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Modelling PAH curvature in laminar premixed flames using a detailed population balance model

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ABSTRACT

A detailed population balance model, which includes the kinetic Monte Carlo-aromatic site (KMC-ARS) model for detailed polycyclic aromatic hydrocarbon (PAH) growth, is used to compute the Gauss curvature of PAHs in laminar premixed ethylene and benzene flames. Previous studies have found that capping of an embedded 5-member ring causes curvature in graphene edges. In this work, a capping process is added to the KMC-ARS model with the rate coefficient of the capping reaction taken from the work of You et al. (2011). We demonstrate that the Gauss–Bonnet theorem can be used to derive a correlation between the number of 5- and 6-member rings in a PAH and its Gauss curvature (or radius of curvature), independent of where the 5-member ring is embedded within the PAH structure. Numerical simulation yields satisfactory results when compared to the experimentally determined Gauss curvature reported in the literature. Computed and experimental fringe length distributions are also compared and the results suggest that PAHs smaller than the size required for inception are able to condense onto particles.

1. Introduction

The buckminsterfullerene (C_{60}) was first discovered during the condensation of carbon vapour after the laser bombardment of graphite [1]; subsequently, C_{60} and other fullerenes were discovered in flames [2]. Fullerenes are a class of 3-D closed shells which contain exactly 12 pentagons. Their shape and size depends on the arrangement of pentagons as well as the number of hexagons. One can also consider them to be 2-D as the carbon atoms only form a molecular sheet [3]. Sheets containing less than 12 pentagons are open shells with the limiting case being a flat sheet. In a comment on the role of fullerenes in soot formation in flames, Frenklach and Ebert [4] argue that polycyclic aromatic hydrocarbons (PAHs) can curve through the incorporation of 5-member rings and can grow through sequential buildup of benzene and acenaphthylene to form fullerenes. They further argue that partially closed carbon clusters may collide and stick together while open shells continue to grow forming layers around the adducts; an explanation that is consistent with experimental high-resolution transmission electron microscopy (HRTEM) images of soot collected from flames which show multiple centres surrounded by concentric circles (see, e.g., Ref. [5–9]). Quantitative measurements of these sheet-like PAHs otherwise referred to as lattice fringes have been made including measurements such as the fringe length, interlayer spacing and, more rarely, radius of curvature [5,6].

To model the 3-D evolution of PAH structures in different flame environments, Violi et al. [10–12] employ a fully-coupled kinetic Monte Carlo-molecular dynamics (KMC-MD) code which has a detailed PAH growth mechanism. Frenklach and co-workers [13–15] use a similar model which includes many more reactions creating 5- and 6-member complexes and more recently has been extended to include oxidation reactions [16]. However, these simulations are computationally very expensive. Therefore, these simulations are limited to the tracking of a single, non-interacting PAH; whereas experimental HRTEMs show that soot particles are made up of multiple layers of stacked PAHs. Kraft and co-workers employ a detailed population balance model [17] which is solved using a stochastic numerical method [18]. The model describes particles as

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aggregates composed of primary particles which are in turn composed of individual PAHs, thus containing information on particle size, morphology, and the internal structure of the particles. These particles undergo coagulation, sintering and particle rounding due to condensation and surface growth. This is the PAH-primary particle (PAH-PP) model [19]. The KMC-aromatic site (KMC-ARS) model tracks each of the PAHs in the particles which evolve according to a list of jump processes [20,21] which make use of the steady-state assumption [22] for all intermediate species to reduce the computational expense of the simulations. This particular modelling approach has been used to simulate soot formation in laminar flames (see, e.g., Ref. [17–19,23,24]) and engines (see, e.g., Ref. [25]). The KMC-ARS model is unable to predict curvature because it does not allow the incorporation of 5-member rings and it only tracks the coordinates of the carbon atoms which describe the edge of the PAH. But the Gauss–Bonnet theorem [26,27] which relates the integral of the Gauss curvature over a compact surface, i.e. its total Gauss curvature, with an integer naturally associated to it, i.e. its Euler characteristic, may be of help to us.

The purpose of this paper is to extend the PAH-PP/KMC-ARS model such that we can not only track PAHs but also allow the inclusion of 5-member rings and to track the associated change in curvature using the Gauss–Bonnet theorem. Computed fringe length distributions are also compared with experimental measurements [6]. As fringe length is thought to be related to PAH size, these comparisons allow us to investigate the minimum PAH sizes required for inception and condensation which may be different. The influence of different fuels is also briefly studied. First, the flame chemistry and structure are computed using a steady-state burner-stabilised premixed laminar flame code. Second, the particle dynamics is solved using a detailed population balance model where the PAH growth mechanism is extended to allow for the incorporation of 5-member rings which leads to PAH curvature.

