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Effect of Nucleation Reversibility on Predicting Soot Particle Size Distributions in Premixed Flames

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Abstract

A novel approach to model soot particle nucleation has been implemented in a detailed combustion and sectional soot particle dynamics model. The new nucleation model makes allowance for the reversibility of the soot dimerization process. The reversible rate of dimerization has been calculated based on the equilibrium constant of the polycyclic aromatic hydrocarbon (PAH) dimers. The equilibrium constant is determined based on intermolecular forces of the nucleating PAHs. The new model has been employed to simulate soot particle size distributions (PSD) in a series of burner-stabilized, laminar premixed stagnation ethylene flames. The reversible nucleation model makes it feasible to obtain good agreement with the measured soot PSDs of the premixed flames which were impossible to model using the preceding models. The effect of PAH molecules' vibration frequencies on the predicted soot particle size distribution has been investigated. Being developed based on statistical mechanics theories, the reversible nucleation model eliminates the dependency of the nucleation model on dimerization efficiencies.

1. Introduction

In view of the PAH-based soot formation pathway, the formation and growth of aromatic species bridges the main combustion zone chemistry and soot formation. PAH molecules after growing to a certain size begin to stick to each other after collision, forming PAH dimers. PAH dimers can collide with PAH molecules forming PAH trimers or with other dimers forming PAH tetramers, and so on. Meanwhile, individual PAH species keeps increasing in size via molecular chemical growth reactions. In this manner, the PAH clusters evolve into solid particles. As a practical measure, the formation of dimers is normally assumed to mark the emergence of the solid particle phase [1]. In addition, soot particles could grow via the collision and the resultant deposition of PAH species on soot surface. This process is often referred to as PAH-soot surface condensation. Not all collisions lead to nucleation or condensation. Efficiencies are used to account for the probability of sticking in each collision. In a recent study [2], it was shown that the relative efficiency of nucleation vs condensation heavily influences soot primary particle diameter predictions. Lower nucleation efficiencies resulted in larger prediction primary particle diameters, while lower condensation efficiencies produced smaller primary particle predictions. In addition, no combination of efficiencies were able to predict the correct order of magnitude of soot concentration when the soot model with the constant sticking efficiencies were employed to model soot particle size distribution in the burner-stabilized stagnation premixed ethylene/air flames. These observations were the initiative to study sticking probability in the PAH nucleation and growth processes and develop models that better represent the physics of these processes. Following the work by Eaves et al. [3], a fully reversible nucleation model has been developed. The PAH composition of dimers are necessary to determine nucleation reverse rates. Therefore, additional conservation equations have been solved for the sectional aerosol dynamic model to track PAH content of the dimers. The reversible nucleation model along with the condensation efficiency proposed by D'Alessio et al. [4] has been employed to simulate a series of soot particle size distribution (PSD) in the burner-stabilized stagnation premixed ethylene/air flames [5]. There are several advantages associated with modeling and using these measurements. The PSD data provides the details necessary for soot morphology modeling as compared to diffusion flame measurements, which only consist of average quantities. Being one dimensional, modeling the premixed flame provides the opportunity to conduct several simulations and optimizations in a cost effective manner. Finally, these flames are ideal to test nucleation/condensation models since soot formation in these flames are dominant by PAH growth. The sensitivity of PSDs to reversibility of dimerization and collision efficiencies for the condensation of PAH molecules on the soot particles is explored in detail along with that to principal modelling assumptions.

2. Approach

The flame is modeled using the OPPDIF code [6]. Soot is modeled using a detailed fully coupled sectional aerosol dynamics approach. In this approach the continuum soot particle mass distribution is divided into a discrete number

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of soot clusters, each with an assigned mass. Conservation equation of soot aggregate number densities, and primary particle number densities are solved for each soot section. The soot sectional model considers nucleation, surface growth, PAH surface condensation, surface oxidation, coagulation, fragmentation, particle diffusion and thermophoresis.

