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Impact of the maturation process on soot particle aggregation kinetics and morphology

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Abstract

Mature soot aggregates exhibit a morphology which is currently mimicked by diffusion-limited aggregation (DLCA) codes, i.e. with a sticking probability = 1 when two aggregates collide. Nevertheless, nascent soot particles may grow in the reaction-limited aggregation regime (RLCA), i.e. with a sticking probability $\ll 1$. Yet, it remains to be seen how fast the transition from RLCA to DLCA occurs for soot particles and what is the impact on aggregation kinetics, particle size distribution and morphology. This work intends to fill this gap by exploring the aggregation of soot particles formed in a laminar premixed flame through numerical simulations. Results show that the transition from RLCA to DLCA is very fast and produces a moderate impact on soot formation dynamics and morphology. However, soot particles mass bulk density is found to play an important role and should be considered in future simulations of soot formation in flames.

Keywords: Soot, Maturity, Aggregation, Electrostatic, Van der Waal, Rebound

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1. Introduction

The incomplete combustion of hydrocarbon fuels leads to the formation of a variety of complex Polycyclic Aromatic Hydrocarbon (PAH) molecules. The clustering of these PAH molecules commonly leads to the formation of spheroidal nascent soot primary particles, which can reach sizes around a few nanometer [1–6]. This PAH clustering process is very complex. Molecular Dynamics simulations have provided important insights into the formation of these nascent soot primary particles. For instance, they have provided an estimation of soot available reactive sites and surface properties [7–9], molecular PAH cluster morphology [3, 10], internal structure [11, 12], detailed PAH molecules interactions and clustering [13]. These simulations have shown that smaller soot particles coalesce faster than larger ones [3, 12]. In this context, it is reasonable to consider a critical time t_2 (corresponding to a limit diameter d_c) after which^{Rev} agglomeration replaces coalescence leading to ramified structures also called fractal-like aggregates (see Fig. 1). This article focusses on what occurs after this stage, in particular on the role played by soot maturity (here the change in chemical composition and particles bulk density) on the aggregation kinetics and morphology.^{Rev} The formation of these complex aggregates can be modeled by classical Diffusion-limited Cluster Aggregation (DLCA) or Reaction-limited Cluster Aggregation (RLCA) codes when detailed information on aggregate’s morphology is intended [14]. In this type of simulations, the motion of each individual particle is explicitly solved and agglomeration can occur when two particles collide. More precisely, DLCA and RLCA simulations assume that particles undergo purely diffusive motion

25 (i.e. convective transport by an underlying flow is neglected). This means
 26 that these methods are restricted to small particles, typically within the col-
 27 loidal range (i.e. lower than a few micrometers, for which gravity forces are
 28 negligible compared to Brownian motion). DLCA and RLCA simulations are
 29 able to produce morphologies similar to soot aggregates. The main difference
 30 between DLCA and RLCA simulations lies in the treatment of collisions be-
 31 tween two particles: DLCA assumes that agglomeration is driven by particle
 32 diffusion while agglomeration is driven by the physico-chemical interactions
 33 between particles in RLCA codes. To put it differently,^{Rev} in DLCA codes,
 34 every collision between a pair of particles leads to their adhesion and, hence,
 35 to the formation of aggregates (i.e. the sticking probability is 1). In RLCA
 36 codes, the sticking probability is close to 0, meaning that only a few collisions
 37 are successful to form an aggregate. In reality, nascent soot particles may
 38 have a very low sticking probability, i.e. they may rebound after collisions
 39 due to their higher mobility and lower potential well depths compared to
 40 mature soot [15]. On the contrary, mature soot have a higher tendency to
 41 form aggregates due to a sticking probability ≈ 1 . Therefore, a second criti-
 42 cal diameter d_s has to be considered as the transition between both regimes,
 43 as illustrated in Fig. 1. Little attention has been paid to this second critical
 44 diameter. Therefore, in the present work, we focus on identifying d_s . The
 45 question we intent to answer in the current investigation is the d_s to simulate
 46 the transition from RLCA to DLCA and what would be the consequences on
 47 soot aggregation kinetics, morphology and size distribution?^{Rev}

48 This transition is expected to be related to the evolution of particle mo-
 49 bility and their composition. In fact, nascent particles are small (a few

50 nanometers diameter) and have a mass bulk density $\sim 1.2 \text{ g/cm}^3$ at typi-
 51 cal flame temperatures [16] whereas, mature soot primary particles have a
 52 larger diameter, are solid, with a graphitic structure and a bulk mass density
 53 of $\sim 1.8 \text{ g/cm}^3$ [16, 17]. Similarly, the chemical composition, parametrized by
 54 the C/H ratio, increases with maturity due to soot dehydrogenation [5, 18].
 55 Indeed, soot maturity evolution has many physico-chemical consequences
 56 as further discussed in Refs. [19, 20]. These progressive modifications of
 57 the physico-chemical properties of soot particles may consequently induce a
 58 change of particle mobility but also affect their sticking probability [15, 21].

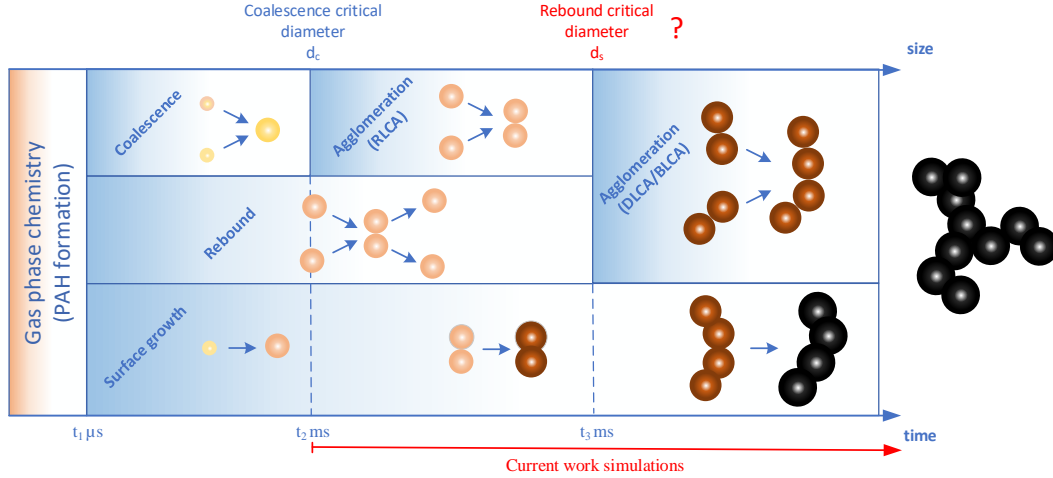


Figure 1: Different processes and mechanisms involved in soot formation in flames.