2. Computational method

The computational method consists of two parts. In the first part, species profiles are computed using a modified version of PREMIX [28], including calculation of the source terms by the method of moments with interpolative closure (MOMIC) using the code published by Revzan et al. [29]. The ABF mechanism, which includes combustion chemistry and the formation and growth pathways of PAHs up to pyrene, and species thermodynamics and transport properties [30,31] are supplied as input. Note that the ABF mechanism includes the mechanism for benzene combustion. The experimental temperature profile [32,33] is imposed to ensure full agreement between the experimental temperature and that seen by the soot model. The transport equations of the moments of the particle size distribution (PSD) are solved to account approximately for the production and consumption of key gas-phase species due to inception, condensation, surface growth and oxidation. A total of six moments, including the zeroth moment, are solved using MOMIC to close the moment transport equations. In the second part, a detailed population balance model is applied as a post-processing step where the imposed temperature and computed species profiles from PREMIX are supplied as input.

We investigate two different flames and the flame conditions are summarised in Table 1. These are atmospheric pressure sooting flames where the main difference is that flame A [32] is an ethylene flame ($\phi = 2.4$) while flame B [33] is a benzene flame ($\phi = 2.0$). PREMIX simulations are performed using windward differencing and considering multicomponent transport and thermal diffusion. About 150 grid points are found to be sufficient for convergence.

3. Detailed population balance model

A detailed population balance model [17] is used to model soot formation by postprocessing the PREMIX simulations of the burner-stabilised laminar premixed flame. The growth of PAH species within the model is described by a kinetic Monte Carlo-aromatic site (KMC-ARS) model [20], starting from pyrene. The dynamics of the soot particle population is described by the Smoluchowski coagulation equation with additional terms for particle inception, condensation, sintering and surface growth. A brief description of the most important aspects of the particle model is given below. Further details may be found elsewhere [17,19,20].

In the model, soot particles are represented as aggregates composed of primary particles, where each primary particle is composed of a number of PAHs [19]. The edge of each PAH is described by a list of contiguous site types. These elementary sites include free-edge, zig-zag, armchair and bay sites [20,34,35]. This representation allows the exact structure of each individual PAH to be resolved. A primary particle is represented as a set of two or more PAHs. An aggregate is represented as a set of two or more primary particles. Each aggregate stores a list of neighbouring primary particles and resolves the common surface area between each pair of neighbours, where each pair of neighbours can be in point contact, can be fully sintered or can be anywhere in between [19]. The degree of sintering is described by a *sintering level*, $s \in [0, 1]$ [36]. A sintering level of 0 corresponds to point contact and a sintering level of 1 corresponds to completely sintered.

There are five different particle processes in the model:

Inception. A primary particle is formed when two PAH molecules stick following a collision. The rate of collision is determined by a transition regime coagulation kernel [37] which is dependent on the mass and collision diameter of each collision partner [23]. The sticking probability of these two PAHs is determined by a simple collision efficiency model [17]. If the number of 6-member aromatic rings in each of the collision partners exceeds 16 then they will stick, which provided the best agreement between experimentally derived and computed optical band gap [24]. This implies a unit sticking probability.

Coagulation. An aggregate is formed when two (primary or aggregate) particles stick following a collision. The rate of collision is calculated as per the transition regime coagulation kernel. After a coagulation event, two primary particles (one from each collision partner) are assumed to be in point contact. These primaries may undergo subsequent particle rounding due to mass addition [19] via surface growth and condensation, and due to sintering [36].

Surface growth. PAHs in a primary particle may grow via surface reactions with gas-phase species. The rate of surface growth is a function of the structure of the PAH and is described by the KMC-ARS model. Two parameters are introduced to differentiate the rate of growth of PAHs in a primary particle versus those in the gas phase: the growth factor, g, and the critical number of PAHs in a primary particle, n_{crit}. The *growth factor* $g \in [0, 1]$ [19] is a multiplier that is applied to the growth rate of PAHs within primary particles once the number of PAHs (n_{PAHs}) exceeds n_{crit}. It is intended to account for the possibility that PAHs in large primary particles grow more slowly than PAHs in the gas-phase. We assume $n_{\text{crit}} = 4$ because Totton et al. [38] showed that the average stack size for clusters of coronene molecules is around 4. Reactions take place on the edge of a molecule and the edges of PAHs in stacks are exposed to the chemical environment.