THE SIMULTANEOUS AGGREGATION AND SURFACE GROWTH OF SOOT PARTICLES FORMED IN AN ETHYLENE LAMINAR PREMIXED FLAME

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TITLE

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RESUME

L'agrégation et la croissance de surface des particules de suie sont simulées numériquement à l'aide d'un code aux éléments discrets de type Monte Carlo où chaque agrégat est suivi dans le temps. La croissance de surface n'a pas un impact notable sur la dimension fractale des agrégats. En revanche, elle augmente considérablement la compacité locale des agrégats comme le révèle le « packing factor ». Le taux de recouvrement et le nombre de coordination des monomères en sont à l'origine. Les agrégats produits sont notamment similaires à ceux observés expérimentalement. Finalement, négliger la croissance de surface peut conduire à des erreurs d'un facteur 8 à 10 sur la fraction volumique de suie.

ABSTRACT

Soot aggregation and surface growth is numerically simulated based on a Monte Carlo discrete element method where each individual aggregate is tracked in time. Surface growth does not highly influence the fractal morphology of aggregates while it leads to a high increase in local compacity as quantified by the packing factor, overlapping, and coordination number of primary particles. The generated aggregates are in remarkable resemblance with those experimentally measured. Finally, neglecting surface growth leads to an underestimation of soot volume fraction by a factor of 8-10.

MOTS-CLÉS : Suie, Agrégat, Croissance Surface / **KEYWORDS:** Soot, Aggregation, Surface growth, Overlapping

1. INTRODUCTION

The collision and subsequent agglomeration of soot nanoparticles in flames lead to the formation of morphologically complex clusters. These clusters have unique physicochemical properties making them valuable for industrial applications, such as reinforcers in tires. However, these properties can be also a problem when these particles are released to the atmosphere or when entering to the human lungs where they may be carcinogenic. A better understanding of soot aggregates physicochemical properties involves an accurate description of their morphology. This morphology can be dependent on the simultaneous change of fluid-particle and particle-particle regimes (Morán *et al*., 2020b). In addition to soot particle evolution by aggregation, the mass transfer with the surrounding gas is suspected to play an important role on the kinetics of aggregation, particle size distribution, and particle morphology. Indeed, surface growth may provide nearly all the mass of the ultimately formed soot particles. Surface growth is also suspected to increase the overlapping between primary particles as typically observed in Transmission Electron Microscopy (TEM) images (Bourrous *et al*., 2018; Cortés *et al*., 2018). Primary particles overlapping plays an important role in soot particle radiative properties. It can consequently affect climate models and particle sizing by optical techniques such as time-resolved laser-induced incandescence (Johnsson *et al*., 2013). Indeed, the latter requires an accurate determination of aggregate's volume and surface area but also the amount of overlapping between monomers which influences the heat transfer (notably conduction) rates with the surrounding gas.

Along with the increase in monomers overlapping, surface growth can increase the coordination number (*i.e*. the number of intersections with touching neighbor monomers). Along with the overlapping, this parameter determines the physicochemical properties of aggregates such as heat/electrical conduction, catalytic/chemical performance, radiative properties, and mechanical resistance (Rumpf, 1958; Yon *et al*. 2015a). Although the importance of the aforementioned morphological parameters, they have not been quantified and systematically studied for soot particles in flames, and consequently this work aims at filling this gap. Finally, a fundamental question that arises when studying aggregates formed under coagulation and surface growth is about the variation of their fractal structure, and notably their fractal dimension. This is studied with special attention in the present work by quantifying the morphology of individual aggregates based on the recently introduced generalized pair correlation function (Yon *et al*., 2020). Large uncertainties currently exist

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in the literature regarding the increase in aggregates local compacity, therefore this is quantified and reported in the present work.

