THE PROPERTIES OF SELF-PRESERVING SIZE DISTRIBUTION OF SOOT AGGREGATES

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TITLE

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ABSTRACT

Aggregation process is, in certain cases, a self-similar phenomenon whose modeling can be done through the so-called kernel homogeneity parameter. A new approach for the determination of this parameter is introduced. It is based on analytical expressions derived from the self-preserving theory and applied to the 1st and 2nd moments of the particles size distribution. As aggregation evolves in time, the so determined kernel homogeneity is found to variate in a different way depending on the initial soot volume fraction. The relative convergence between the homogeneity coefficients derived from the 1st and 2nd moments of the particles size distribution is used as a criterion to estimate the time-lag for self-preserving. It is found to be 5 times the characteristic time of coagulation with no relevant dependence on the initial soot volume fraction.

KEYWORDS: Soot, Fractal Aggregates, Self-Preserving, Time-Lag

1. INTRODUCTION

The Brownian motion of soot particles in flames naturally leads to random collisions between particles and therefore the formation of polydisperse fractal-like aggregates. However, depending on the physico-chemical conditions, this polydispersity may achieve a natural limit where the shape of the particles size distribution becomes invariant in time (Friedlander, 2000), this is called the self-preserving size distribution (SPSD). It is a fundamental concept that allows a considerably simplified solution for the Smoluchowski equation. It also explains why a low limit for the polydispersity of particles size is observed for particles under coagulation and finally, it allows subsequent theoretical developments for example to study the interaction of aggregates with light (Eggerdorfer & Pratsinis, 2014).

$$\frac{dn_N}{dt} = \frac{1}{2}\sum_{i=1}^{N-1} K(i,i-1)n_i n_{N-i} - n_N \sum_{i=1}^{\infty} K(i,N)n_i \quad (1)$$

In the Smoluchowski equation, n_N is the number density of aggregates consisting of N primary particles, and $K(i,j)$ is the coagulation kernel determining the rate of aggregation. In certain cases, this kernel is a homogeneous function, i.e. $K(\alpha i, \alpha j) = \alpha^{\lambda} K(i,j)$ where λ is the aggregation kernel homogeneity parameter and $\alpha > 0$ is a constant value. This λ parameter is very important for the kinetics of aggregation and the resulting SPSD (Oh & Sorensen, 1997). It has been proposed to be dependent on both the gas Knudsen number, i.e. the ratio between the gas mean free path and the aggregate mobility diameter and the diffusive Knudsen number, i.e. the ratio between the particle persistant distance and the nearest neighbor distance (Pierce *et al*., 2006; Heinson *et al*., 2014). Also, these authors showed a dependence on the fractal dimension of the generated aggregates. However, these relationships are not well understood. The determination of λ parameter typically relies on the scaling hypothesis, i.e. by calculating the kinetic exponent $z = 1/(1-\lambda)$ as proposed by Dongen & Ernst, (1985). This kinetic exponent z is determined from the time variation of the inverse number concentration based on the power-law $1/n \sim t^z$. Despite its simplicity, the scaling hypothesis is widely used however, its accuracy is rarely discussed.

2. PROPOSED APPROACH

2.1. The volume based self-preserving size distribution

Let's consider $p(v)dv$ the probability to find a particle with a volume between v and $v + dv$. We can demonstrate that under the conditions of self-preserving size regime, in an analogous fashion to Oh & Sorensen (1997) we can find the following expression for the SPSD,

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$$p(v) = \frac{(1-\lambda)^{1-\lambda} x^{-\lambda} e^{-(1-\lambda)x}}{\bar{v}\Gamma(1-\lambda)} \quad (2)$$

Where $x = v/\bar{v}$ and $\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}dt$ is the Gamma function. By considering the volume equivalent diameter $d_v = v^{1/3}6/\pi$, the q-moment of this distribution is,

$$\overline{d_v^q} = \widetilde{d_v}^q (1-\lambda)^{-q/3} \frac{\Gamma(1-\lambda+q/3)}{\Gamma(1-\lambda)} \quad (3)$$

Where $\widetilde{d_v} = \overline{d_v^3}^{1/3}$, calculated for each residence time. In the proposed method the homogeneity coefficient is calculated by solving eq. (3) for the first ($q = 1$) and second ($q = 2$) moments of the volume equivalent diameters distribution. The corresponding homogeneity coefficients, denoted as $\lambda_{M1}$and λ_{M2}, respectively are calculated as a function of the particles residence time.