59 Another factor, commonly overlooked in the literature, is the role played
 60 by the particle electric charges. Different works have found soot particles
 61 to acquire a natural electric charge in flames due to chemi-ionization reac-
 62 tions and ion attachment to PAH clusters or primary particles [22–26]. The
 63 interaction between charged colloidal particles leads to the presence of re-

64 pulsive electrostatic forces that can hamper agglomeration. Indeed, when
 65 the kinetic energy of the approaching particles is not strong enough to over-
 66 come the repulsive electrostatic forces, particles repel each other and prevent
 67 agglomeration [27]. Therefore, accurate predictions of the outcome of soot
 68 particle interactions require simulations that include both the sticking and
 69 the collision probabilities. To the authors' knowledge, such modifications of
 70 electrical properties have never been taken into account to study the morpho-
 71 logical properties and kinetics of soot aggregation. The present work intends
 72 to fill this gap by considering the bulk density, sticking probability and elec-
 73 trostatic forces evolving in time. To this end, the Monte Carlo Aggregation
 74 Code (MCAC) [28] is used. This code allows the simultaneous transition in
 75 flow regime (from free-molecular to continuum) and agglomeration regime
 76 (from ballistic to diffusive) to be taken into account. It has been previously
 77 used to simulate soot agglomeration [29], and more recently agglomeration
 78 and surface growth [30]. As shown in Fig. 1, it is important to note that
 79 the dynamics of PAH molecular cluster formation is out of the scope of the
 80 present work. Here, we investigate the kinetics of non-coalescing soot pri-
 81 mary particle aggregation and surface growth in a laminar premixed flame
 82 together with detailed calculations of inter-particle interactions.^{Rev}

83 **2. Methodology**

84 To answer the main question raised by the current investigation, a phys-
 85 ical evaluation of the collision and sticking probabilities of soot aggregates
 86 (described in Section 2.1) is carried out and then implemented in a Monte
 87 Carlo discrete element code as explained in section 2.3. The principle of the

collision and sticking probabilities determination relies on fine-scale evaluations of the interaction energy between two soot aggregates (more details are provided in Section 2.2).

2.1. Interaction energy between particles

2.1.1. Interaction between primary spheres

Drawing on the previous study by Hou et al. [15], the interaction energy E between two spherical soot particles separated by a distance h is obtained by integrating the Lennard-Jones interactions between atoms over the volume of each body. This integration results in the sum of an attractive force and a repulsive force (more details can be found in [15] or a brief summary in Section 1 of the Supporting Material).

$$E_{\text{L-J}} = E_{\text{att}}(h) + E_{\text{rep}}(h) \quad (1)$$

The attractive term due to the van der Waals contribution can be written as

$$E_{\text{att}}(h) = -\frac{A_{\text{ham}}}{6} f_a(R_{p,1}, R_{p,2}, h) \quad (2)$$

where h is the separation distance between the two spheres, A_{ham} the Hamaker constant and f_a a function containing geometrical factors. The repulsive term is due to the overlap of electron orbitals occurring at very short separation distances. It is given by [15]:

$$E_{\text{rep}}(h) = \frac{1}{37800} A_{\text{ham}} \left(\frac{\sigma_{ab}}{2R_{p,1}} \right)^6 (U_{\text{rep},1} + U_{\text{rep},2} + U_{\text{rep},3} + U_{\text{rep},4}) \quad (3)$$

with σ_{ab} the distance of zero potential between atoms. Each of the four components $U_{\text{rep},i}$ are detailed in Section 1 of the Supporting Material.

107 In addition to these short-ranged intermolecular forces, we also account
 108 for electrostatic interaction between charged soot particles. The formula for
 109 the potential energy of two charged spherical particles (each one having a
 110 given number of elementary charge z_p) is given by:

$$E_{\text{electro}}(h) = \frac{k_0 z_{p,1} z_{p,2} e^2}{h} \quad (4)$$

111 where $k_0 = 8.9875517923 \times 10^9$ is the Coulomb constant (in $kg\ m^3\ s^{-2}\ C^{-2}$)
 112 and e is the elementary charge.

113 As a result, the total interaction energy E_{tot} between two primary soot
 114 particles is given by:

$$E_{\text{total}}(h) = E_{\text{att}}(h) + E_{\text{rep}}(h) + E_{\text{electro}}(h) \quad (5)$$

115 2.1.2. Parametrization

116 To solve Eq. (5), further information is required on particle properties.
 117 The Hamaker constant A_{ham} is estimated using the number density of carbon
 118 atoms (C) and hydrogen atoms (H) within each soot particle as well as the
 119 particle mass bulk density (similarly to the procedure in [15]). This means
 120 that, by changing the chemical composition of one particle and/or its den-
 121 sity to account for maturity effects, the Hamaker constant is automatically
 122 updated to fit this new composition. Further details on the parametriza-
 123 tion used here are provided in Section 1 of the Supporting Material. [Soot](#)
 124 [particles charging may be determined by different mechanisms including the](#)
 125 [attachment of ions and electrons to soot molecular clusters, primary parti-](#)
 126 [cles, and soot aggregates. Positive and negative ions are naturally produced](#)
 127 [in the flame as it has been experimentally observed \[22, 31, 32\]. These ions](#)

128 and electrons are believed to be produced mainly by chemi-ionization reac-
 129 tions [24]. However, thermo-emission may be an important mechanism to
 130 be considered. Indeed, Balthasar and Mauss [33] suggested that this mech-
 131 anism might explain the appearance of charged molecular clusters. More
 132 recently, Starik et al. [24] found no relevant role played by thermoemission.
 133 The relation between soot charging and maturity seems *a priori* not strong
 134 since flames with different fuels and different flame conditions show similar
 135 charge distributions [23, 25, 34, 35]. The detailed modeling of soot charging
 136 dynamics is beyond the scope of the present work (interested readers can
 137 refer to [24, 33, 36]). In this work, the electric charge of soot particles^{Rev}
 138 is estimated using available measurements on the charge distribution of soot
 139 particles in premixed flames [25]. Aggregates electric charges are obtained by
 140 randomly sampling a number of elementary charges (z_p) from the Boltzmann
 141 distribution [25],

$$f(z_p) = \left(\frac{K_E e^2}{\pi d_m k_B T} \right)^{1/2} \exp \left(\frac{-K_E z_p^2 e^2}{d_m k_B T} \right) \quad (6)$$

142 where $K_E = 9.0 \cdot 10^9 \text{ Nm}^2/\text{C}^2$, k_B is the Boltzmann constant, e is the ele-
 143 mentary charge, and d_m is the mobility diameter of the aggregate obtained
 144 from the friction coefficient of the aggregate [28, 30].

