



Simulating the morphology of clusters of polycyclic aromatic hydrocarbons: The influence of the intermolecular potential



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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, indeed uncertainties remain on the molecules involved in the process and on their intermolecular potential function. A study of the evolution of coronene ($C_{24}H_{12}$) at a temperature of 500 K and additional analysis on the morphology of particles obtained have been performed in this paper by using a molecular dynamics approach. Four intermolecular potentials, which differ for their function forms and magnitudes of the interaction involved, have been tested in order to outline the difference in cluster formation and morphology. The cluster formation is strongly dependent on the magnitude of potential interaction, while it is weakly dependent on the differences in the repulsive branch of the potential function. Potentials which have a similar interaction intensity but have two different repulsive branches, exhibit very similar percentage of clustered molecules, number of cluster formed and cluster mean sizes. The electrostatic interactions do not remarkably affect the cluster formation propensity, but different morphologies are found. The electrostatic term increases the disorder in the structure of the formed clusters for all the investigated potentials, due to an increased number of molecules not arranged in parallel planes. The use of a systematic approach to analyze the internal structure and shape of the formed cluster allowed to have a better comparison between the potentials and their capability to reproduce realistic configurations.

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1. Introduction

The nucleation of particles in hydrocarbon-rich combustion remains the least understood step in the process of particulate matter – soot – formation because of the difficulty to experimentally isolate and systematically study the process in hostile combustion environments.

Nucleation is the passage from gas-phase high molecular mass molecules to compounds having condensed phase features. Aromatic compounds have been recognized as the precursor molecules because they have been detected, at not-negligible concentrations, in flames [1–2] and are collected in soot samples as adsorbed material [3–4]; moreover, soot particles, observed via high resolution transmission electron microscopy (HR-TEM), have been found to be constituted by aromatic layers generally organized in a turbostratic structure [5–6]. These layers have been interpreted as the stacking of large polycyclic aromatic hydrocarbons (PAHs). Experimental findings also show that soot extracted in

the post-flame region can contain significant amounts of aliphatic components relative to aromatics [7–8]; it suggests that aliphatic chains or bridge formation between aromatic parts can also play an important role in soot formation.

Although a consensus is found in the literature about the central role of PAHs in the nucleation process [9–15], the presence of many different compounds in soot particles gives uncertainties on the exact nature of the gas-phase PAHs involved in the process. It is worth to remind that nucleation strongly influences the total amount of soot formed because soot loading occurs through reactions of gas-phase species with the existing nuclei surface, consequently a correct modeling of the nucleation process is a prerequisite for the modeling, in a predictive way, of the soot formation in combustion.

Several possible pathways have been presented in literature for soot nucleation. The first hypothesis considers fullerene-like structures as the nuclei for soot particles [16–17]. Although fullerene species has been detected in flames [18], it is known that their formation is too slow to be taken into account for soot nucleation. Other pathways involves the stacking of moderate-sized PAHs [9–13] and/or the reaction or chemical coalescence of PAHs into crosslinked three-dimensional structures [12–13,19–20].

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Despite the several pathways proposed in literature for soot nucleation, many research groups agree on moderately sized PAH stacking [14] as the initial nucleation step. Pyrene ($C_{16}H_{10}$) stacking, also referred as dimerization, is widely used as the first nucleation step in many soot models [21–26] although Molecular Dynamics and/or ab initio calculations indicate that the percentage of clustered pyrene molecules at flame temperature is negligible [27–28]. Coronene on the other hand has a non-negligible dimerization efficiency [27–28], but its concentration in flames is significantly lower than pyrene and hence the global dimerization rate, i.e., the probability of two coronene molecules to meet and to remain attached, is also low.

The dimerization efficiency depends on the interaction potential among colliding molecules. The intermolecular potential between two molecules is given by the sum of non-bonded atom-atom pair potential functions. The latter is the sum of three contributions: the repulsive and attractive terms and the electrostatic term. A good knowledge of the nature and magnitude of intermolecular forces is necessary to fully understand the interaction and to have a reliable prediction of their capability to form dimers [28–29].

The calculation of intermolecular potential energy can be done with accurate ab-initio techniques, with semi-empirical quantum mechanical methods or with empirical atom-atom potentials parametrization. Semi-empirical and empirical methods are computationally much faster than ab-initio calculations [30]. Semi-empirical potential methods are more accurate than empirical potential parametrizations because they are based on a quantum mechanical model, but their use is limited to small size systems and short timescales, of the order of picoseconds, due to computational costs [31–33].

