

Molecular Dynamics Simulations for Structural Analysis of Combustion-Generated Particles

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Abstract

Combustion-generated particle nucleation remains the least understood process of particle formation. Stacking of polycyclic aromatic hydrocarbons (PAHs) has been recognized as key step of particle inception, but uncertainties remain on the PAHs involved in the process and on their interaction mechanism that determine the characteristic soot structure. In this paper, a study of the evolution of PAHs and analysis on the structure of particles obtained has been made using a molecular dynamics (MD) approach. Simulations of evolution of homomolecular systems at 500K have been performed using a MD code (GROMACS). Two different types of PAH molecules have been analysed in order to understand if they exhibit a different coagulation efficiency: coronene ($C_{24}H_{12}$) representative of pericondensed aromatic hydrocarbons (PCHAs), and dicoronene ($C_{48}H_{22}$) representative of aromatic aliphatic linked hydrocarbons (AALHs). A significative dependence of the coagulation efficiency has been found whether PCHAs or AALHs are considered. Successively, particle morphology has been systematically studied analysing the distribution function of the distances between the centres of mass of the coagulated aromatics. A different size and morphology of the nascent particles has been found. Looking at this indicator of internal disposition of molecules in the clusters, coronene clusters show mainly an ordered arrangement of stacked molecules whereas, an enhancement of disorder in the structure has been observed for clusters of dicoronene molecules.

Introduction

Combustion-generated particle nucleation remains the least understood process of soot formation, mainly due to the difficulty to isolate and systematically study nucleation process in combustion environment. Polycyclic Aromatic Hydrocarbons (PAHs) have been detected in flames and soot samples [1] and these molecules have been recognized being precursor compounds in the nucleation process in hydrocarbon-rich combustion [2]. The presence of amorphous regions and well-organized layered structure within soot particles, observed with high resolution transmission electron microscopy (HR-TEM) [3], has been interpreted as stacking of large PAHs. Uncertainties remain on the nature and structure of PAHs involved and on their capability to form three-dimensional structures.

The possibility of stacking gas phase PAHs has been largely discussed and it has been initially treated with a semi-empirical approach [4]. Nowadays more systematic approaches have been proposed and, from this point of view, molecular dynamics (MD) approach is a valid tool to explore the nature of the nucleation process. MD codes have been applied to study the evolution of PAHs in controlled temperature environment, starting from their reciprocal interactions, described as an interaction potential [5-9]. Frenklach and co-workers have used MD simulation with on-the-fly quantum forces to investigate lifetimes of dimers of aromatic molecules linked by aliphatic chains (AALHs) and peri-condensed aromatic hydrocarbons (PCAHs) [5,6] known to be both present in a flame environment [10]. They show that PAH dimerization is physically realistic at flame conditions and AALH dimers appear to have lower lifetimes than PCAH dimers of comparable mass. Similar studies have been made by Violi and co-workers using a classical MD approach [7,8]. They have modelled the clustering behaviours of small molecules of PCAHs and AALHs and fullerenes with different molecular masses at different temperatures providing information on the clustering behaviour of the different aromatic structures. Similarly, Kraft and co-workers have performed MD simulations on clustering of different PCAHs [9]. The aim of this work is to gain insights on the nucleation mechanism of PAHs and their different clustering behaviours in dependence on different morphologies of precursor molecules. Internal organization of clusters has been systematically analysed and correlated to initial molecular structure. Finally, cluster images obtained with different starting PAHs have been compared with HR-TEM images of nascent soot particles.

Molecular dynamics simulations

MD simulations were performed using GROMACS v4.6 [11] to study cluster nucleation of PCAHs and AALHs [10]. Particularly, the attention was focused on coronene ($C_{24}H_{12}$), representative of PCAHs, and on the aromatic molecule containing two coronene connected by a σ -bond, dicoronene (1,2-coronil-coronene, $C_{48}H_{22}$), as representative of AALHs. These molecules were chosen in order to understand the effect of the structure of precursor molecules on the clusterization and on the morphology of nascent particles. The methodology is the same used in a similar work presented last year [12] in which the effect on the clusterization of molecular mass of precursor molecules has been studied. Homomolecular systems were simulated at temperatures of 500K using the canonical NVT ensemble. Velocities and positions of all atoms in the system were obtained solving Newton's equation of motion. The simulations were performed by using the velocity Verlet algorithm [13] as integration method, with an integration time step of 1fs, coupled with a Nosè-Hoover thermostat [14] with a time constant of 0.05ps. In each simulation, 1000 molecules of coronene or 500 molecules of dicoronene were initially casually located in a cubical box. The different number of initial molecules ensured a constant number of aromatic sub-units in the systems because dicoronene have two aromatic sub-units inside the molecule. The concentration used is $2 \cdot 10^{18}$