145 2.1.3. Interaction between aggregates

146 We further extend the previous work of Hou et al. [15] to compute the
 147 interaction energy between aggregates composed of a number of primary
 148 soot particles. As displayed in Figure 2, the difficulty that arises when com-
 149 puting the interaction between two aggregates is that it should take into
 150 account the aggregate morphology and its orientation with respect to the

151 other aggregate/particle. In fact, depending on the aggregate morphology
 152 and orientation, one or several primary particles within a first aggregate can
 153 be in close proximity to other particles in the second aggregate. Hopefully,
 154 recent evaluations of van der Waals interactions between fractal DLCA ag-
 155 gregates have shown that the van der Waals interaction between aggregates
 156 is actually governed by the interaction between the closest pair(s) of primary
 157 particles [37]. This result is mainly due to the short-range nature of van der
 158 Waals forces, which usually act within the nanoscopic scale. As a result, we
 159 have simplified the present calculations of aggregate-aggregate interactions
 160 by accounting only for the interaction between the closest pair of primary
 161 particles.

162 Concerning electrostatic forces between aggregates, a similar issue arises
 163 since the exact repartition of charges within an aggregate is unknown. Sev-
 164 eral simplifications can be considered, including: (a) placing all charges on
 165 the closest pair of primary particles, (b) considering aggregates as full spheres
 166 with an equivalent radius where charges are homogeneously distributed and
 167 (c) placing all charges on the furthest pair of primary particles within ag-
 168 gregates. Since one of the objectives of this study is to assess the impact
 169 of electrostatic interaction on soot aggregation, we report here only the re-
 170 sults obtained with case (a), which tends to overestimate the electrostatic
 171 contribution and thus corresponds to the worst case scenario.

172 *2.2. Collision efficiency*

173 As mentioned in the introduction, simulations of particle agglomeration
 174 require to couple a model for the aggregate transport (collision step) and a
 175 model for aggregate interactions (adhesion step). However, these two phe-

176 nomena occur at various spatial and temporal scales: soot particles can
 177 indeed be transported near the flame over several centimeters while inter-
 178 aggregate forces are composed of short-ranged Lennard-Jones forces (within
 179 the nanoscopic scale) and long-range electrostatic forces. Since precise cal-
 180 culations of the combined motion of interacting aggregates at the nanoscopic
 181 scale are out of scope of the present study (it will require much smaller
 182 time steps for the transport model), the coupling of the two phenomena is
 183 obtained using energetic considerations that are similar to boundary condi-
 184 tions used in standard CFD simulations (see also [38]). This means here
 185 that only reduced information on the interaction energy is extracted from
 186 the whole energy-versus-distance curve (see also Fig. 2): the potential well
 187 $E_{well} \leq 0$ (i.e. the minimum of the interaction energy) and the energy bar-
 rier $E_{barr} \geq 0$ (i.e. the maximum of the interaction energy). As displayed in

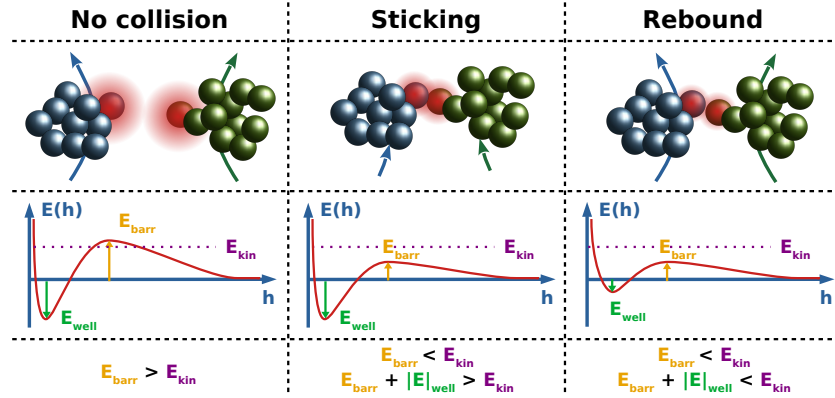


Figure 2: Sketch showing the three possible outcomes of a collision between two aggregates and the corresponding criteria (based on the potential well E_{well} , the energy barrier E_{barr} and the relative kinetic energy E_{kin}).

188

189 Fig. 2, three possible outcomes of an interaction are considered depending
 190 on the following energetic criteria:

- 191 1. no collision occurs when the repulsive energy barrier E_{barr} overpowers
 192 the relative kinetic energy along the direction of collision E_{kin} , i.e.
 193 $E_{kin} < E_{barr}$;
- 194 2. a collision occurs when the relative kinetic energy along the direction of
 195 collision E_{kin} is high enough to overcome the repulsive energy barrier
 196 E_{barr} , i.e. $E_{kin} > E_{barr}$. Once a collision occurs, two subsequent results
 197 are possible:
 - 198 2.a. The two particles/aggregates stick to each other when the particle
 199 cannot escape the potential well, i.e. $E_{kin} < |E|_{well} + E_{barr}$;
 - 200 2.b. The two particles/aggregates rebound when their kinetic energy
 201 (again taken equal to the incoming one) prevails over the potential
 202 well, i.e. $E_{kin} > |E|_{well} + E_{barr}$;

203 Drawing on this scenario for the outcome of an interaction between soot
 204 particles/aggregates, a collision probability and a sticking probability are
 205 evaluated. The formula for these probabilities are obtained by analogy with
 206 a Brownian diffusion of particles in a force field (more details are provided
 207 in Section 2 of the Supporting Material):

$$P_{coll} = 1 - \operatorname{erf}\left(\sqrt{\widetilde{E_{barr}}}\right) + \sqrt{\widetilde{E_{barr}}} \times \exp\left(-\widetilde{E_{barr}}\right) \quad (7)$$

$$P_{stick} = \operatorname{erf}\left(\sqrt{\widetilde{E_{stick}}}\right) - \sqrt{\widetilde{E_{stick}}} \times \exp\left(-\widetilde{E_{stick}}\right) \quad (8)$$

208 with the dimensionless potential energies $\widetilde{E_{barr}} = E_{barr}/(k_B T)$ and $\widetilde{E_{stick}} =$
 209 $(|E|_{well} + E_{barr})/(k_B T)$ (k_B being the Boltzmann constant and T the flame
 210 temperature).

