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Molecular dynamics simulations of incipient carbonaceous nanoparticle formation at flame conditions

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Particle nucleation remains one of the most intriguing steps in the process of particle formation in flames. Although stacking/clustering of polycyclic aromatic hydrocarbons (PAHs) has been identified as a key step in the nucleation process, uncertainties remain about the size of the PAHs undergoing clustering, the organisation of the PAHs in the forming clusters and the factors affecting the relative amounts of order and disorder present in the texture organisation. A molecular dynamics approach is presented to study the influence of the molecular weight and structure of PAHs on the nucleation and coagulation processes and on the morphology of the formed clusters. Two different types of macromolecules have been analysed: pericondensed aromatic hydrocarbons (PCAHs) and aromatic aliphatic linked hydrocarbons (AALHs), known to be present in flame environments depending on flame temperature, equivalence ratio and fuel chemical structure. Clustering of six organic molecules has been analysed at two extreme temperatures, namely 500 K and 1500 K. The six molecules have been chosen on the basis of their molecular weight (pyrene and coronene) and molecular structure (single molecules, covalent-bonded dimers and covalent-bonded trimers). Nucleation of single pyrene molecules is negligible at low temperature and practically absent at high temperature. Conversely, nucleation of single coronene molecules involves 33% of the initial molecules at low temperature. Molecules within the clusters are highly mobile at flame temperatures and just 5% of the initial molecules are in clusters. The presence of covalent bonds among the aromatic sub-units improves clustering and growth, both for pyrene and coronene sub-units. Looking at the structure and the fractal dimensionality of the formed clusters, an enhancement of the disorder of the clusters is observed in the case of the AALHs (dimers and trimers) with an increased number of molecules not arranged in parallel planes. The same behaviour is found for the higher temperature.

Keywords: molecular dynamics; particle inception; PAH; fractal dimensionality

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the main precursors of particles in flames. They are formed close to the flame front and grow through chemical reaction pathways in the post-flame regions, reaching molecular masses in the order of 200–1000 u. These molecules are the building blocks of incipient particles with sizes of few nanometres that are formed on timescales in the order of milliseconds.

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The transition from gas-phase molecules to particles is not well understood although the use of new and sophisticated diagnostic techniques in recent years has increased our knowledge of particle inception and growth as well as of particle morphology [1–7]. The presence of stacked PAH molecules was revealed by HR-TEM [5,8–10] and AFM [11] in nascent soot particles. These particles are characterised by the concurrent presence of well-organised and amorphous regions. Many hypotheses have been advanced. The most intriguing one is that the order arises due to stacking of planar PAHs to form parallel atomic layers; the disorder is due to the presence of randomly oriented and/or non-planar PAHs. The hypothesis is also corroborated by the evidence that the combustion environment, in which particles are formed, producing different amounts and types of PAHs, determines the final concentration of the particles as well as the organisation at atomic scale [1,9,12]. Moreover, the PAH pool formed in flames contains a large amount of non-planar PAHs, i.e. those containing a 5-membered ring or an alkyl-side chain or covalent σ-bonds, so that their role in soot inception cannot be excluded a priori [13–15]. Therefore, it appears that the chemical structure of PAH molecules, their concentration, together with the combustion environment in which they are formed, may control the morphology of the particles.

Based on this experimental evidence many modelling attempts have been implemented [16–24]. Despite the general good agreement of the proposed models, the inception problem is still modelled by lumped reactions and a semiempirical coagulation efficiency. Recently more detailed treatment of the inception problem has become possible due to more sophisticated approaches, especially molecular dynamics (MD) methods [25–33]. By means of MD it is possible to get a detailed description of molecule evolution, monitoring the internal coordinates over the time. The trajectories of atoms and molecules in a control volume are determined by numerically solving the Newton’s equations of motion, where forces between the interacting entities in the system and their potential energies are calculated using interatomic potentials or molecular mechanics force fields.