Nucleation is modeled based on dimerization of pair of PAH molecules with more than 5 aromatic rings which serves as a connection between the gaseous phase reaction mechanism and the first soot section. The dimerization process is considered to be reversible. The forward rate of dimerization is determined by the rate of physical collision of the nucleating PAH molecules in the free-molecular regime. The forward rate of dimerization and the forward rate coefficient (k_{FWD}) are calculated according to equation (1) and (2), respectively:

$$\left(\frac{\partial N_{Dim}}{\partial t}\right)_{FWD} = k_{FWD}[PAH]^2 \quad (1)$$

$$k_{FWD} = \frac{2.2}{\rho} \sqrt{\frac{4\pi k_B T}{C_{mass} N_{C,PAH}}} d_{PAH}^2 A_v^2 \quad (2)$$

where k_B is the Boltzmann constant; C_{mass} is the mass of a carbon atom; $N_{C,PAH}$ is the number of carbon atoms in the incipient PAH species; d_{PAH} is the diameter of the incipient PAH species; A_v is Avogadro's number; $[PAH]$ denotes the mole concentration of the incipient PAH species. The reverse rate coefficient (k_{REV}) is calculated from the relation between equilibrium constant and rate coefficients, Eq. (3).

$$\frac{k_{FWD}}{k_{REV}} = K_p / RT \quad (3)$$

Utilising statistical mechanical principles to find gibbs free energy of dimerization, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, the equilibrium constant could be expressed as a function of monomer vibrational frequencies, binding energy and temperature. The details of enthalpy and entropy calculation could be found in [3]. Additional transport equations are solved to track concentration dimers of different pair.

The condensation rate is calculated based on the collision theory between PAH molecules and aggregates [7]. PAH-soot surface condensation efficiency proposed by D'Alessio et al. [4] is used to account for the probability of sticking in each collision. The sticking probability function given by Eq. (4) derived from the Lennard-Jones potential and the assumption that a moving particle does not experience friction caused by collisions with the surrounding gas.

$$\gamma = 1 - \left(1 + \frac{\Phi_0}{k_b T}\right) \exp\left(-\frac{\Phi_0}{k_b T}\right) \quad (4)$$

In Equation (4) k_b is the Boltzmann constant and Φ_0 is the potential well depth which is calculated using a Hamaker constants typical of polybenzenoid structures suggested by Sirignano and D'Anna [7]. The HACA mechanism [7] is used to describe soot particle surface growth. Particle diffusion and thermophoresis velocity are given by [9] and [10]. Details of the sectional model, and transport equations can be found in [6, 7]. A kinetic mechanism developed for C1–C4 fuels [11] incorporated to describe gas phase reactions.

3. Results and Discussion

The developed soot sectional model has been employed to model the centerline of laminar premixed atmospheric burner-stabilized stagnation ethylene-oxygen-argon flame [5] for six stagnation-surface positions. The burner spacing ranges from $H_p = 0.55$ – 1.2 cm. The inlet flow composed of 16.3% C_2H_4 , 23.7% O_2 and 60% Ar (equivalence ratio $\phi = 2.07$). The inlet cold gas velocity is 8 cm/s (STP) and the temperature boundaries equal to the measured burner temperature.

Predicted soot volume fraction and soot particles number density using the reversible nucleation model and the measurement data at the stagnation plate for all H_p values are displayed in Figure 1 and Figure 2, respectively. Included in those plots, calculated soot volume fraction and number density using a non-reversible nucleation model. The non-reversible nucleation model considers a constant low sticking probability ($\gamma_{Nuc} = 10^{-5}$). Soot volume fraction has been over predicted in most of flames with both reversible and non-reversible models. However, the reversible model better captured the trend of decrease in the soot concentration as the H_p decreases. The measured number density in Figure 2 shows an increase of total number of particles as the separation distance increased to 0.8 cm where it reaches its maximum value and then number densities decrease after this point. The reversible model has been able to correctly predict the experimentally observed changes of soot particles number density with variation of separation spacing. The non-reversible model on the contrary, fails to capture this trend. Despite the fact that a very

low nucleation efficiency has been considered which tends to lower the total number of particles [2], the non-reversible model highly overpredicts the total number of particles.