The formation of clusters and their morphologies, i.e., bigger size systems evolving on longer timescales, can be studied with reasonable computational costs only by using empirical potentials. Different empirical potentials are reported in the literature. A Buckingham potential (exp-6 potential) parametrization has been proposed by Williams [34] and has been used for the calculation of the intermolecular interactions of homo-molecular and hetero-molecular clusters of PAHs by Miller and co-workers [29,35]. A Lennard-Jones (LJ) type parametrization has been proposed by Van de Waal [36]. It was calculated by fitting the position and depth of the minima of the Buckingham potential sets of Williams [34]. Violi and co-workers have used this LJ-type potential to model the clustering behaviors of small PAHs and fullerenes at different temperatures [27,37]. Both empirical potentials proposed by Williams [34] and Van de Waal [36] are parametrized to match the heat of sublimation of aromatic hydrocarbons and crystallographic data.

An anisotropic potential developed by Kraft and co-workers has been parametrized using ab initio results, to model interactions between PAHs (PAHAP potential) [38]. Comparing with the reference energies taken from ab initio symmetry-adapted perturbation theory -SAPT(DFT)- calculations performed by Podeszwa and Szalewicz [39], the PAHAP potential accurately models interaction energy for a variety of dimer configurations for different PAH molecules [38]. An isotropic form of the PAHAP potential (iso-PAHAP potential) was developed successively by the same group. It differs from the PAHAP potential because it is no longer orientation-dependent. This potential has been used to perform MD simulations on clustering of PAHs with sizes ranging from pyrene ($C_{16}H_{10}$) to circumcoronene ($C_{54}H_{18}$) in a wide range of temperatures (500–1500 K) [28]. Recently, Iavarone et al. have used the iso-PAHAP potential [40] to simulate the organic molecules in the same range of temperatures.

The choice of the interaction potential seems to affect the obtained result. Indeed, MD studies on the stacking of PAHs that used the potential functions above described [27–28,37,40] show different results in terms of capability of PAH molecules to stack and

form clusters. In the papers reported in the literature, great attention was paid to the effect of the shape and the intensity of the potential well on the total amount of the PAH clustered, but less attention is paid to the effect of the interaction potential on the morphology of the formed clusters.

Few works on cluster morphology are present in the literature. Rapacioli et al. have studied the most stable configurations of clusters of PAHs using a global optimization approach [41]. Clusters of PAHs have been modeled using the LJ potential parametrization of Van de Waal [36]. Kraft and co-workers have done a similar work where they presented a study of the clusters assembled from PAHs molecules similar in size to small soot particles using a stochastic ‘basin-hopping’ global optimization method [42]. Most of these studies report calculations of potential energy of pre-assembled PAH clusters to outline what are the lowest-energy cluster structures. Systematic or statistic studies of the morphology of the clusters dynamically formed from PAH clustering has not been done, yet. Cluster morphology represents a key aspect and it is crucial in determining the reactivity of the formed condensed structures.

The aim of this work is hence to study the effect of intermolecular forces with different parametrization forms and magnitude not only on the global clustering behaviors but also on the morphology of the formed clusters. For the first time, statistical analysis of the morphology of the formed cluster is reported, introducing the internal distance distribution and a structural parameter. The homo-molecular coronene cluster formation at a temperature of 500 K is analyzed using a MD code (GROMACS) [43]. The internal organization and shape of the clusters is systematically analyzed to show the main differences related to the intermolecular potential function used.

2. Methodology

2.1. Molecular dynamics simulations

In order to study the stacking of PAHs, a classical MD approach has been used. The molecular dynamic approach allows to study the evolution of PAHs into clusters considering that the clustering process is a non-equilibrium process. Cluster formation and evolution from a gas-phase homo-molecular system of coronene molecules at fixed temperature of 500 K were simulated using the canonical NVT ensemble (Number, Volume and Temperature). A low temperature (500 K) was chosen to simulate the systems, in order to have a large number of formed clusters, necessary to carry out a statistical analysis of the cluster morphology. As reported in other papers, the choice of a higher temperature does not lead to the formation of a significant number of clusters [27–28]; a good analysis of cluster morphology is hence not allowed.

MD simulations were performed using GROMACS v4.6 [43]. 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 [44] as integration method, with an integration time step of 1 fs, coupled with a Nosé–Hoover thermostat [45] with a time constant of 0.05 ps, according to best practice in literature for these systems [28].

In each simulation, 1000 molecules of coronene were initially casually located in a cubical box. The molecule concentration was $2 \cdot 10^{18}$ PAHs/cm³. This concentration value is not reasonable; 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) [37]:

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

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