The possibility to investigate the interaction between colliding PAH molecules by means of a potential describing their reciprocal interactions is an interesting approach to obtain information on the morphology of the forming clusters. In this paper a MD code has been implemented to study the clustering characteristics, in terms of cluster morphology, of two different types of aromatic macromolecules: pericondensed aromatic hydrocarbons (PCAHS), such as pyrene and coronene, solely constituted by fully-condensed aromatic islands, and aromatic-aliphatic-linked hydrocarbons (AALHS), constituted by aromatic molecules linked by σ-bonds, such as in the bi-phenyl molecule. MD can help understanding if the clustering of these two types of PAH molecules results in different morphologies of the nascent particles.

It is beyond the purpose of the study to analyse the effect of adopting different interaction potentials in the modelling of the nucleation process, knowing how important it is to replicate the intermolecular interactions. Our aim is to examine differences and similarities in the morphology of the incipient particles when the homomolecular clusterisation of PCAHs and AALHs occurs by using an isotropic intermolecular potential recently proposed and assessed in the literature; see [28] and references within. In particular, attention is focused on two representative PAH molecules, pyrene (C_{16}H_{10}) and coronene (C_{24}H_{12}), and on aromatic molecules containing pyrene and coronene connected by one σ-bond, i.e. bi-pyrene (C_{32}H_{18}) and bi-coronene (C_{48}H_{22}) or by two σ-bonds, i.e. tri-pyrene (C_{48}H_{26}) and tri-coronene (C_{72}H_{32}). A schematic representation of the coronene molecules and its oligomers, bi- and tri-coronene, is reported in Figure 1. In our calculations, these compounds are the colliding entities and hence the interacting molecules. The model is tested for a typical concentration of aromatic molecules in a hydrocarbon rich flame at two extreme
temperatures, namely 500 K and 1500 K, in order to investigate the morphology of the clusters generated during combustion and during the cooling process at the exhausts.

**MD simulations of PAH clustering**

The MD code used in this work is a modification of the code developed by De Candia et al. [34]. To mimic molecule interactions, MD is performed at constant number, volume and temperature (NVT) using the velocity Verlet algorithm [35], to integrate Newton’s equations of motion, and the Nosé–Hoover thermostat [36,37] with a time step of $1 \times 10^{-3}$ times the simulation time step $t_0$, to keep the temperature steady and to avoid continuous energy drifts caused by the accumulation of numerical errors during the simulations [38]. The simulations time step is calculated from the units of energy, mass, and length, chosen a priori, in the following way:

$$t_0 = \sqrt{m_0 \sigma_0^2 / \varepsilon}$$

(1)

where $m_0$, $\sigma_0$ and $\varepsilon$ are the mass unit, the length unit, and the energy unit expressed in $k_B T$, respectively ($k_B$ is the Boltzmann constant and $T$ is the temperature in K).

Following Totton and co-workers [28], an isotropic potential for molecule interaction specifically developed for PAHs is adopted in this work. Atom–atom intermolecular potentials approximate the total interaction energy $U$ as a sum over all pairwise atomic interactions between molecules. Molecules, indicated by $A$ and $B$, were constituted by atoms $a$ and $b$ respectively, and were modelled as rigid bodies, neglecting relative molecular orientation. The total atom–atom interaction potential as a function of the atom–atom separation, $R_{ab}$, is therefore:

$$U = \sum_A \sum_{A < B} \sum_{a \in A} \sum_{b \in B} U_{ab} (R_{ab}) .$$

(2)

The form of the isotropic PAH potential is given by:

$$U_{ab} = G \exp \left[ -\alpha_{ab} (R_{ab} - \rho_{ab}) \right] - f_6 (R_{ab}) C_{6,iso} / R_{ab}^6 + q_a q_b / R_{ab} .$$

(3)

The atom–atom interaction potential in Equation 3 is calculated as sum of three terms: the first term is the short-range Born–Mayer term, the second is the dispersion term and the third is the point-charge electrostatic term. The short-range contribution is damped with a constant $G$, whereas the dispersion term is damped with a Tang–Toennies damping function
Table 1. Interaction parameters used in the calculations for different pairwise atomic interactions. The damping coefficient $\beta$ has been set equal to 1.6485 and the pre-exponential factor $G$ to 0.001, according to Totton et al. [28].

