

# COAGULATION EFFICIENCY OF CORONENE AT FLAME CONDITION USING A MOLECULAR DYNAMICS APPROACH

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## Abstract

Stacking of polycyclic aromatic hydrocarbons is recognized as a key step in particle inception process in hydrocarbon-rich combustion. A conclusive description of the process is not reached yet. Indeed uncertainties remain on the molecules involved in the process and on their intermolecular potential function. A study of the evolution of coronene (C<sub>24</sub>H<sub>12</sub>) in a range of temperature (500 K-1500 K) have been performed in this paper by using a molecular dynamics approach in order to understand if coronene dimerization can be a key step in particle formation at flame temperatures. In order to relate the MD findings with soot formation models, the coagulation efficiency of coronene has been determined. At 1500 K, the coagulation efficiency is estimated to be 10<sup>-5</sup>, a value also used in some soot formation models presented in literature. To have a better estimation of this value, it is necessary to extend the study to a larger system or to perform a higher number of simulations for each case, so that the statistical analysis can be more accurate.

## Introduction

The nucleation of particles in hydrocarbon-rich combustion remains the least understood step in the process of soot formation because of the difficulty to experimentally isolate and systematically study the process in combustion environments. Nucleation is the passage from gas-phase high molecular mass molecules to compounds having condensed phase features. Polycyclic Aromatic Hydrocarbons (PAHs) have been recognized as precursor molecules in the nucleation process in hydrocarbon-rich combustion. They have been detected in flames [1-2] and they have been found in soot samples as adsorbed material [3-4].

Although the possibility of stacking gas phase PAHs in the nucleation process has been largely discussed in the literature [5-8], uncertainties remain on the exact nature of gas-phase PAHs involved and on their effective capability to form nanoparticles.

Pyrene (C<sub>16</sub>H<sub>10</sub>) stacking, also referred as dimerization, is widely used as the first nucleation step in many soot models [9-12] although Molecular Dynamics and/or ab initio calculations indicate that the percentage of clustered molecules at flame temperature is negligible for small PAHs molecules [13-14]. Coronene is also often

used as staking PAH to treat nucleation process in soot models. Also its coagulation has been studied previously with MD approach [14]. The aim of this work is to study the coronene dimerization in a range of temperature (500 K-1500 K) to understand if coronene dimerization can be a key step in soot particle formation. The homo-molecular coronene cluster formation is analyzed using a MD code (GROMACS) [15]. The coagulation efficiency is calculated for the system in all the range of temperatures considered and these values are compared with the values used in the soot kinetic model presented by D'Anna and Kent [11].

### Methodology

A classical MD approach has been used to study the clusterization of coronene molecules. Cluster formation from a gas-phase homo-molecular system of coronene molecules in a range of temperature (500 K-1500 K) were simulated using the canonical NVT ensemble (Number, Volume and Temperature).

MD simulations were performed using GROMACS v4.6 [15]. The simulations were performed by using the velocity Verlet algorithm [16] as integration method, with an integration time step of 1 fs, coupled with a Nosè-Hoover thermostat [17] with a time constant of 0.05 ps, according to best practice in literature for these systems [14]. In each simulation, 1000 molecules of coronene were initially casually located in a cubical box. The molecule concentration was  $2 \cdot 10^{18}$  PAHs/cm<sup>3</sup>. This concentration value is not reasonable, because it is much higher than that found in a flame environment but allows us to follow the clusterization events on a much shorter timescale. Indeed, according to the Eq. (1) [18]:

$$\Delta t_{\text{real}} \approx \Delta t_{\text{MD}} \left( \frac{n_{\text{MD}}}{n_{\text{real}}} \right)^2 \quad (1)$$

each nanosecond of simulation at  $2 \cdot 10^{18}$  PAHs/cm<sup>3</sup> corresponds to 4 ms for a concentration of  $1 \cdot 10^{15}$  PAHs/cm<sup>3</sup>, typical of rich hydrocarbon flames [19].