2. METHODOLOGY

2.1. Surface growth model and implementation

Soot particles are considered to be exposed to an incoming specific surface mass flux density φ in (kg/m^2/s) of gas molecules (mainly acetylene molecules) producing the surface growth of soot particles. In this context, the radius of each primary particle $r(t)$ evolves during a time step Δt as,

$$r(t+\Delta t) = r(t) + u\Delta t \tag{1}$$

Where $u = \varphi/\rho_p$ is the surface growth rate in (m/s), and ρ_p is the soot particle mass bulk density. This methodology is consistent with Mitchell and Frenklach (1998). The Monte Carlo Aggregation Code (MCAC), introduced and validated by (Morán *et al*., 2020a,b) to purely aggregation is used in the present work. It is consequently adapted to particle surface growth. One of the most important properties for particles dynamics is the friction coefficient of aggregates in the transition flow regime. The method proposed by Yon *et al*. (2015b) is used, it consist on the following power-law $f_{agg} = f_p(v_{agg}/v_p)^{\Gamma/D_f}$, where f_p is the primary particle friction coefficient, Γ is a function of the monomer flow regime, D_f is the aggregate fractal dimension, v_{agg} and v_p are the aggregate and average primary particle volume. Determining v_{agg} is however not evident when primary particles are highly overlapped. Some accurate method exist (Cazals *et al*., 2011), however they are prohibited in terms of CPU time for the current purposes. A new method to determine v_{agg} is consequently proposed. It is a semi-analytical method considering a multi-sphere correction term, this is very important but commonly ignored in the literature due to the lack of approximative methods (Brasil *et al*., 1999; Morán *et al*., 2018; Lindberg *et al*., 2019).

2.2. Numerical simulations

An ethylene premixed flame environment as studied by Harris (1990) is considered to simulate the simultaneous aggregation and surface growth of soot particles. In this context, a constant temperature of 1700 K and ambient pressure is considered. Experimentally measured time-resolved surface growth flux φ is considered based on this work by assuming a constant soot density $\rho_p = 1.8$ g/cm^3. Cases will be referred all along this manuscript in terms of the initial surface growth rate, i.e. $u_0 = 0.4\ \mathrm{nm/ms}$ corresponding to a flame having $\mathrm{C/O} = 0.82$, and $u_0 = 0.6\ \mathrm{nm/ms}$ corresponding to $\mathrm{C/O} = 0.94$ as experimentally measured by Harris (1990). As a reference case, pure aggregation without surface growth is also simulated ($u = 0$). Considering the available experimental data, the simulations cover the $8.3 - 30\ \mathrm{ms}$ range in residence time, corresponding approximately to $5 - 25\ \mathrm{mm}$ in terms of height above the burner. At the initial residence time ($8.3\ \mathrm{ms}$) soot particles agglomeration can be neglected due to the coalescence of particles after collision (D'Anna *et al*., 2010). In this context, the initial primary particle size distribution is considered lognormal with a geometric mean of $8\ \mathrm{nm}$, and a geometric standard deviation $\sigma_{p,\mathrm{geo}} = 1.2$ in accordance with the data from premixed ethylene flames. Initial soot volume fraction is $f_v = 0.118\ \mathrm{ppm}$ for all cases except one case having $u_0 = 0.6\ \mathrm{nm/ms}$, where $f_v = 0.357\ \mathrm{ppm}$ is considered. For each simulated case, a total of 1024 primary particles are considered at the beginning of the simulation and a total of 10 simulations are done per condition. The results reported later are averaged over these 10 simulations. The reference case ($u = 0$) has been successfully validated by comparison with macroscopic Population Balance simulations in terms of aggregation kinetics and particle size distribution.

3. RESULTS AND DISCUSSION

As shown in **Fig. 1a**, soot volume fractions is increasing in time due to the mass transfer with the gas phase. The increase in f_v is proportional to the surface growth rate and seems not highly dependent on the initial f_v value since both cases consisting of $u_0 = 0.6$ show an almost equivalent percentual increase in time. It is important to note that neglecting surface growth can lead to a factor of 10 in the predicted particle volume fraction. **Fig. 1b** shows the effect of surface growth on the inverse of the aggregate number concentration $1/n(t)$ as a function of time. For all the cases consisting of initial $f_v = 0.118\ \mathrm{ppm}$ no relevant difference is observed up to a residence time of around $15\ \mathrm{ms}$ showing that despite surface growth is stronger at the beginning it is not able to change the kinetics of small aggregates consisting of a few or isolated monomers. In addition, at short times, the initial particle volume fraction seems much more important in terms of aggregation kinetics. The reported kinetic exponent (z) for larger residence times shows a degradation in aggregation kinetics produced by surface growth.