211 2.3. Integration in an Aggregation Code

212 The Monte Carlo Aggregation Code (MCAC) is a recent code developped
213 to simulate the aggregation of nanoparticles by considering the transition in
214 both flow and aggregation regimes. The latter corresponds to the transi-
215 tion between ballistic-limited cluster aggregation (BLCA) and DLCA dur-
216 ing time [28, 29]. More recently, surface growth process has been imple-
217 mented, enabling a physically-driven generation of realistic soot aggregates
218 consisting of overlapping primary particles [30]. In the context of the cur-
219 rent work, MCAC has been adapted to non-unitary collision and sticking
220 probabilities. In this context, a collision-check step is done each time two
221 aggregates come to close contact. The outcome of this check depends on
222 a uniformly distributed random number $\delta_1 \in [0, 1]$ such that, particles col-
223 lide when $\delta_1 \leq P_{coll}$, or repel each other when $\delta_1 > P_{coll}$. If collision is
224 found, a second random number is generatd $\delta_2 \in [0, 1]$ such that, particles
225 stick together after collision when $\delta_2 \leq P_{stick}$, or rebound when $\delta_2 > P_{stick}$.
226 This procedure is inspired by the classical RLCA codes found in the litera-
227 ture [39, 40]. As explained in previous sections, P_{coll} and P_{stick} depend on
228 both the electrostatic barrier, and Lennard-Jones potential well depth, re-
229 spectively. These properties depend on the flame temperature, aggregate’s
230 mobility diameter, primary particle size and soot maturity. To simulate a
231 time-evolving soot maturity, the properties of individual aggregates are in-
232 troduced as new parameters in MCAC (includig the C/H ratio, the density
233 ρ_p , and electric charge). The C/H ratio is correlated to the average primary
234 particle size (within an aggregate) and used to determine ρ_p (see section 3
235 of the Supporting Material). The potential well depth is determined based

on the diameter of the colliding primary particles. The electrostatic barrier is determined based on the electric charge of the interacting aggregates. Indeed, the mobility diameters of the approaching aggregates is obtained based on the friction coefficient of aggregates [28, 41]. Thus, equation (6) is used to sample a given charge for each aggregate that respects the Boltzmann distribution. This new version of MCAC allows to investigate the kinetics of aggregation, the particle size distribution, and aggregates morphology.

Kinetics of aggregation is studied by quantifying the time evolution of the aggregate number concentration $N(t)$ in $\#/m^3$ and the monodisperse equivalent coagulation kernel k_{ii} in m^3/s . The latter is determined from the local slopes of $1/N(t)$ as done in Ref. [29].

Particle size distribution is studied in terms of the volume-equivalent radius. The morphology of particles is studied in terms of the population-based fractal dimension, and fractal prefactor obtained by a log-log fit of the fractal-law expressed as,

$$\frac{V_{agg}}{\bar{V}_p} = k_f \left(\frac{R_g}{R_{pv}} \right)^{D_f} \quad (9)$$

where, V_{agg} is the aggregate volume corrected by overlapping monomers and obtained based on the SBL library [42], $\bar{V}_p = 1/N_p \sum_{i=1}^{N_p} (\pi/6) d_{p,i}^3 = (4\pi/3) R_{pv}^3$ is the average primary particle volume, and R_g is the aggregate's radius of gyration obtained by discretizing the aggregate [41] (see section 4 of the Supporting Material). In addition, the pair correlation function for representative aggregates is calculated and fitted to search the packing factor φ which is an indicator of the local compacity in the cluster. The details on its determination are given elsewhere [43, 44] and the fitting procedure is the same than in Ref. [30]. Further details can also be found in section 5 of the

260 Supporting Material.

261 3. Results

262 3.1. Case studied and parametrization

263 A premixed ethylene flame ($C/O = 0.82$) is selected as a test case. This
264 flame has been already simulated by considering the simultaneous aggrega-
265 tion and surface growth [30] but change of maturity was not considered and
266 thus, the collision and sticking probabilities were fixed to 1. In order to start
267 the current simulation with smaller primary particle size than in the afore-
268 mentioned work, surface growth rates (u in nm/ms) from Ref. [30] have been
269 linearly extrapolated to shorter residence times. Current simulations start
270 at $t = 3.5$ ms, with 1024 spherical primary particles [45] corresponding to a
271 lognormal size distribution with a geometric diameter of $d_p = 2.4$ nm and
272 geometric standard deviation of 1.2. The domain size is set to respect the ini-
273 tial volume fraction to $f_v = 0.002$ ppm. Constant temperature $T = 1700$ K
274 and 1 atm of pressure are considered. The simulation ends at $t = 30$ ms.

275 In this study, based on a literature survey, nascent soot are considered
276 to have $C/H = 1.1$ and a corresponding bulk density of $\rho_p = 1.2$ g/cm³. In
277 contrast, mature soot are characterized by $C/H = 10$ and $\rho_p = 1.8$ g/cm³.
278 Mass bulk density of nascent and mature soot particles are obtained from [17],
279 being in good agreement with [16].

280 Different cases are considered in order to evaluate the role played by
281 maturity and electrostatic forces (see Table 1). The first one called “mature
282 (no potentials)” consists in keeping the properties of mature soot during
283 all the simulation and considering systematic collision and sticking when

two aggregates approach each other (i.e. whatever the size of the colliding primary spheres). This corresponds to the usual DLCA approach. The second one called “nascent (no potentials)” is identical to the previous one but now considering the physical properties of nascent soot. The comparison with the previous case is then used to study the role played by the bulk density.

Cases 3 and 4 called respectively “mature (only LJ)” and nascent “(only LJ)” will also conserve the physical properties of respectively mature and nascent soot, but for these cases the sticking probabilities are evaluated based on the colliding primary particle radii according to their composition.

Case 5 “variable maturity (LJ+electrostatic)” considers a transition of soot maturity induced by a variation of C/H and consequently in ρ_p according to the primary sphere radius based on Refs. [5, 46] (see the section 3 of the Supporting Material for further details). This case also considers the electrostatic forces as described in Section 2.1.

For each case studied, a total of 10 simulations are conducted and results presented later are averaged over these ten simulations as done in previous works [29, 30].