Simulations were run for 1 ns and the initial velocities were generated by a Maxwell-Boltzmann distribution at the reference temperature.

For the intramolecular interactions the OPLS-AA (Optimized Potential for Liquid Simulations-All Atom) force field parameters for bonds, angles and dihedrals were used [20]. The non-bonded term ( $U_{\text{nb}}$ ) is an atom-atom intermolecular interaction, sum over all pairwise atomic interactions between molecules (Eq. (2)).

$$U_{\text{nb}} = \sum_A \sum_{A < B} \sum_{a \in A} \sum_{b \in B} U_{ab}(R_{ab}) \quad (2)$$

Molecules are indicated by symbols A and B and atoms of these molecules are indicated by symbols a and b, respectively. The pairwise atomic interaction,  $U_{ab}$ , is function of the atom-atom separation  $R_{ab}$ . The iso-PAHAP potential developed by Kraft and co-workers has been used. The parameters and the form of the interaction potential have been taken from Ref. [14].

The output of the simulations was a trajectory up to 1 ns that represented the time evolution of all the atoms locations and velocities. Five trajectories for each temperature were run and all the data were averaged over these runs. Once the spatial location of all atoms, hence of all molecules, was known from trajectories, clusters were identified. For identifying a cluster, it was necessary to define a cut-off distance ( $r_{\text{crit}}$ ) measured between molecule centers of mass and a critical period of time ( $t_{\text{crit}}$ ). Two molecules were considered in the same cluster if the distance of their centers of mass was lower than  $r_{\text{crit}}$  for a time longer than  $t_{\text{crit}}$ . In this work, according to literature [14], stable clusters were identified by using  $r_{\text{crit}}=1.2$  nm and  $t_{\text{crit}}=16$  ps. Larger critical distances and interaction times did not modify significantly the results. The count of the clusters allowed to track total clustering vs time and to evaluate the cluster efficiency for the given system.

### Evaluation of the coagulation efficiency

In order to relate the MD findings with soot and nanoparticle formation models, we determined the collision efficiency  $\gamma$  of coronene from Eq. (3).

$$Z = \sqrt{\frac{8k_bT}{\pi\mu}} \gamma \pi \sigma^2 C^2 V t \quad (3)$$

where:

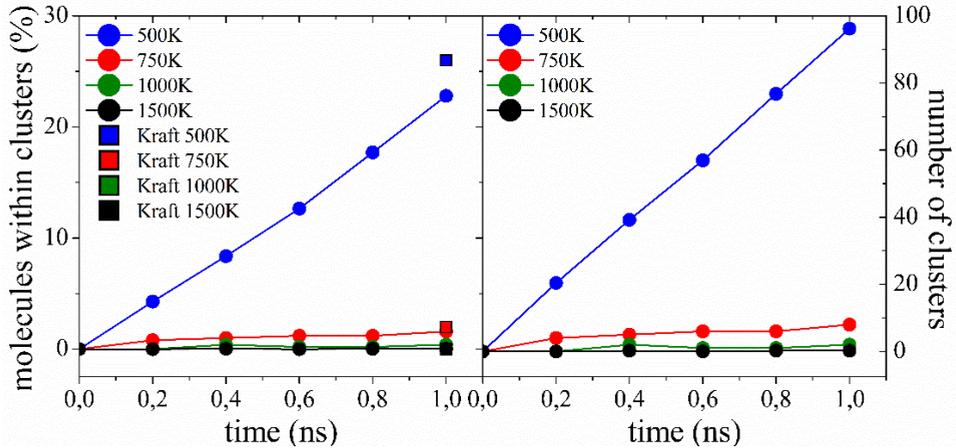
- $Z$  is the number of effective collision in the volume investigated assumed equal to the number of cluster formed.
- $k_b$  is the Boltzmann constant
- $T$  is the temperature
- $\mu$  is the reduced mass of two coronene molecules
- $\sigma$  = the coronene diameter
- $C$  = number concentration of coronene molecules in the system
- $V$  = volume investigated
- $t$  = time in which the collisions are considered.