PAHs/cm³ is unreasonable in a flame environment but allows us to follow the clusterization events on a much lower timescale. In fact, each nanosecond of simulation at $2 \cdot 10^{18}$ PAHs/cm³ corresponds to 4ms for a concentration of $1 \cdot 10^{15}$ PAHs/cm³, typical of a rich hydrocarbon flame [7]. Simulations were run for 6ns and the initial velocities were generated by a Maxwell-Boltzmann distribution at the reference temperature.

The interaction potential was computed as sum of the non-bonded and the bonded terms. The non-bonded term is an atom-atom intermolecular interaction, sum over all pairwise atomic interactions between molecules. The pairwise atomic interaction contains a repulsion term and a dispersion term expressed as Lennard-Jones (LJ) potential form. The electrostatic interactions were neglected. The parameters used in the Lennard-Jones potential are the same used in ref. [12]. These parameters were set such that the used LJ interaction potential had a potential well value similar to the isotropic potential used to model interactions between PCAHs (iso-PAHAP) developed by Totton et al. [9]. For the intramolecular interactions, the OPLS-AA force field parameters for bonds, angles and dihedrals were used [15]. The hydrogen bonds, that have the highest stretching frequencies in these systems, were treated as constraints in the equation of motion. The reason for this choice is that the algorithm can use larger time steps when the highest frequencies are removed.

The output of the simulations is a trajectory up to 6ns that represents the time evolution of molecules locations and velocities. Five trajectories for each PAH system were run and the clustering data were averaged over these runs. Once the spatial location of all atoms is known from trajectories, stable clusters can be identified. For identifying a cluster, it was necessary to define a cut-off distance (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} . Stable clusters were identified by using $r_{\text{crit}}=1.2\text{nm}$ and $t_{\text{crit}}=16\text{ps}$ [9]. Larger critical distances and interaction times do not modify significantly the results. The internal structure of clusters was analysed by calculating the distances between centers of masses of monomers, i.e. the aromatic sub-unit, in the same clusters. The obtained distance distribution function (DDF) is a first indicator of order within the structure.

Results and discussion

Figure 1 reports the percentage of stable clustered molecules and the number of stable clusters formed as a function of MD time for the two systems investigated at temperatures of 500K. In both cases the percentage of stable clustered molecules increases with time. The amount of clustered molecules reaches in the coronene system a value of 40%, after 6ns. The σ -bonded molecules show a higher clusterization propensity than the respective PCAHs. The percentage of clustered molecules is slightly higher in dicoronene with respect to coronene. The strongest clusterization of σ -bonded molecules (AALHs) is associated with their capability

to accommodate the collision energy through vibrations, bending and rotations around the σ -bond increasing the lifetimes of formed cluster.

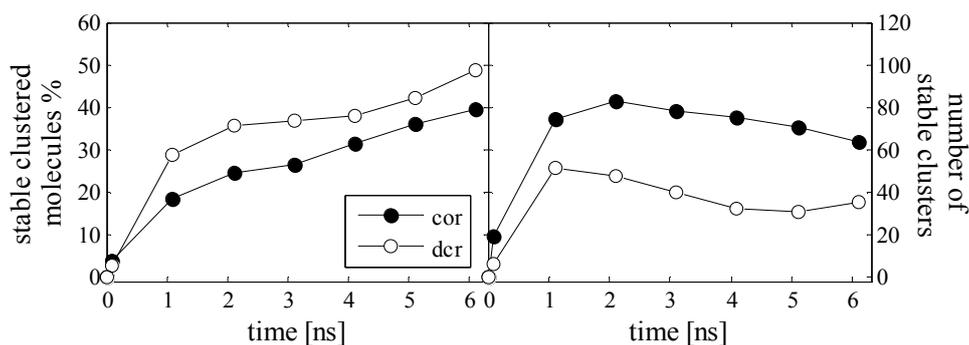


Figure 1. Percentage of stable clustered molecules (left column) and number of stable clusters (right column) vs MD time for coronene (cor-●) and dicoronene (dcr-○) at 500K.