3.2. Collision and sticking probabilities of soot particles

3.2.1. Effect of maturity

We first assess the role of soot maturity (expressed through particle size, mass bulk density and composition) on the collision and sticking probabilities. To this end, we evaluate the behaviour for mature soot, nascent soot and soot with variable maturity but zero electric charges. In that case, since no repulsive forces act on a range longer than van der Waals forces, no energy

Table 1: Selected cases for numerical simulations.

| Case | Description |
|---|--|
| Mature (no potentials) | $P_{coll} = 1$ and $P_{stick} = 1$, $\rho_p = 1.8 \text{ g/cm}^3$ |
| Nascent (no potentials) | $P_{coll} = 1$ and $P_{stick} = 1$, $\rho_p = 1.2 \text{ g/cm}^3$ |
| Mature (only LJ) | $P_{coll} = 1$, and P_{stick} is evaluated, $\rho_p = 1.8 \text{ g/cm}^3$, $\text{C/H} = 10.0$ |
| Nascent (only LJ) | $P_{coll} = 1$, and P_{stick} is evaluated, $\rho_p = 1.2 \text{ g/cm}^3$ $\text{C/H} = 1.1$ |
| Variable maturity (LJ + electrostatic) | P_{coll} and P_{stick} are evaluated, ρ_p and C/H evolve in time electrostatic forces considered |

309 barrier occurs (not shown here). Hence, the collision probability is always
310 equal to unity. However, the balance between van der Waals forces and
311 Born repulsion leads to an existing potential well whose value depends on
312 the particle size as well as on the particle properties.

313 Figure 3 displays the evolution of the potential well and sticking probab-
314 ity as a function of the reduced particle radius $R_{red} = R_{p,1}R_{p,2}/(R_{p,1} + R_{p,2})$,
315 where $R_{p,i}$ expresses the radius of the i 'th colliding primary particle. Several
316 conclusions can be drawn from this figure:

- when the particle properties are fixed (“mature” or “nascent” cases), the depth of the potential well increases with increasing reduced particle diameter. This is consistent with previous studies of neutrally charged particles (e.g. [15]). As a result, the sticking probability quickly increases from 0.1 at $R_{red} = 0.5$ nm to values close to 1 around $R_{red} = 3$ nm. Based on the definition of the reduced particle radius, we can evaluate the critical primary diameter at which the sticking probability is roughly equal to 1, which happens to be around $d_s \sim 8$ nm for nascent particles (resp. $d_s \sim 12$ nm for mature soot). This means that, except for very small particles, a collision does induce agglomeration of the two particles involved. This result is comparable to the one obtained by Hou et al. [15], who obtained $d_s \sim 14$ nm for soot particles at $T = 1500$ K. The slight difference is due to the different formula used to evaluate the sticking probability (see section 2.3 of the Supporting Material) as well as to differences in the density and C/H ratio considered for nascent or mature soot.
- the depth of the potential well for mature particles (and consequently the sticking probability) is higher than the one for nascent particles. This is related to the fact that mature particles have a higher Hamaker constant due to their higher density and C/H ratio, leading to stronger short-ranged repulsive forces.
- the results obtained with the variable maturity case are bounded by the two limit cases of “nascent” and “mature” particles. When one of the particle diameter is fixed, the depth of the potential well (and con-

sequently the sticking probability) increases with the reduced particle diameter. Moreover, it clearly appears that the results obtained for the variable maturity case are very close to the “nascent” case when the reduced size is below 0.7 nm while they become very close to the “mature” case when the reduced size is above 4 nm (in which case, the sticking probability reaches a plateau value $P_{stick} \simeq 1$).

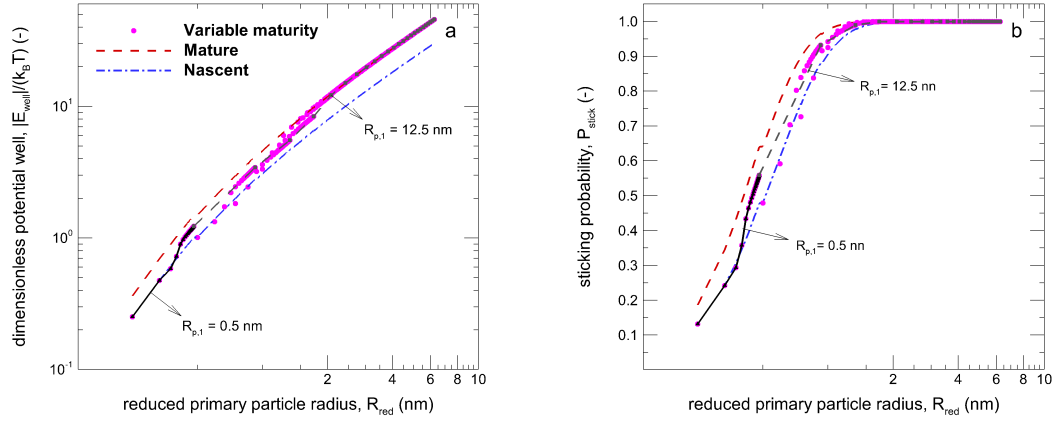


Figure 3: Evolution of the potential well (left) in absolute value, and sticking probability (right) as a function of the reduced particle radius $R_{red} = R_{p,1}R_{p,2}/(R_{p,1} + R_{p,2})$. Results obtained for spherical soot particles with zero electric charge and a size ranging between 1 and 25 nm. The particle density and C/H ratio are obtained either in the case of nascent soot, mature soot or variable maturity.

3.2.2. Effect of electrostatic forces

The role of electric charges on the interaction between soot particles has been assessed by changing the value of each particle charge between $-6e$ and $+6e$ while keeping all other properties fixed. [Experimental determination of](#)

soot charge distribution in ethylene premixed flames [34] have reported to be narrow and symmetric within the $-2e$ to $+2e$ range for soot particles with mobility diameter $d_m \approx 13$ nm. As time evolves, this distribution considerably broadens but remains symmetric within the $-4e$ to $+4e$ for $d_m \approx 62$ nm. Indeed, Eq. (6) shows that the distribution of charges (z_p) is Gaussian distribution whose variance is $\sigma^2 = (d_m k_B T) / (2K_E e^2)$, thus increasing with mobility diameter of the aggregate (see section 7 in the Supporting Material). Based on these measurements, we have opted to consider a range of charges between $-6e$ to $+6e$ to ensure that all possible situations are covered.^{Rev}

In the following, we consider the case of “variable maturity” particles with a fixed particle radius of 5 nm.