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>$\rho$</th>
<th>$\alpha$</th>
<th>$C_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>6.0434</td>
<td>1.8783</td>
<td>30.282</td>
</tr>
<tr>
<td>C-H</td>
<td>4.9562</td>
<td>1.7560</td>
<td>12.605</td>
</tr>
<tr>
<td>H-H</td>
<td>4.1195</td>
<td>1.4043</td>
<td>5.2179</td>
</tr>
</tbody>
</table>

$[39] f_n(R_{ab})$, given by Equation 4:

$$f_n(R_{ab}) = 1 - \exp(-\beta R_{ab}) \sum_{k=0}^{n} (\beta R_{ab})^k / k!$$

(4)

Three pairwise atomic interactions are possible: C-C, C-H and H-H. Table 1 reports the values of the parameters $\rho$, $\alpha$ and $C_6$ in the literature [28].

The interaction potential for pyrene and coronene is calculated following the procedure reported above. Pyrene and coronene molecules are treated as rigid bodies, i.e. the constituting atoms keep their initial positions and the intramolecular interactions, as well as vibrational modes, are not modelled. As PAH molecules are relatively rigid and possess high intramolecular frequencies, the capability of accommodating collision energy into intramolecular modes is limited and thus intermolecular modes will be most important in determining cluster stability [28]. Moreover, the nucleation efficiency is determined by intermolecular interactions, depending on the relative position of the whole aromatic islands and not by the positions of the atoms within them.

When considering dimers and trimers, an additional strong interaction between pairs of pyrene and coronene molecules is added as schematised in Figure 1. This bond allows the relative bending and rotation of pyrene and coronene. Unlike the intramolecular interactions within the pyrene or coronene molecule, the $\sigma$-bond is modelled using a strong interaction potential in order to avoid its break-up while allowing its stretching, shrinking and vibration.

The number of molecules, i.e. pyrene, bi-pyrene and tri-pyrene and coronene, bi-coronene and tri-coronene, the volume and the temperature are fixed. We consider 1000 PAHs (either pyrene or coronene) for each simulation, i.e. the dynamic behaviour of 1000 monomers, 500 dimers and 333 trimers is simulated separately. The size of the ensemble is chosen as a compromise between computational efforts and physical carefulness, as the number of collision is statistically relevant to draw conclusions on nucleation efficiency.

A system of particles of the same type is considered, arranged at the initial time on a regular cubical lattice, in a vacuum, with no force of viscous friction nor any kind of thermal noise. No additional interactions (physical and chemical) are considered, besides the ones existing between the PAHs and described by an intermolecular potential. This assumption is well established in MD approaches, although it is well known that in flame-like environments, chemical reactions between PAHs and the surrounding gases can occur as well as other phenomena like the pyrolysis of hydrocarbons.

The interaction potential as a function of the intermolecular distance is truncated to a distance of $3.5\sigma_0$. For each particle, the three components of the velocity are correlated to
\[ \langle V_x^2 \rangle = \langle V_y^2 \rangle = \langle V_z^2 \rangle = \frac{T}{m} \]  

This average value is multiplied by a factor smaller than 1, which is generated in a pseudo-random function, included in the code, so that the kinetic energy of all the particles respects the Maxwell–Boltzmann distribution. For each time step, the forces acting on the particles are derived from the interaction potential, the equations of motion are solved and new positions of the particles are determined.

One of the problems in MD simulations is to relate MD timescales to the real process timescale. The nucleation of soot takes place over milliseconds [24] and running MD simulations for such time periods with a suitably small time step would be impractical. If we assume that collisions between molecules are distributed randomly, such that the event of a collision does not affect the probability of a subsequent one, then the behaviour seen over real nucleation timescales can be approximated by observing denser systems over shorter timescales, as already reported [28,32]. However, there are some limitations to this approach: by using inflated system densities, the oversaturation of the system is increased, which in turn reduces the critical cluster size according to classical nucleation theory [40]. While soot nucleation, in the sense of the formation of critical clusters, cannot be studied in this way, the approach is still valid when the purpose is to study the morphology of inception particle.