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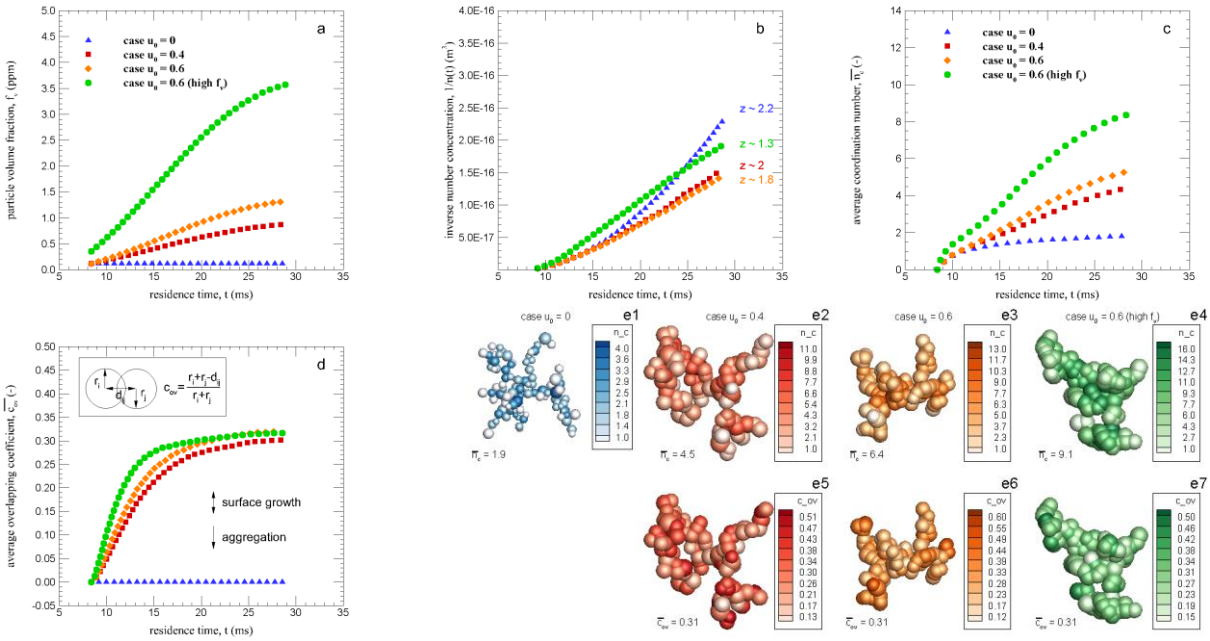

Figure 1: Soot volume fraction (a), inverse of the particle number concentration (b), average coordination number (c), average overlapping coefficient (d) as a function of time. Local coordination number (e1-e4), and local overlapping coefficient (e5-e7).

Fig. 1c shows the evolution of the population average coordination number $\overline{n_c}$ as a function of time. First, it is found to monotonically increase in time reaching an asymptotic value of 2 when no surface growth is present (Yon *et al*. 2020). However, when surface growth is present this value can increase up to $3-8$ depending on both the surface growth rate and initial particle volume fraction. The larger value of n_c observed for the case $u_0 = 0.6$ (high f_v) is not related to particle morphology, it is rather related to the enhancement of aggregation kinetics which leads to a quick increase in aggregates size than other cases. Although maximum average coordination numbers are within the $2-8$ range, local values as observed in **Fig. 1(e1 – e4)** can be as high as 16. This means that surface growth produces a very complex interaction between monomers and considerably increases the compactness of primary particles.