### Results and Discussion

The percentage of clustered molecules and the number of clusters formed as a function of MD time at temperatures of 500 K, 750 K, 1000 K and 1500 K, is reported in Fig. 1. This percentage increases with time and it grows approximately linearly up to 20% after 1 ns at 500 K. As temperature increases, the percentage of clustered molecules decreases and it becomes very small at temperature higher than 750 K. Similar considerations can be done on the number of formed clusters. The results obtained are in good agreement with the results obtained by Kraft and co-workers [14] in the same conditions (1000 starting molecules and 5 trajectories for each system) and using the same interaction potential between molecules (Fig. 1). They conclude that in low-temperature regions of the flame (500 K– 1000 K), physical nucleation may still be a competitive route for particle inception and growth for molecules larger than pyrene and only circumcoronene was found to

dimerise at 1500 K [14].

To understand if coronene dimerization is not a competitive route in soot formation at flame temperature, in this work the MD results were related with soot formation models evaluating the coagulation efficiency of coronene.



**Figure 1.** Percentage of clustered molecules and number of clusters formed vs MD time at 500 K, 750 K, 1000 K and 1500 K. Squares refer to the result reported by Kraft and co-workers [14] at the same simulation conditions.

The collision efficiency  $\gamma$  has been computed from Eq. (3) at every temperature. The number of effective collision  $Z$  has been set equal to the number of clusters formed. This assumption is reasonable when every effective collision generates a new dimer in the system. This is true for all the system where the mean and maximum sizes are equal to 2, hence where  $T > 750$  K (Table 1). The results are displayed in Table 1.

**Table 1.** Mean and maximum sizes, number of effective collision and coagulation efficiencies after 1 ns, at 500 K, 750 K, 1000 K and 1500 K.

T	500 K	750 K	1000 K	1500 K
mean cluster size	2.37	2	2	2
maximum cluster size	7	2	2	2
$Z = n_{\text{clust}}$	96.2	8	2	0.2
$\gamma$	$3.5 \cdot 10^{-2}$	$2.5 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$4 \cdot 10^{-5}$

The calculated collision efficiency is of the order of  $10^{-5}$  at flame condition. This value is lower than the value used by D'Anna and Kent to model soot formation [11]. They use a collision efficiency of  $10^{-4}$  at 1500 K for two colliding particles with 1 nm of diameter. The difference between the two different values is probably related to a mean value of the number of clusters (0.2) obtained with a small

statistical sample. In fact, the clustering data was averaged over only five trajectories of 1 ns for each coronene system. All the papers using MD on PAHs clustering presented in literature use five trajectories for each case [13-14]. It might be probably the result of an inaccurate statistical analysis. The mean value of clustered formed at 1500 K is reported as example. As it is possible to observe from the results of the different runs reported in Table 2, the statistical sample seems not very representative.

**Table 2.** Coagulation efficiencies and other

Trajectory	1	2	3	4	5
Number of cluster	0	0	0	0	1
Mean value	0.2				

In order to have a more detailed and accurate statistical analysis:

- the clustering data should be averaged over an extended number of trajectories;
- the clustering data should be evaluated starting from a larger number of starting molecules.

### Conclusions

In this work, a study of the clusterization of coronene at different temperatures has been made using a MD approach. Same conditions and interaction potential of Ref. [14] has been used. We obtained a very small number of clusters formed at temperature higher than 750 K, with a collision efficiency of the order of  $10^{-5}$  at 1500 K, a value similar to that one used by D'Anna and Kent for modelling soot formation [11]. In our opinion, however, we cannot conclude that coronene dimerization is not a competitive route in soot formation, as stated in Ref. [14], as the statistical analysis seems to suffer for the limited dimension of the sample. In fact, a more accurate statistical analysis should be done extending the system dimension, or averaging the results over a larger and more representative number of trajectories. Only in this way, we could really understand if coronene dimerization plays an important role in the particle nucleation process.

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