A TIME-SCALE PROBLEM FOR THE FORMATION OF SOOT PRECURSORS IN PREMIXED FLAMES

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Introduction

This paper applies a previously developed tool to study the molecular transformations that occur in combustion conditions during the transition from gas phase precursors to soot particles.[1-2] To help resolve issues such as identification of pathways leading to soot formation, it is important to characterize the soot precursors, in terms of chemical structure/components. Questions like structure-pathways and structure-property relationships may lead to a deeper understanding of soot growth mechanisms. We want to address these questions theoretically by studying the growth of molecules in combustion environments, using Kinetic Monte Carlo (KMC) and Molecular Dynamics (MD) methodologies.

The processes involved in soot precursor formation exhibit a wide range of time scales, spanning pico- or nanoseconds for intramolecular processes that can occur on a particle surface to milliseconds for the formation of the first soot precursors. In order to accurately describe the soot formation process, we need to model the reactions happening at different time scales. The coupling of KMC and MD methodologies allows us to do so. The code, named KMC/MD, combines the strengths of KMC for long-time sampling, and MD for relaxation processes is based on that developed at LLNL.[2] The time-duration between Monte Carlo events can be arbitrarily long (depending on the kinetics, model. etc), while in Molecular Dynamics, we require time steps which are a small fraction of a vibrational period. So the combination of the two techniques spans two time- and equilibrium scales. The reaction rates among the compounds present in the system are calculated using electronic configuration methods, and they are specified as probabilities.

This approach is designed to preserve atomistic scale structure: a single particle evolves in time with real three-dimensional structure (bonds, bond-angles, dihedral angles). Some preliminary results have been reported in an earlier publication for the simulation of the evolution of soot precursors in an ethylene premixed laminar flame.[1,3]

In this paper the KMC/MD code is used to study the growth of aromatic structures to a nano-size range in the soot inception zone of aromatic and aliphatic laminar flames. The aromatic growth process strongly depends on the specific local regime, which is characterized by several experimental factors such as temperature, concentration of hydrogen, PAH, etc., and it is interesting to understand the influence of different environments on structural properties of the compounds formed. The use of this approach enables the investigation on the physical as well as chemical properties of the carbonaceous nanoparticles formed, such as H/C ratio, and particle morphology. After summarizing in the following section the methodological details of the computations performed, the results of hydrocarbon compounds growth are discussed in two different environments represented by low pressure aromatic and aliphatic flames.

Methodology

Molecular Dynamics, in which one chooses an appropriate interatomic potential to describe the forces between atoms and then integrates the classical equation of motion, is the most direct approach among atomistic simulations. However, the limitation in the accessible simulation time represents a substantial obstacle in making useful predictions with MD. Resolving individual atomic vibrations requires a time step of approximately femtoseconds in the integration of the equations of motion, so that reaching times of even microseconds is very difficult. In order to solve this time scale problem, MD methodology has been coupled to KMC to allow the extension of the accessible time scale by orders of magnitude relative to direct MD, while retaining full atomistic detail. During the KMC module[4-6] one escape path is chosen randomly from a list of possible transition events, weighted by the rate constant, and the system is advanced to that new state. The clock is then incremented in a way that is consistent with the average time for escape from that state, which can be determined easily from the rate constants for the possible escape paths in the list. The two methods differ in their ability to explore phase space. The ability of the KMC method to make non-physical moves can significantly enhance its capacity to explore phase space in appropriate cases. Its capability to generate states directly has many advantages, including bypassing configurations which may be difficult to escape dynamically. And so the method can be used to study the configurations of systems which may be expensive or impossible to access via MD.

Molecular Dynamics may not be able to cross the barriers between the conformations sufficiently often to ensure that each conformation is sampled according to the correct statistical weight. MD can be very useful for exploration of the local phase space whereas the KMC method may be more effective for conformational changes which jump to a completely different area of phase space.

The time-step for a single KMC iteration is a "real time," determined by the kinetics system. The reaction rates among the compounds present in the system are specified as probabilities and the surface configuration over time is then given by a master equation, describing the time evolution of the probability distribution of system configurations.

A more detailed description of the methodology is reported elsewhere.[1-3]

Conditions analyzed

Below we report the computational results obtained for the growth of aromatics in two premixed laminar flames of aliphatic and aromatic fuels in order to determine the influence of different environments, and hence reaction pathways, on the structures of particles. A low-pressure benzene-oxygen flame C/O=0.8 with an unburned velocity of 42 cm s^{-1}, p= 2.66 kPa,[7] and an acetylene/oxygen flame at a pressure of 2.67 kPa[8] have been experimentally studied by Homann and co-workers, who measured PAH and PAH radicals for these flames by mean of resonant (REMPI) and nonresonant multiphoton ionization with a frequency-doubled, pulsed dye laser and separation with a time-of-flight mass spectrometer, equipped with an ion reflector. These experimental data are used to validate the code in terms of structure properties, such as H/C ratio.

