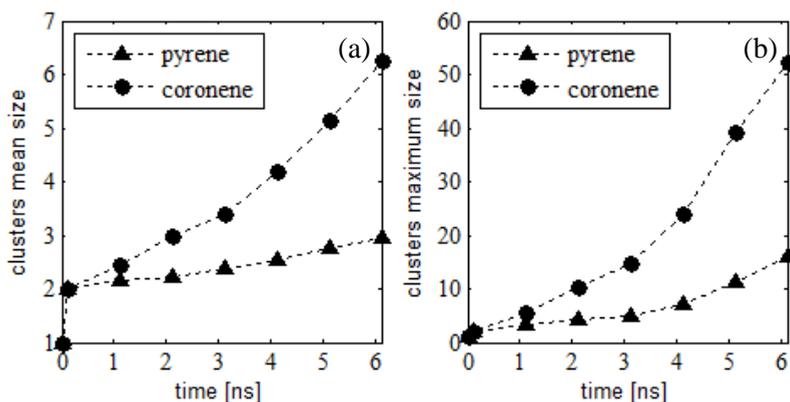
Figure 1 reports the percentage of stable clustered molecules and the number of stable clusters formed as a function of time for the two different systems investigated.



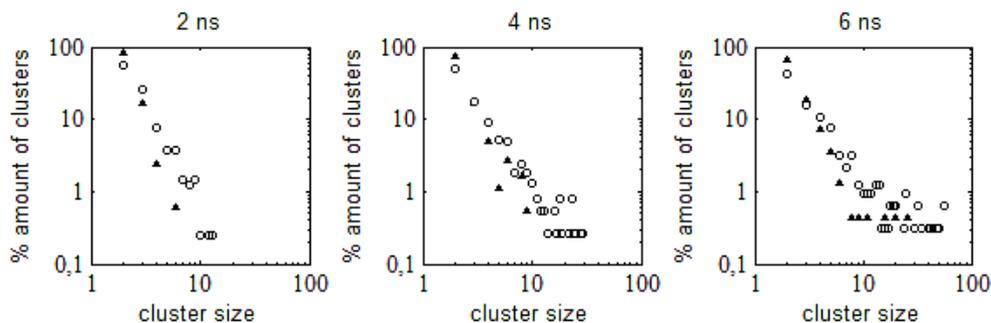
**Figure 1.** (a) Percentage of stable clustered molecules and (b) number of stable clusters formed vs MD time for coronene (circles) and pyrene (triangles) at 500 K.

In both cases, the percentage of stable clustered molecules increase with time: with coronene, the amount of clustered molecules reaches a value of 40%, more than three times higher respect to the pyrene system (14%). In addition, for the coronene system the number of clusters formed increases initially rapidly, reaching a maximum at 2 ns of simulation, and then it decreases slowly. The decrease of the number of cluster is a net result of cluster formation and cluster coagulation. Cluster formation, i.e. when two molecules stack together, increases the number of clusters, while particle coagulation, i.e. the collision between two clusters to form a bigger one, decreases the number of clusters. Initially cluster formation prevails on particle coagulation, Due to the large amount of free molecules in the system. Successively, cluster coagulation becomes predominant, due to the increase in number of formed cluster and the simultaneous decrease of free molecules in the systems. In this stage, the number of clusters decreases. This is also confirmed looking at the mean and the maximum cluster size evolution reported in figure 2. It is possible to note that in the coronene clusters reach large size up to 50 molecules) suggesting a more important coagulation process taking place. In the pyrene system, the number of clusters increases continuously with time suggesting that cluster formation rate is always faster than cluster coagulation. The mean and the maximum cluster size confirm this behaviour showing values significantly smaller than those found for coronene (2.8 and 16 molecules, respectively).

In figure 3, the cluster size distributions (CSD) for the coronene and pyrene systems are reported. In both cases, CDSs evolve towards the formation of clusters of increasing sizes. For the pyrene system, the amount of particle bigger than 10 molecules remains negligible also at 6ns. On the contrary, in the coronene system, the formation of clusters of size up to 50 molecules is clearly visible, although a large part of the clusters is mainly constituted by 2-4 molecules.



**Figure 2.** (a) Mean sizes and (b) maximum sizes of clusters formed vs MD time for coronene (circles) and pyrene (triangles) at 500 K.



**Figure 3.** Cluster size distribution for the coronene system (circles) and pyrene system (triangles) at 500 K after 2 ns, 4 ns and 6 ns of simulation.

## Conclusions

This article addressed a preliminary study of particle nucleation process by a molecular dynamics approach. Two PAHs molecules, pyrene and coronene, were chosen as starting molecules to analyze the effect of different masses of precursor molecules on the clusters obtained. The results show that the physical interaction between PAHs is a key step for the cluster formation. At 500 K, the molecules of coronene clusterize more than pyrene molecules, due to their strongest interaction. In the coronene case, a rapid increase in the number of particles formed is observed in the first 2 ns of simulation, whereas after that point the coagulation process becomes prevalent, making the number of cluster decrease and leading to the formation of particles of size up to 50 molecules. This is not observed for the pyrene system, where the number of cluster increases monotonically with the time and the clusters reaches a smaller size (16 molecules).

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