The characteristic nucleation time in a flame can be related to the simulation nucleation time in a denser system using Equation 6:

\[ \Delta t_{\text{flame}} = \Delta t_{\text{MD}} \left( \frac{n_{\text{MD}}}{n_{\text{flame}}} \right)^2 \]  

In this study, the number of molecules and the volume are set for all the cases equal to \(2 \times 10^{18}\) PAHs cm\(^{-3}\). This concentration is higher than that usually found in rich flames. By using the relationship between the MD time and the flame residence time, a simulation of 1 ns at a density of \(2 \times 10^{18}\) molecules cm\(^{-3}\) corresponds to approximately 4 ms in real flame conditions, i.e. in a flame containing aromatic concentrations of the order of \(1 \times 10^{15}\) molecules cm\(^{-3}\) [22]. This gave us a plausible way to approach experimental timescales.

Clusters are defined in the code on the basis of the distance between molecule centres of mass, introducing a cut-off distance, \(R_{\text{crit}}\), related to the size of the molecules involved and their interaction potential, i.e. the position of the potential well. This definition accounts for both long-living clusters and instantaneous ones. The first ones can be considered stable clusters, whereas the latter ones can be the result of an inefficient collision due to high repulsive forces or too high kinetic energy involved. In order to discern between these two types of clusters, a critical time, \(t_{\text{crit}}\), is set to distinguish the stable clusters, with lifetime longer than \(t_{\text{crit}}\) from the unstable ones. \(R_{\text{crit}} = 1.5\) nm and \(t_{\text{crit}} = 20\) ps are set for the present study [28].

An analysis of the dependence of the number of stable clusters on the critical time is performed; by increasing the critical time, the number of stable clusters decreases until a plateau value is reached for times as long as 15 ps. To avoid any influence of the choice of the critical time on the results, a value of 20 ps has been set in the present work.
Results and discussion

Five trajectories, i.e. time evolution of molecule location and velocity, up to 1 ns are run for each different PAH system. At the selected conditions (number of molecules, concentration, simulated time), the computational cost of each trajectory is about 24 h on four-processor machine. The number of trajectories is considered sufficient to draw a plausible statistics on the number of stable and unstable clusters, as reported in the literature [28,33]. Data analysis is made on the values averaged over all the runs. Stable clusters, unstable clusters and not clustered molecules are identified according to the definition above reported. Figure 2 shows the percentage of clustered (stable and unstable) molecules at the two temperatures for the different molecules, after 1 ns. As temperature increases, the percentage of clustered molecules decreases for all the analysed cases. As expected increasing the size of the molecules, i.e. from pyrene to coronene, the number of clustered molecules increases. Even at 500 K very few pyrene clusters are formed, about 5% of the total molecules, in agreement with literature results [6,28], indicating that the interaction potential is too weak to allow pyrene molecules to stick together after a collision, whilst cluster formation slightly increases if bi-pyrene and tri-pyrene molecules are considered.
The average number of molecules in a cluster increases from three to four and six moving from pyrene to bi-pyrene and tri-pyrene at low temperature. At low temperature, about 50% of the formed clusters are unstable, i.e. their lifetime is below the critical value, except for tri-pyrene, which forms only 5% of unstable clusters over a total of 27% clustered molecules.

At low temperature coronene already shows a much higher tendency to form clusters, being 33% of the initial molecules in clusters, constituted by at most seven elements. It is noteworthy that a very low percentage of unstable clusters is formed in this case. These results, as well as that for pyrene, are in good agreement with the results of Totton and co-workers [28], who used similar methodology.