The two major inputs to the KMC/MD code are represented by the number and concentration profiles of the species that characterize the gas phase and that can contribute to the growth process and by the reaction rates that describe the velocity with which the gas-phase species are added to the growing seed. Acetylene, H, naphthalene, and acenapthylene species are considered in this work as key contributors to the PAH growth process and used as input to the

KMC/MD code. The choice of the input PAH is due to their presence in high concentrations in the PAH inventory, and to the importance that PAH with peripherally fused five-membered rings (CP-PAH), which include acenaphthylene, have in the flame formation chemistry of soot[9-10,11,12,13,14,15] and fullerenes.[16] Acetylene is the most abundant building block[17] and contributes to the HACA mechanism. The concentration profiles have been calculated using the CHEMKIN package[18] together with a kinetic model previously developed.[19]

In using these concentrations in the atomistic model, no allowance was made in the calculated hydrocarbons and H profiles for species depletion or temperature change. A detailed description of the gas-phase species involved, and the reactions that can occur in the system, together with their rates is reported elsewhere.[20]

Results and Discussion

Homann and co-workers reported the molecular formulas of PAH in a C/H diagram for the two flames, where each point corresponds to a certain compound C_xH_y. The experimental data have been re-plotted in **Figure 1** as diamond points for the aromatic[7] *(1a)* and aliphatic[8] flames *(1b)*.

The totality of points represent the ensemble of PAH and PAH radicals with different molecular formulae. The formulae of six-ring PAH with most peri-condensed ring structures like coronene, ovalene, etc. lie on the dotted line in the diagrams. The points above the line represent PAH that are H-rich and those below that are H-poor with respect to these most condensed 6-ring structures. The authors also emphasized that large H-rich PAH play an important role in reactions, both with respect to growth and consumption, irrespective of whether they are molecules or radicals.[7] As most of the PAH are pericondensed, enriched hydrogen in their structure means 4C bays or larger coves at which reactions could take place preferentially. The results obtained through the use of KMC/MD code are plotted as filled circles on the same figure. The use of the KMC/MD methodology allows us to follow the evolution of structures in a chemically specific way. The computed data are in good agreement with the experimental results in terms of H/C ratio, and show the formation of H rich compounds corresponding to open elongated PAH with bays and coves. PAH formation does not follow a narrow path in the C-H diagram but a broad band due to the variance in H content for the same number of C atoms; the molecular formulas of the PAH form a band that widens toward larger PAH. This observation indicates that with an increase in the number of C atoms, the bandwidth for the H content becomes larger. This behavior becomes more pronounced when the fuel is changed from acetylene to benzene. The KMC/MD method is able to reproduce this trend too and this is due to the different contribution of the reaction pathways to the growth of the aromatic compounds. Having a diverse molecular base and not only the reaction sequence of hydrogen abstraction and addition of acetylene molecules to the radical site previously formed may lead to a network of aromatic-aliphatic linked structures.

The results reported in **Figure 1** are both relative to two conditions within the oxidation zone of the flames. We did that in order to emphasize the influence that the two environments have on the structures of the compounds formed. The relative contribution of the different types of growth reactions seems to depend on the fuel. In the case of aromatic fuels polymerization reactions can occur early since aromatics are in relatively large concentrations in the fuel, whereas in the case of aliphatic fuels such as acetylene, ethylene or methane the first aromatic ring must be formed from fuel decomposition products by a sequence of elementary reactions and therefore the concentrations of aromatic soot precursors are in lower concentrations than in the aromatic flames.
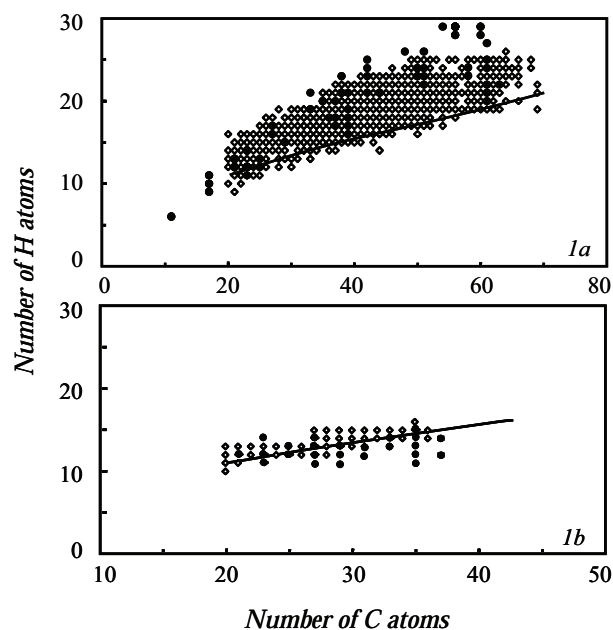

Figure 1. Hydrogen and carbon content for the aromatic (a) and aliphatic (b) flames.