2.2. Numerical simulations

The aim is to simulate aggregation of initially monodisperse spherical primary particles. The simulation scheme is an improved version of the classical diffusion limited cluster-cluster aggregation. It starts with a total of N_0 = 3200 randomly placed monomers in a cubic box. Particles are displaced by following the individual positions in time, periodic boundary conditions are applied to avoid artificial effects due to the interaction between particles and the containing box. Particles are displaced individually in a random direction along a persistant distance $\sqrt{18D\tau}$ and the corresponding physical time step is $\Delta t = 3\tau$ where $\tau = m/f$ is the momentum relaxation time, i.e. the ratio between the particle mass and friction coefficient. If the displaced particle collides with a neighbor one, they irreversibly stick together otherwise, a new particle is selected randomly to be displaced. The probabilities for selecting and displacing one particle are based on the individual time steps Δt_i to obtain an equivalent residence time for the whole population of particles in the box $p_i = \Delta t_i^{-1} \sum_j \Delta t_j^{-1}$. Both the probabilities of particles displacements and the persistant distances of individual particles depend on the friction coefficient. In order to take into account the possible change of flow regime due to the aggregation process, we use the method proposed by Yon *et al*., (2015) consisting on a power law between the aggregate friction coefficient and the number of primary particles. Finally, when the initial number of monomers N_0 decreases up to $N_0/8$ then each side of the box is duplicated and the number of aggregates is increased 8 times by introducing periodic images of the existing ones. Soot primary particles consist of constant bulk density ρ_p = 1.8 g/cm^3 and monodisperse diameter of 20 nm. They are suspended in air at temperature 1700 K and pressure 101.3 kPa (flame conditions). Three different volumes fractions are simulated, i.e. 1, 1000 and 10^5 ppm in order to study the impact of the diffusive Knudsen number on λ and its corresponding time-lag for SPSD.

3. RESULTS AND DISCUSSION

Fig. 1a presents the time evolution of the geometric standard deviations (GSD) of the gyration ($\sigma_{geo,dg}$), mobility ($\sigma_{geo,dm}$) and volume equivalent ($\sigma_{geo,dv}$) diameters for aggregates generated at different volume fractions. Results are presented as a function of dimensionless time t/τ_c, where $\tau_c = 0.5 n_0 K_0$ is the characteristic time of coagulation (n_0 is the initial number concentration and $K_0 = 4\sqrt{12kT/\rho_p}\, {R_{pp}}^{1/2}$, here R_{pp} is the radius of primary particles). For times larger than t/τ_c = 5, the three GSD's are within the 1.9-2.2, 1.5-1.7 and 1.5-1.6 ranges, respectively for gyration, mobility and volume equivalent. Both $\sigma_{geo,dg}$ and $\sigma_{geo,dm}$ are in good agreement with those simulated by Goudeli *et al*., (2014) however, $\sigma_{geo,dv}$ are about 10% larger than the values reported by these authors. The GSD presented in Fig. 1a can be also compared with experimental measurements. For soot particles generated in an ethylene diffusion flame (Caumont-Prim, 2013), Transmission Electron Microscopy (TEM) analysis provided $\sigma_{geo,dg}$ = 2.1 and a fractal dimension of $D_f = 1.73$ in good agreement with our simulations. Similarly, Differential Mobility Analyzer measurements gave $\sigma_{geo,dm}$ = 1.72. This agreement is also found with TEM measurements done by Cortés *et al*., (2018) who obtained $\sigma_{geo,dg}$ = 2.1-2.9 for similar fractal dimensions for soot particles measured at similar residence times in the centerline of the flame at two different soot loadings.