Moving from coronene to bi-coronene and tri-coronene, a strong cluster formation is observed together with the almost complete absence of unstable clusters. The strongest formation of clusters, when bi- and tri-molecules are considered, is associated with the strongest interaction between the molecules. Indeed, even though the size of the aromatic island remains the same, in a collision event involving two bi-coronene molecules the two colliding entities account for four aromatic islands. The presence of the $\sigma$–bond increases the global interaction, increasing the probability to form a stable cluster. Comparing bi-pyrene and coronene cluster formation at low temperature, it appears that bi-pyrene has a lower tendency to form clusters with respect to coronene although both molecules, coronene and bi-pyrene, have a comparable interaction potential, i.e. seven aromatic rings for coronene and eight aromatic rings for bi-pyrene. This result indicates that the inclusion of a $\sigma$–bond between aromatic islands reduces the capability of the whole molecule to interact, probably because the $\sigma$–bond induces a non-planarity to the molecule, for the effect of bending and rotation around the bond, thus reducing the molecule interaction. The effect can be noted also comparing tri-pyrene and bi-coronene. In tri-pyrene, the presence of two $\sigma$–bonds creates a more tridimensional shape for the molecule reducing the capability of the $\pi$ electrons to reach an interaction distance.

At high temperature, the amount of clustered molecules reduces, as expected. Moreover, the number of unstable clusters increases: more than 50% of the clusters are unstable for all the configurations. In the case of pyrene, stable clusters at high temperature are not observed.

Looking at the number of clusters, stable and unstable, formed by bi-pyrene and coronene molecules at 500 and 1500 K, the tendency to form clusters decreases as temperature increases and the reduction is more severe for coronene than for bi-pyrene. The same behaviour can be observed comparing tri-pyrene and di-coronene and can be related to the presence of the $\sigma$–bond between aromatic islands. The overall potential well is wider for bi-pyrene and tri-pyrene, compared to coronene and bi-coronene respectively, because of their geometry. At high temperature, a monomer, e.g. coronene, is less attracted by the potential well of another approaching monomer with respect to the case of two colliding dimers, e.g. bi-pyrene, given the same distance between their centres of mass. As a result, the $\sigma$–bond can mitigate the negative effect of increasing temperature on cluster formation efficiency, so that bi-pyrene seems to form clusters easily, compared to coronene, and tri-pyrene and bi-coronene show a comparable tendency to form clusters.

At high temperature the $\sigma$–bond reduces the stability of the formed cluster, as the relative percentage of unstable clusters over the total number of clusters is higher for bi-pyrene and tri-pyrene, with respect to coronene and bi-coronene. This result is in agreement with the work reported by Wong et al. [26], who studied bi-collisions of AALH dimers using MD and reported substantially lower lifetimes for AALH than for PCAH of comparable masses.
The mean number of molecules per cluster remains small, around three molecules/cluster, at high temperature, for coronene, bi-coronene and tri-coronene.

In order to study the morphology of the formed clusters, the total MD time was increased up to 10 ns at 500 K and 20 ns at 1500 K. In this way the number of molecules constituting the cluster increases, reaching a plateau value. Figure 3 shows the number of elements clustered as a function of the MD time for coronene, bi-coronene and tri-coronene at 500 K. The final number of elements in the cluster is much lower than the total number of molecules in the control volume, so that the critical size of the cluster cannot be attributed to a lack of molecules, which limits cluster formation, but to a reduced average velocity of the larger clusters, which hinders the probability that they can meet other colliding entities. It is also interesting to note that tri-coronene forms clusters with the largest number of molecules at lower MD times whereas bi-coronene forms clusters with the highest number of molecules at larger MD times.

Cluster morphology is analysed by calculating the fractal dimension of the clusters. Fractal analysis is used to characterise irregularly shaped objects on the basis of their volume variations relative to their sizes. Several studies have been performed on carbonaceous aerosol aggregates aiming to describe their morphology through the fractal analysis of TEM images [41,42], whereas studies on the fractal analysis of incipient particles are missing. Hence, our data cannot be compared with experimental data.

The fractal dimension $D$ relates the mass of the incipient cluster, $M$, to the radius, or in general a characteristic size of the object, $L$. In particular:

$$M \propto L^D, \quad (7)$$

where $M$ is the mass of a cluster calculated from the number of molecules within it. Figure 4 shows the dependence of the cluster size, i.e. the number of clustered coronene molecules, on its radius at 500 K after 5 ns. The continuous line in the figure represents the characteristic curve of a compact spherical configuration; the dashed line represents the characteristic curve of elongated structures. Clusters up to about 1.25 nm, i.e. six molecules/cluster, are clearly compact, while, as the size increases, the dependence suggests the presence of
Figure 4. Coronene clusters size as a function of radius, at 5 ns and 500 K. The continuous line represents the characteristic curve of a compact spherical configuration, while the dashed line represents the characteristic curve of elongated structures.