In benzene flames, PAH are formed in concentrations about 100 times those found in aliphatic fuel flames of the same C/O ratio.[21] Their maximum concentrations occur within the oxidation zone and decrease at the end of it where most of the carbon is formed. Polyacetylenes arise in the oxidation zone but their concentration does not decrease as rapidly in the region where molecular oxygen has been consumed. An important difference consists in unsaturated hydrocarbons present in the oxidation zone, i.e. C_2H_2 in acetylene flames, and benzene and PAH in benzene flames. During the combustion of benzene, the benzene molecule itself is an important reactant for the formation of higher molecular weight PAH. In contrast to acetylene, benzene is completely consumed, even before the end of the oxidation zone. In the vicinity of the temperature maximum benzene is no longer available as a building block for larger molecules or particles. Within a benzene flame C_2H_2 is formed as the temperature increases. At the end of the oxidation zone, C_2H_2 is present in nearly the same concentrations as those found in acetylene flames.
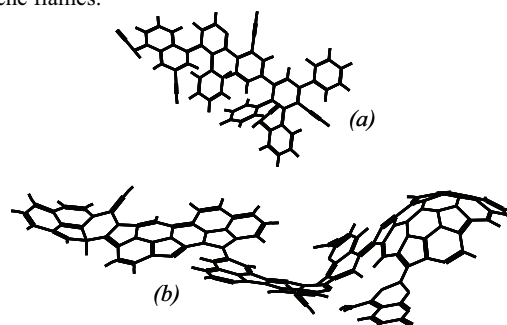

Figure 2. Intermediate compounds formed in aliphatic (a) and aromatic (b) flames.

Figure 2 reports the structures of two intermediate compounds formed in the aliphatic *(2a)* and aromatic flame *(2b)*. In the first case

the compound formed is still mainly planar and the contribution of acetylene is significant. In the lower part of the figure, the structure formed in the aromatic flame shows already three-dimensional characteristics and the contribution of aromatic hydrocarbons, such as benzene, naphthalene is prevalent.

Another important characteristic of these particles is their morphology. Ellipticity parameters are often used to characterize particle shape.[22] In order to characterize ellipticity, the aspect ratio AR is computed

$$AR = a/b$$

where a and b are the axes of the ellipse that has as its center the object's centroid.

A series of diameters of the particles are sampled. The average of these diameters is used as the spherical diameter r_s of the configurations, and an average of the longer diameters is used as "a", and an average of the shortest ones is used as "b". A better evaluation of *a* and *b* can be obtained using the Legendre ellipse that has the same geometrical moments up to the second order as the original object area. The Legendre ellipse is often used instead of the original object. The aspect ratio of the particle, defined as a/b, is reported in **Figure 3** as a function of the diameter (ED) calculated for an equivolume spherical particle.
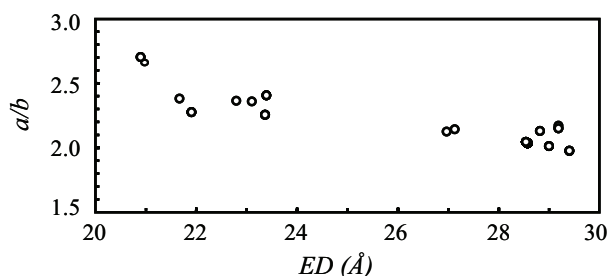

Figure 3. The aspect ratio of soot precursor molecules as a function of equivalent spherical diameter in acetylene flame (in Angstroms).

The aspect ratio of a circle is one and of an ellipse with the ratio of axes 2:1 is equal to two. The aspect ratio for the ellipse increases with an increase in the ratio of the major and secondary axes. The aspect ratio is seen to increase with increasing particle size.

The elongated shapes exhibited by the young nanoparticles is supported by "in situ" measurements on soot evolution in flames. Light scattered by nanoparticles is more depolarized than that scattered by soot particles and the depolarization ratio increases as the particle deviate from the spherical shape.[23]

Concluding Comments

The paper presents the application of Kinetic Monte Carlo and Molecular Dynamic to study soot inception in aliphatic and aromatic flames. Formation of carbonaceous nanoparticles can be followed in a chemically specific way. Properties of the particles, such as H/C ratio and morphology have been computed, showing the presence of elongated shapes for young nanoparticles. The influence of two different environments, an aromatic and aliphatic flame, is assessed in terms of structures of the particles formed. The use of this approach will enable the investigation on the physical (e.g., porosity, density, sphericity) as well as chemical (e.g., H/C, aromatic moieties, number of cross-links) properties.

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