The number of clusters formed in the coronene and dicoronene systems initially rapidly increases, reaching a maximum at 2ns and at 1ns of simulation, respectively, and successively slowly decreases. The decrease of the number of clusters is a net result of cluster formation and cluster coagulation. Cluster formation, i.e., when two free molecules stack together, increases the number of clusters, while cluster coagulation, i.e., the collision between two clusters to form a bigger one, decreases the number of clusters. Initially cluster formation prevails over cluster coagulation, due to the large amount of free molecules in the system. Successively, when cluster coagulation becomes predominant, due to the increase in number of formed clusters, the number of clusters decreases.

Additional analysis has been made to have a quantitative description of cluster internal structure. Cluster morphology has been analysed by calculating the distances between centers of mass of aromatic sub-units in the same clusters. Figure 2 reports DDF of the clusters formed after 6ns at 500K.

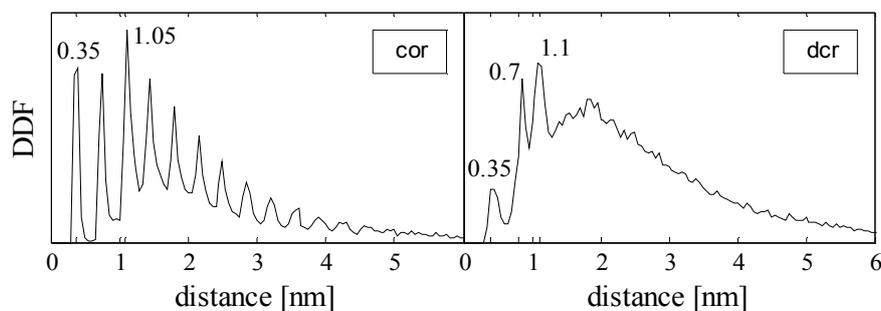


Figure 2. DDF after 6ns of MD time at 500K: coronene (left column) and dicoronene (right column).

This is due to a stacked arrangement of the molecules in the structure. The major peak is located at around 1.05nm that is a multiple of 0.35nm and incidentally also corresponds to the distance between two coronene placed side by side and it suggests the presence of stacks of molecules placed side by side. Looking at the DDF for dicoronene, the peaks mostly disappears and a broader distribution can be seen. Also, for dicoronene it is possible to distinguish the peak of the internal distance between aromatic sub-unit centers of mass (1.1nm) are evident. Finally, in the dicoronene case, a peak at 0.7nm can be distinguished suggesting that a large number stacks of 3 monomers are still present within the clusters. This latter result suggests that in dicoronene the cluster structure is characterized by the concurrent presence of well-organized regions (presence of sharp peak at 0.35 nm and 0.7 nm) and amorphous regions (broader distribution for distances larger than 1nm). In Fig. 3 clusters sections of the biggest cluster formed in both systems are compared to HR-TEM images of a nascent soot particle [3]. The σ -bonded molecule clusters show a good similarity with experimental images. PCAHs form more organized structures and they tend to assume cylindrical shape. On the contrary, the σ -bonded molecules clusters exhibit a more spherical morphology.

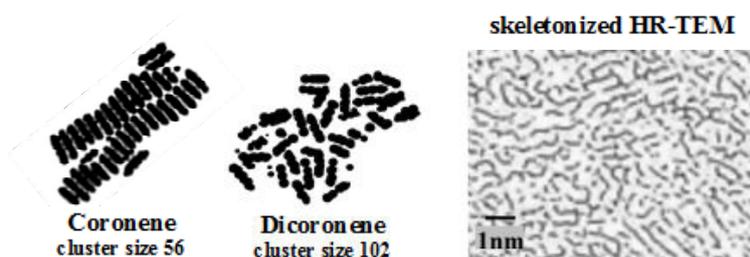


Figure 3. Cluster section of biggest cluster formed and HR-TEM image of nascent ethylene soot adapted from Ref. [3]. The cluster size is defined as the number of aromatic sub-units present globally in the cluster.

Conclusions

MD simulations were performed for two different type of aromatic molecules, PCAHs (coronene) and σ -bonded aromatic molecules (dicoronene) at 500K to investigate cluster formation. At this temperature clusters were formed for both the aromatics; the σ -bonded molecules are more effective than the corresponding PAHs, suggesting that the presence of the σ -bond improves the inception of clusters. Analysis of internal structure of formed clusters shows that ordered structures are formed in coronene clusters. The presence of the σ -bond in the stacking aromatics gives disorder to the structure of the formed clusters, due to an increased number of molecules not arranged in parallel planes. The DDF for dicoronene appears broad and not structured. Analysis of the sections of the formed cluster confirm this finding, suggesting that σ -bonded molecules form cluster with more similar internal structure to what found through HR-TEM images.

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