Figure 5. Simulated images of two clusters of coronene formed at 500 K and 5 ns (left hand side) and 10 ns (right hand side). Each coronene molecule is represented as a disk.

elongated structures up to 2.2 nm (equivalent spherical diameter) with 15 molecules in the cluster. Larger particles are not formed because the number of molecules in the cluster remains constant.

Figure 5 reports a typical image of simulated clusters formed by coronene at 500 K and 5 and 10 ns of MD time. Stacked PAH structures and less ordered structures can be seen. Columnar PAHs never exceed three or four molecules in reasonable agreement with experimental high-resolution transmission electron microscopy (HR-TEM) images of young soot particles [8–10].

Bi-coronene molecules show similar behaviours in terms of morphology. Figure 6 reports the number of bi-coronene molecules in the cluster as a function of the radius of the sphere in which they can be comprised at 500 K after 10 ns MD time and 1500 K after 20 ns MD time. The two MD times correspond to the same residence time in the flame, considering the effect of the temperature on the molecule velocity and on the sticking efficiency [43].

Clusters having the same size, i.e. containing the same number of molecules, are less compact at high temperature. The different morphology at high temperature is also clearly
Figure 6. Bi-coronene clusters size as a function of radius, at 10 ns and 500 K (triangles) and at 20 ns and 1500 K (crosses). The insert reports the region of the graph between 1 and 3 nm where the morphological differences at high temperature are more evident. The continuous line in the insert represents the characteristic curve of a compact spherical configuration; the dashed line represents the characteristic curve of an elongated structure.

seen in the inset of Figure 6: at 500 K the bi-coronene cluster grows as an almost compact sphere while at 1500 K the cluster has an enhanced random growth with a less compact morphology.

Conclusion
A MD approach is presented to study the influence of the molecular structure and molecular weight of PAHs on the nucleation and coagulation processes and on the morphology of the formed clusters. Simulations were conducted in a canonical NVT ensemble with cubical periodic boundary conditions, coupled with a Nosé–Hoover thermostat. The intermolecular interactions were modelled using a PAH isotropic potential and the molecule trajectories were integrated using the velocity Verlet algorithm.

Two different types of macromolecules were analysed: PCAHs and AALHs, known to be present in the flame environment depending on flame temperature, equivalence ratio and fuel chemical structure. Simulations were performed at two extreme temperatures, namely 500 K and 1500 K for six molecules, namely pyrene, bi-pyrene and tri-pyrene, and coronene, bi-coronene and tri-coronene.

Nucleation of single pyrene molecules was almost absent at low temperature and not observed at high temperature. Nucleation of coronene molecules at low temperature occurred through the formation of clusters consisting of not more than seven molecules: only a maximum of four molecules were organised in parallel planes (columnar phase) while the remaining ones were arranged in a disordered patterns (amorphous phase). The total percentage of clusters, stable and unstable, formed by coronene turned out to be almost 33% at low temperature and only 5% at high temperature. These results are comparable
with those obtained by other groups \[28,32\] and show that the molecules of PAHs within particles are highly mobile at flame temperatures.

The presence of covalent bonds connecting two or more aromatic islands improved the inception and growth mechanisms of the clusters and mitigated the negative effect of increasing temperature on cluster formation efficiency, although at comparable interaction potentials the inclusion of a \(\sigma\)–bond between aromatic islands reduces the capability of the whole molecule to form stable clusters.

Looking at the structure and the fractal dimensionality of the formed clusters, an enhancement of the disorder of the clusters in the case of the AALH (dimers and trimers) was observed with an increased number of molecules not arranged in parallel planes and elongated structures, but organised in a spherical texture. Increasing the temperature, and looking at clusters formed by the same type of molecule, a decrease of the compactness was found.

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**Disclosure statement**

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