Figure. 4 displays 2D contours of the energy and probability values (E_{barr} , E_{well} , \mathcal{P}_{coll} , \mathcal{P}_{stick}) as a function of the elementary charge present in each particle. It can be seen that a range of values can be obtained depending on the elementary charge present in each particle. In particular, the collision and sticking probabilities are close to 1 only when particles have high but opposite charges. On the contrary, when both particles have a high and similar charges, the collision and sticking probabilities quickly drop to values close to 0.

Due to the symmetry in the effect of particle charges (see also Eq. (4)), we further analyse the effect of electrostatic charges by plotting the same results as a function of the product of the particle elementary charges $z_{12} = z_{p,1} z_{p,2}$. This is displayed in Figure 5. This allows to confirm and quantify the two aspects mentioned before. First, for similarly charged particles, the potential well is close to zero (except for $z_{12} \ll 1$) while the energy

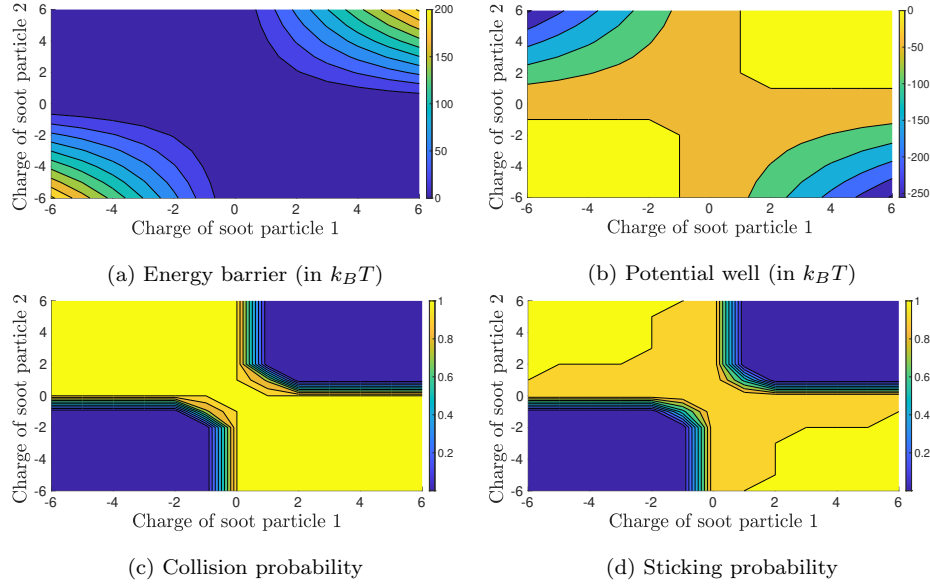


Figure 4: 2D plot showing the evolution of $(\widetilde{E}_{barr}, \widetilde{E}_{well}, \mathcal{P}_{coll}, \mathcal{P}_{stick})$ as a function of the electric charge of each particle. Results obtained for spherical soot particles with $R_{p,1} = R_{p,2} = 5$ nm and variable maturity (density and C/H ratio).

376 barrier increases linearly with z_{12} . As a result, the collision probability (and
 377 hence the sticking probability) quickly drops to very small values when the
 378 particle charge increases. Second, for oppositely charged particles, no energy
 379 barrier occurs (except for $z_{12} \ll 1$) while the depth of the potential well is
 380 increased due to the attractive electrostatic force. In that case, both collision
 381 and sticking probabilities have values close to 1.

382 Although these results indicate a clear effect of soot maturity and electro-
 383 static forces on the collision probability and sticking probability, it remains
 384 to be seen how this affects the actual agglomeration of soot particles. This
 385 is done in the next sections where these collision & sticking probabilities are
 386 coupled to the MCAC code to simulate the formation and growth of soot

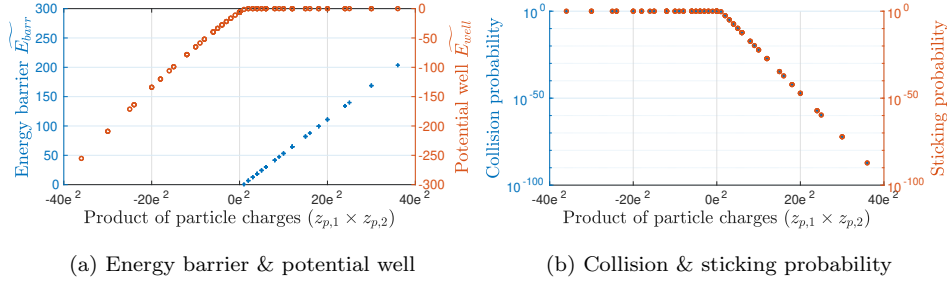


Figure 5: Evolution of $(\widetilde{E_{well}}, \widetilde{E_{barr}}, \mathcal{P}_{coll}, \mathcal{P}_{stick})$ as a function of the product of the particle electric charges. Results obtained for spherical soot particles with a size of 5 nm. The particle density and C/H ratio are obtained with variable maturity.

aggregates.

3.3. Agglomeration of soot particles

Figure 6a presents the time evolution of the inverse particle number concentration $1/N(t)$. The local slope of this curve in log-log correspond to the kinetic exponent z , which indicates how fast aggregation is. The $1/N(t)$ is naturally increasing in time due to irreversible aggregation in the absence of continuous nucleation and fragmentation. All cases show a similar evolution except in the cases of nascent soot particles. Indeed, nascent soot particles have a lower mass bulk density, consequently they move faster and more ballistically. This leads to an enhanced kinetics of aggregation that becomes more evident over time. When comparing the two cases involving nascent soot (no potentials and only LJ), a clearer difference is observed at early residence times. Agglomeration is initially faster for the case without potential which is explained by the larger sticking probability (unity). However, the role played by bulk density seems relatively more important than taking into account of a time evolving sticking probability. This conclusion is reinforced

403 by the comparison with the three remaining cases (mature with and without
 404 potentials and variable maturity). This means that considering the change
 405 of collision and sticking probability induced by the maturation process have
 406 a reduced impact on the aggregation kinetics. This is explained by the fact
 407 that d_s is very small, and also by the large surface growth efficiency (SGE)
 408 as shown in section 6 of the Supporting Material. This parameter has been
 409 introduced by [41] and quantifies the predominance of surface growth over
 410 aggregation to explain soot mass growth. For example, $\text{SGE} \rightarrow \infty$ means
 411 that surface growth dominates soot mass growth over aggregation, while
 412 $\text{SGE} \rightarrow 0$ means the opposite. In this work, non-unitary sticking or colli-
 413 sion probabilities lead to larger values of SGEs, which is especially evident
 414 for early residence times. However at these residence times, the SGE is still
 415 high even without considering LJ or electrostatic potentials. The later is ex-
 416 plained by the low nascent soot volume fractions making difficult to observe
 417 a big impact on the soot formation process.