The calculated soot PSDs obtained using sectional model are shown in Figure 3. Reasonable to good agreement is obtained. The model is able to predicts the bimodal distribution of PSDs in the $H_p=1.0$ cm and $H_p = 1.2$ cm flames. The model also shows a transition from unimodal distribution to bimodal distribution as the separation distance increases. Consistence in all PSD predictions is the overpredictions of the larger particles. These are the particles that have been formed in the high temperature regions where the reverse rates are high. One explanation for the overprediction is that condensation rate is not modeled as reversible.

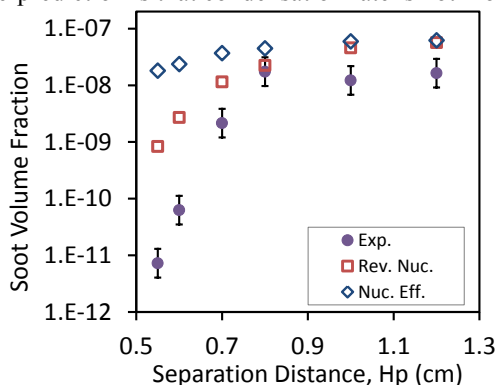


Figure 1. Comparison of experimental soot volume fraction [5] (particle diameter, $D_p > 2.5$ nm) with prediction of the reversible nucleation and constant efficiency nucleation models as function of separation distance.

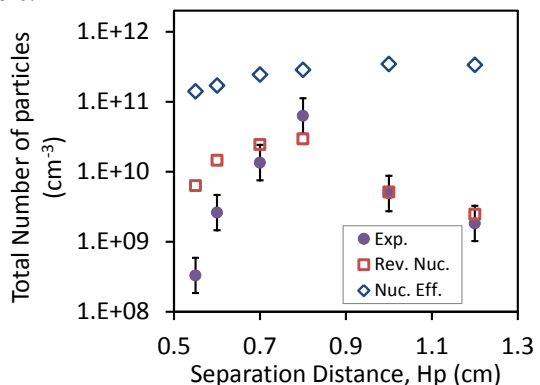


Figure 2. Comparison of measured soot particle number density [5] (particle diameter, $D_p > 2.5$ nm) and those computed with the reversible nucleation and constant efficiency nucleation model as function of separation distance.

3.1 Sensitivity Analysis

The reverse rate of dimerization is calculated based on the equilibrium constant of dimerization. The enthalpy and entropy of dimerization required for K_p has been derived from statistical mechanical principles [1]. The resulting equilibrium constant of dimerization is a function of vibrational frequencies of the PAH molecules that are

