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# The importance of reversibility in modeling soot nucleation and condensation processes

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## Abstract

Given the upcoming EURO 6 regulations, which include limits on particle number density (and hence size) for soot emissions from land vehicles, soot models must be capable of accurately predicting soot particle sizes. Previous modeling work has demonstrated the importance of the relative strengths of nucleation and condensation in predicting soot primary particle size; however, fundamental models still rely on tunable constants for modeling both processes, which limits predictive capability. Recent investigations into nucleation and condensation processes suggest that both processes are not thermodynamically favored to occur from 5-ringed PAHs, yet 5-ringed PAHs have been experimentally observed in abundance within nascent soot particles. This contradiction leads to the understanding that nucleation and condensation from 5-ringed PAHs is plausible, although they are likely highly reversible processes.

A fundamental reversible model for nucleation and condensation is developed through the use of statistical mechanics and the results from several recent works. The model is highly sensitive to both the binding energy and the vibration frequencies created during the nucleation and condensation processes, although reasonable values are obtained through an extensive literature review. A model for tracking the PAHs on the surface of soot particles is developed, which allows for the calculation of the reverse rate of nucleation and condensation. The inclusion of reversibility in the nucleation and condensation subroutines enables the model to accurately reproduce all relevant soot morphological parameters determined experimentally for the atmospheric pressure, laminar, ethylene–air Santoro flame. This is due to more accurate partitioning of PAH mass through the nucleation and condensation processes. The developed reversible model represents an advancement in fundamental soot formation modeling by replacing tunable constants with fundamental physics.

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## 1. Introduction

Reducing soot emissions from combustion processes is important due to the negative health and environmental effects of atmospheric soot. In

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order to achieve this goal, there has to be a fundamental understanding of the mechanisms of soot formation to allow for the determination of economically viable methods of reducing these emissions. Due to the highly complex nature of soot formation, detailed numerical models are employed to gain fundamental understanding of the factors that affect each mechanism of soot evolution. The current theories of how soot forms involve three main mechanisms; those being nucleation, hydrogen-abstraction-carbon-addition (HACA) surface growth, and polycyclic aromatic hydrocarbon (PAH) condensation. Extensive studies have been performed to characterize the nature of HACA surface growth; however, the processes involved in nucleation and PAH condensation are still unclear. Nucleation, which is the birth of a soot particle, is theorized to occur from the dimerization of gas phase PAHs. PAH condensation is the process by which gas phase PAHs can condense onto the surface of a soot particle. Both of these processes rely on physical PAH bonds; however, one acts to create new soot particles, while the other one acts to increase the size of existing soot particles.

The upcoming European emission standard for land vehicles, EURO 6, will include regulations on particle number density in addition to total particle mass (and hence particle size), thus accurate modeling of particle number density and size is important. In a recent study [1], it was shown that the relative efficiency of nucleation versus condensation heavily influences soot primary particle diameter predictions. Lower nucleation efficiencies resulted in larger predicted primary particle diameters, while lower condensation efficiencies produced smaller primary particle predictions. While this study [1] did display the importance in the relative strengths of nucleation to condensation for primary particle diameter predictions, the model relied on introducing tunable constants for nucleation and condensation efficiencies to increase agreement with the experimental results. It should be noted that all other soot formation models in the literature rely on efficiencies. These efficiencies can be tunable constants, or functional forms based on theoretical assumptions [2], predominantly with both processes modeled to occur via pyrene. In order to accurately predict soot particle size for a wide range of conditions, numerical models must be able to accurately model nucleation and condensation, and their relative contributions to total soot mass, without reliance on efficiencies for nucleation and condensation.

### 1.1. Physical PAH bonding processes

There has been a significant amount of recent investigations into the nature of physical PAH nucleation and condensation. In work by Sabbah et al. [3], it was shown that at flame temperatures, the dimerization of two pyrene molecules was not

thermodynamically favored. A temperature-dependent equilibrium constant for the dimerization of pyrene was proposed and based on its very small magnitude at flame temperatures, it was determined that dimerization must be highly reversible. It is asserted in this work that any proposed efficiency for the nucleation process should be a function of equilibrium ratios or constants. There has been some work into attempting to define an equilibrium constant for the dimerization of other PAHs as well. In a review article by Wang [4], statistical mechanics was utilized to define an equilibrium constant for the dimerization of pyrene, ovalene, and circumcoronene using binding energies taken from [5]. Some assumptions had to be made, with the most significant being the average frequency of the vibration modes created during the dimerization process. Investigations have been performed into the magnitude of these vibration modes in the work of Totton et al. [6] for pyrene, coronene, ovalene, hexabenzocoronene, and circumcoronene dimers. In Totton et al. [6], a more advanced model for determining the binding energies between PAHs was developed. Molecular dynamics simulations were utilized to propose a coagulation efficiency for PAH-PAH (nucleation) and PAH-PAH cluster (condensation) collisions that had dependencies on temperature and collisional reduced mass. Rapacioli et al. [7,8] looked at the frequencies of the vibration modes for coronene stacks containing up to 8 coronenes and vibration modes for various PAH dimers. Their conclusion was that in general, as PAH stack sizes increase, as would occur during the condensation process, vibration frequencies reduced. Finally, in Elvati and Violi [9], and Chung and Violi [10], it was determined that the addition of aliphatic chains, and not only a PAH's size, influence whether or not a dimerization was favored. All of these works reached the conclusion that PAHs much larger than pyrene (ovalene and larger) would need to be present for physical PAH attraction to play a role in nucleation and condensation.

The experimental work performed by Teini et al. [11], where High Resolution Transmission Electron Microscopy (HRTEM) was used to investigate the types of species found within nascent soot, seemed to conflict with the results of these recent thermodynamic investigations. The HRTEM showed that the sizes of species within nascent soot were fairly constant at the core and edges, and consistent with PAHs containing approximately 20 carbon atoms, or 5-rings. Even though these smaller PAHs are not thermodynamically favored to physically bond, they have been found within the cores and edges of nascent soot particles, leading to the assertion that species of this size are important to nucleation and condensation processes. This finding is consistent with the much earlier work of [12], where laser

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