418 However, when analyzing the kinetic exponents z obtained by a power-law
 419 fitting $1/N(t) \propto t^z$ for $t \in [23, 35]$ ms, other conclusions can be drawn. First,
 420 all the values correspond to aggregation in the transition regime since z is
 421 smaller than purely ballistic value ($z \approx 2.2$) and larger than purely diffusive
 422 ($z \approx 1$) regimes [29, 47]. Second, comparison between different simulations
 423 suggest that inclusion of the van der Waals sticking and electrostatic colli-
 424 sion probabilities tends to accelerate agglomeration for large residence times
 425 (larger z). Third, comparing both cases involving purely LJ sticking prob-
 426 ability reveals that nascent soot tends to agglomerate faster, with a kinetic
 427 exponent closer to the one for a purely ballistic regime. Nascent soot without

428 potentials shows the lowest kinetic exponent explained by it faster aggrega-
 429 tion at earlier residence times approaching faster to transition regime where
 430 kinetic exponent could be as small as $z \approx 0.8$.

431 Fig. 6b reports the monodisperse equivalent coagulation kernel. This also
 432 expresses the agglomeration kinetics but is of great interest for soot modeling
 433 in CFD codes since kernels are essential to simulate aggregation by popu-
 434 lation balance methods. This representation is also complementary since it
 435 provides a larger sensitivity to the agglomeration processes at early residence
 436 times. Indeed, this highlights the rapid transition from low to high kernels
 437 at early residence times $t < 8$ ms (corresponding to $d_{p,geo} < 5$ nm) of the
 438 nascent soot composition depending on considering the collision and sticking
 439 probabilities or not. For larger residence times, the differences are mainly
 440 explained by the particles mass bulk density. Nascent soot particles coag-
 441 ulate faster due to their more ballistic motion, their larger collision surface
 442 and larger particle size polydispersity (see Fig. 6d).

443 The evolution of the geometric mean $R_{v,geo}$ (Fig. 6c) and geometric stan-
 444 dard deviation $\sigma_{Rv,geo}$ (Fig. 6d) of the volume-equivalent radius of aggre-
 445 gates are also evaluated. The $R_{v,geo}$ parameter increases monotonically in
 446 time due to agggregation. Nascent soot leads to larger aggregate sizes due
 447 to the more efficienct aggregation process driven by lower bulk density as
 448 discussed above. In turn, the impact of maturation process, sticking proba-
 449 bility or electrostatic repulsion is clearly negligible (no significant differences
 450 are observed when comparing all the cases related to mature soot). The
 451 $\sigma_{Rv,geo}$ reported in (Fig. 6d) expresses a more complex trend, in particular
 452 at early residence times. At these early residence times the decrease in poly-

453 dispersity is linked to the dominance of surface growth in the competition
 454 with agglomeration (see section 6 of the Supporting Material), to produce
 455 larger soot aggregates [30]. Both cases considering nascent soot all along
 456 the simulation are characterized by more ballistic aggregation, consequently
 457 leading to larger $\sigma_{Rv,geo}$ for larger residence times, in agreement with previous
 458 observations [29, 30].

459 Table 2 summarizes the main morphological properties of aggregates sam-
 460 pled at the end of the simulation ($t = 30$ ms). The population-based fractal
 461 dimension (D_{fp}) and the corresponding fractal prefactor (k_{fp}) are reported,
 462 and further details on their determination are provided in section 4 of the
 463 Supporting Material. Overall, both D_{fp} and k_{fp} are very close for all the
 464 cases. Notably, the fractal dimension is larger than the one observed for
 465 DLCA aggregates $D_f = 1.78$, but smaller than BLCA $D_f = 1.91$ limits.
 466 Particularly, k_{fp} are considerably larger than those observed for aggregates
 467 formed by pure agglomeration in the absence of surface growth, whose val-
 468 ues attain a maximum quite asymptotic limit ~ 1.4 [29]. The larger fractal
 469 prefactors observed in this work are explained by the increase in local com-
 470 pacity due to the overlapping of primary particles and the increase in the
 471 coordination number due to surface growth [30]. These values seem quite
 472 close to those determined experimentally [46, 48, 49]. The population aver-
 473 aged packing factors $\bar{\varphi}$ are also reported for the “Mature (LJ)” and “Nascent
 474 (LJ)” cases. As explained in the previous section, they are determined by
 475 fitting the pair correlation function for individual aggregates sampled at the
 476 end of the simulation ($t = 30$ ms). This parameter is related to the local
 477 compacity of primary particles, and has been found to increase with the