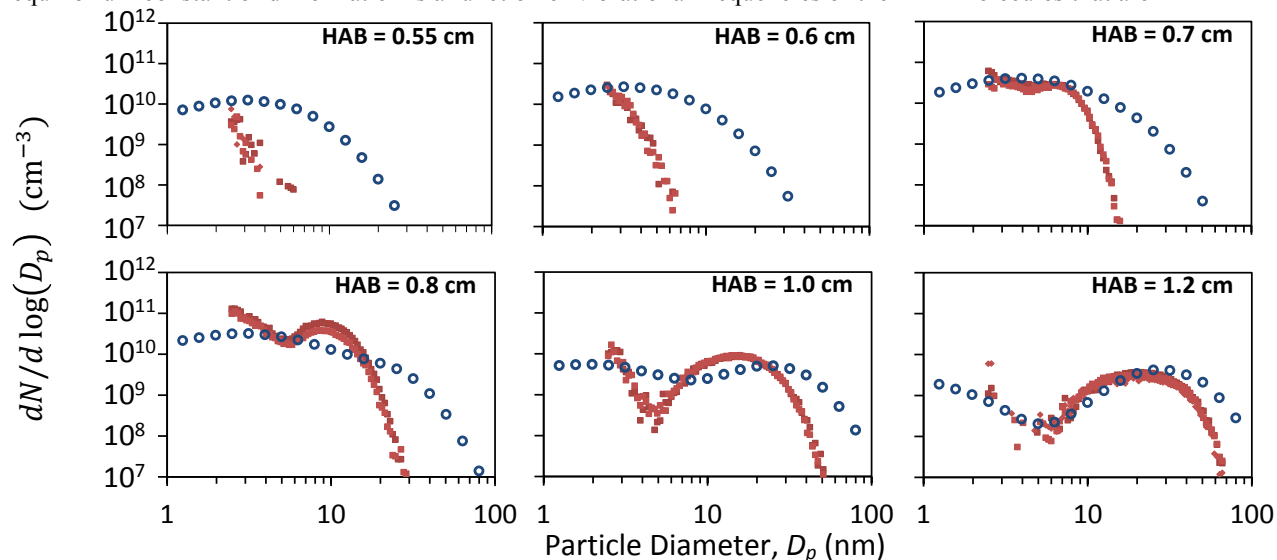


Figure 3. Measured and calculated soot particle size distributions at different separation distance. Measured soot PSDs are shown with squares [5]. Calculated soot PSDs are shown with open circles

participating in the dimerization. The vibrational frequencies of different PAH molecules reported by [3, 12, 13] ranges between $14\text{--}26$ cm^{-1} . Higher vibration frequencies results in higher estimation of dimer's entropy; thus, smaller K_p and favoring dimerization, as shown in Figure 4. In order to investigate the effect of reversibility,

different vibration frequencies have been implemented to calculate soot particle size distribution. Figure 5 displays comparison of the predicted PSDs in the flame with the 1.2 cm separation distance with the experimental data taken from [5]. The consequence of promoting reversibility of dimerization (lower vibration frequencies) is the shift of PSD toward larger particles and a stronger bimodality of the particle size distribution. The reason for the shift is interrelatedness of PAH condensation and nucleation. When the nucleation process is suppressed by increasing reversibility the PAH molecules are absorbed more through the surface condensation as a result although you would have less particles and the soot volume fraction increases. Similar observation has been reported by [3] when the reversible nucleation model has been used to model soot formation in ethylene air diffusion flames.

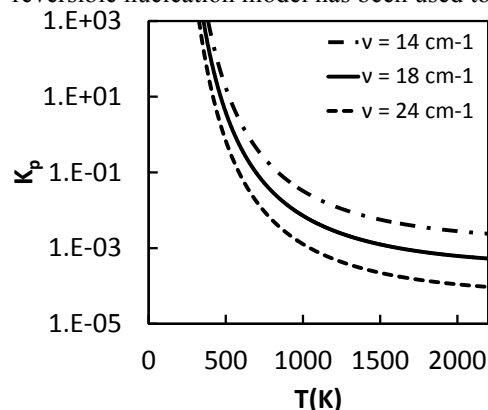


Figure 4. Equilibrium constant for dimerization of PAHs with different average vibration frequencies as a function of temperature.

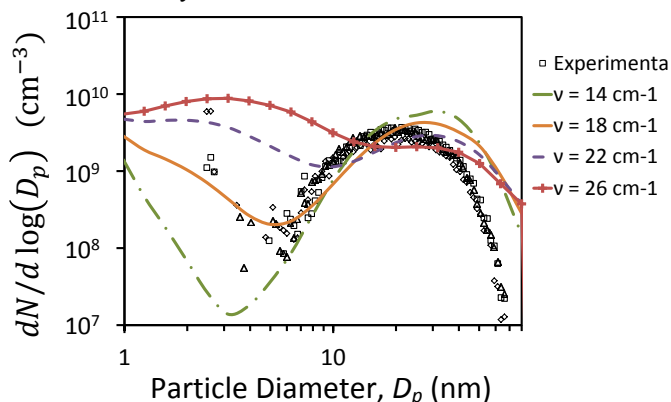


Figure 5. Measured [5] (open squares) and calculated (solid lines) particle size distribution in the Hp=1.2 cm flame using different vibration frequencies.

4. Conclusions

A reversible nucleation model has been developed. The reverse rates of nucleation calculated based on equilibrium constant of the process. Predictive capability of the novel reversible nucleation model in calculating particle size distribution in burner-stabilized stagnation premixed flame has been investigated. Sensitivity of the predicted PSD to vibrational frequencies which has an important role in estimation of equilibrium constant of dimerization has been investigated. It was shown that increasing nucleation reversibility could result in formation of more soot as consequence of competition between nucleation and condensation.

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