Finally, **Fig. 1d** reports the time evolution of the population average overlapping coefficient $\overline{c_{ov}}$. This parameter is measured as $c_{ov} = (r_i + r_j - d_{ij})/(r_i + r_j)$, where $r_i + r_j$ is the sum of the primary particle radii and d_{ij} is the distance between their centers. When particles just agglomerate, they are in a point-touching so $d_{ij} = r_i + r_j$, and consequently $c_{ov} = 0$, this correspond to the case $u = 0$ in this figure. However, when two monomers are totally fused then $d_{ij} = 0$ and $c_{ov} = 1$. As particle are increasing in residence time, their primary particle radii are increasing according to equation (1) leading to a continuous increase in c_{ov}. However, it is less evident why a quite asymptotic value $\overline{c_{ov}} \approx 0.30$ is observed. This is explained by the fact that while aggregation tends to decrease the $\overline{c_{ov}}$, surface growth does both increase and decrease it. This because as primary particles are increasing in size, their overlapping with touching neighbors is increasing however, new intersections between monomers belonging to the same aggregate occur leading also to a decrease in $\overline{c_{ov}}$. In addition, as observed in **Fig. 1(e5 – e7)**, local overlapping coefficient can be up to 2-fold the $\overline{c_{ov}}$. Soot particles from diffusion and premixed flames commonly exhibit an overlapping coefficient (2d from TEM images) between 0.11 to 0.36, being in good agreement with the present simulations (Bourrous *et al*., 2018; Cortés *et al*., 2018).

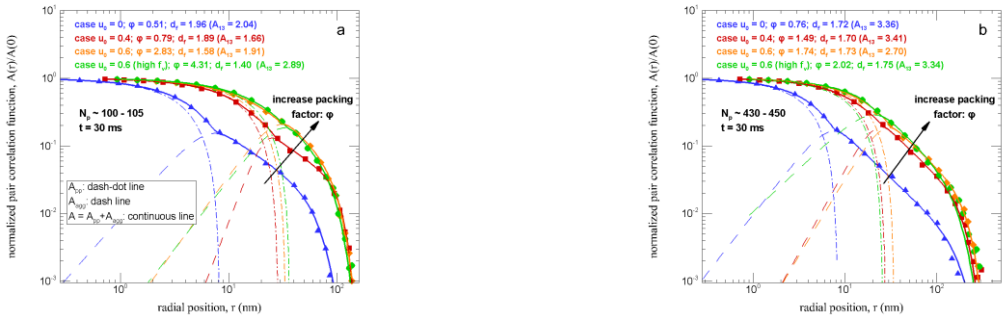

Figure 2: Fitting the pair correlation function of selected aggregates for each condition.

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Fig. 2 shows in symbol the calculated volume-based pair correlation function $A(r)$ for selected aggregates for each simulated case (Yon *et al*., 2020). Aggregates on the left-hand side correspond to a number of primary particles between $100-105$, while those on the right-hand side correspond to $430-450$. All of these aggregates are sampled at the end of the simulation ($t = 30$ ms), and selected for having a representative anisotropy coefficient (A_{13}) of the ensemble of particles in the system. The calculated $A(r)$ is fitted based on a modified version of the model proposed by Yon *et al*., (2020) for taking the intersection of primary particles into account. The fitted packing factor (φ), representing the local compacity of aggregates, is reported for each case. This parameter is clearly increasing with surface growth. Also, the fitted fractal dimension (d_f) describing the overall structure of the aggregate is also reported for each case. When surface growth is present, larger aggregates are needed to observe a self-similar form of the pair-correlation function. This parameter is found to be not strongly dependent on the surface growth level and values are in good agreement with TEM measurements (Bourrous *et al*., 2018; Cortés *et al*., 2018).

4. CONCLUSIONS

The simultaneous aggregation and surface growth of soot particles in an ethylene premixed flame lead to the formation of complex aggregates. They consist in highly overlapped primary particles with local values up to 60% while the global population average attains a robust value around 30%. Also, the local coordination number is in average between 4 to 8, which is respectively 2- and 4-times larger than the maximum values reached by agglomerates formed in the absence of surface growth. Local coordination numbers can be however as high as 16. Surface growth does not strongly affect the overall structure of aggregates (fractal dimension), however it considerably increases the local compacity as quantified by the packing factor. This may explain the large fractal prefactor of experimentally measured soot particles. Finally, neglecting surface growth underpredicts soot volume fraction by a factor of $8-10$ depending on the flame conditions.

ACKNOWLEDGMENTS

This work is financed by ANR ASTORIA (N°ANR-18-CE05-0015) and the Region of Normandy (project RIN Gazpropres). The authors also thank the CRIANN numerical resources supported by the Normandy region.

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