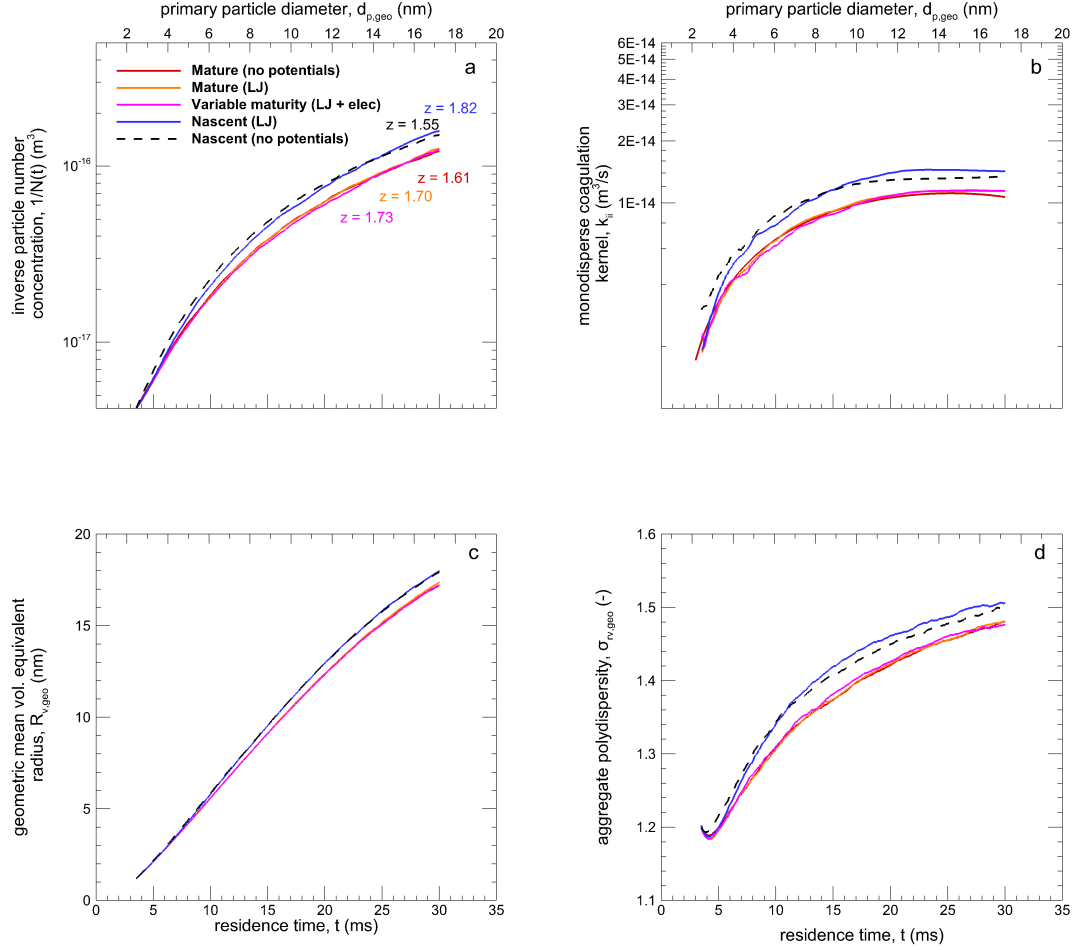


Figure 6: Time evolution of the inverse particle number concentration $1/N(t)$, monodisperse equivalent coagulation kernels, geometric mean volume-equivalent radius, and the corresponding geometric standard deviation.

478 number of monomers per aggregate. It attains a maximum value between 1
 479 to 1.4 for DLCA aggregates consisting of 10^3 point-touching monodisperse
 480 and polydisperse monomers, respectively [44]. Current aggregates contain
 481 ~ 100 monomers per aggregate and their packing factor ($\bar{\varphi} \approx 1.5$) is larger

482 than those found in the referred work. This is explained by primary particle
 483 overlapping [30]. These packing factors are in good agreement with [30] who
 484 obtained $\bar{\varphi} \approx 1.49$ for large aggregates ($N_p \in [430, 450]$) generated under the
 485 same flame conditions. However, no relevant difference is observed in local
 486 compacity for the different cases studied.

Table 2: Morphological parameters characterizing aggregates sampled at the end of the
 simulation ($t = 30$ ms). Population fractal dimension (D_{fp}), and prefactor (k_{fp}) as well as
 average individual packing factor ($\bar{\varphi}$) are reported. Error values lead to the 95% confidence
 intervals.

| Case | Population | | Individual |
|------------------------------|-----------------|-----------------|-----------------|
| | D_{fp} | k_{fp} | $\bar{\varphi}$ |
| Mature (no potentials) | 1.85 ± 0.01 | 2.15 ± 0.01 | - |
| Mature (LJ) | 1.83 ± 0.01 | 2.18 ± 0.01 | 1.57 ± 0.08 |
| Variable maturity (LJ+elec.) | 1.82 ± 0.01 | 2.19 ± 0.01 | - |
| Nascent (LJ) | 1.86 ± 0.02 | 2.19 ± 0.02 | 1.49 ± 0.10 |
| Nascent (no potentials) | 1.83 ± 0.02 | 2.24 ± 0.02 | - |

487 4. Conclusion and perspectives

488 A numerical simulation of soot particles aggregation and surface growth
 489 is performed by a Monte Carlo Discrete Element Method in a laminar pre-
 490 mixed flame. The role played by soot maturity evolution during time is
 491 explored by modeling the collision and sticking probabilities as well as the
 492 evolution of the primary particle bulk density. The possible impact of the
 493 electrostatic repulsion of soot particles has also been investigated. Numerical

494 results showed that both the particle maturity and the electrostatic forces af-
 495 fect the value of the collision and sticking probabilities. One raised questions
 496 was the evaluation of a critical primary diameter from which the sticking
 497 probability achieves its asymptotic value (unity). We evaluated this critical
 498 diameter around $d_s = 10$ nm for mature and nascent soot. However, when
 499 coupling these probabilities within the Monte Carlo Aggregation Code, it
 500 appears that inter-particle interactions do not considerably influence soot
 501 aggregation kinetics, particle size distribution, and morphology. This be-
 502 cause the sticking probability of soot particles tends toward 1 in a very short
 503 period of time (a few milliseconds) that corresponds to a low collision fre-
 504 quency due to the very low soot volume fraction ($\sim 10^{-3}$ ppm) at this time.
 505 Therefore, under the studied conditions, we conclude that the assumption
 506 of a sticking probability = 1 is valid all along the soot formation process
 507 for soot particles even if the simulation begins with particles as small as
 508 $d_p = 2.4$ nm, which is lower than d_s . This tends to neglect the role played
 509 by electrostatic forces at short ranges as well as the effect of maturation on
 510 the collision and sticking probabilities in the simulation of aggregates forma-
 511 tion for example by solving the population balance equation as in Ref. [50].
 512 This also explains why most classical DLCA codes, where a sticking prob-
 513 ability = 1 is assumed, succeed to produce fractal-like aggregates quite in
 514 good agreement with those measured experimentally under different flames
 515 conditions and fuel types [51–54]. Also, classical RLCA simulations show
 516 that a relevant variation in aggregates morphology (at least in terms of the
 517 fractal dimension) is found for extremely low sticking probability in the order
 518 of 10^{-3} [55–57] which is far to be representative of soot formation even when

519 soot particles are still nascent.

520 However, the variation of soot particles bulk density due to maturity
521 evolution in time has been shown to significantly influence the kinetics of
522 agglomeration and thus the related coagulation kernels. Therefore we recom-
523 mand to consider the variation of the bulk density from nascent to mature
524 soot in numerical simulations of nanoparticles formation in flames. This is
525 explained by an increased mobility of the particles having a lower bulk den-
526 sity. Nevertheless, this seems not to have a significant impact on the resulting
527 particles morphology.

528 Finally, the updated version of MCAC is available under the following
529 website <https://gitlab.coria-cfd.fr/MCAC/MCAC/-/releases>.

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