On Fig. 1b we see the time variation of the kernel homogeneities $\lambda_{M1}$and λ_{M2} as determined by using eq. (3) for each studied soot volume fraction. These results are averaged over a total of 10 runs for each case, error bars reported in this figure correspond to 95% confidence intervals based on the standard deviation of these 10 simulations. The λ parameters evolve in time with an important dependence on the volume fraction. For the case f_v = 1000 ppm it converges towards a value λ = 0.25. At the opposite, for the two other volume fractions, an asymptotic behavior is not observed. For both extreme cases f_v = 1 and f_v = 10^5 ppm, λ slowly approaches

to -0.1 and 0.5, respectively. In Fig. 1b we observe a comparison between the numerically determined probability density function (symbols) and the theoretical SPSD (dash lines) based on eq. (2) for the λ_{M1} determined by our method for the largest residence time simulated, i.e. t/τ_c = 19, 18 and 14 for 1, 1000 and 10^5 ppm, respectively. The agreement is also very good.

Fig. 1d presents the inverse of the particle number density as a function of time. This figure is used to determine the kinetic exponent z for each studied configuration (Table 1). As explained before, this exponent is commonly used to determine λ as reported in the third column of Table 1. In this table, we also report a range of observed variations of λ_{M1} based on the proposed 1st moment approach.

Table 1: Comparison of homogeneity coefficients as derived from the kinetics exponent (3rd column) and the propossed approach (4th column).

f_v ppm	z	$\lambda = (z-1)/z$	λ_{M1} (for $t/\tau_c > 5$)
1	1.43	0.30	-0.05 – 0.25
1000	1.53	0.34	0.25 – 0.30
10^5	1.60	0.37	0.32 – 0.49

The proposed method enables a more accurate and sensitive determination of λ than the classical method in the literature. The overall trends are similar. The values determined with the new method are well within the diffusion (λ = -0.25) and ballistic (λ = 0.55) aggregation limits reported in the literature (Heinson *et al*., 2014). This new method for calculating the homogeneity coefficient appears to be more robust than conventional ones.

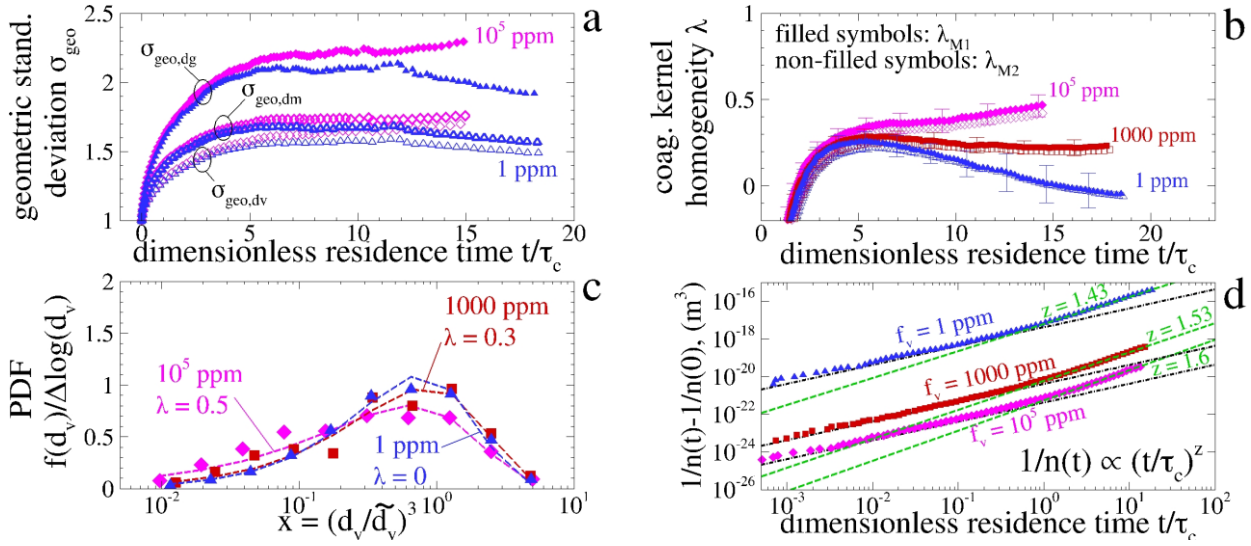

Figure 1. Attainment of the SPSD for soot aggregates.

It can be considered that a certain time is needed in order attain the SPSD. Based on our methodology, "time-lag" can be quantified by observing the convergence between λ_{M1} and λ_{M2} determined by the two moments. This is presented in Fig. 2. It appears that time-lag is around t/τ_c = 5 independently of the initial volume fraction. This observation is important for an accurate use of the Smoluchowski equation based on the self-similar approach.

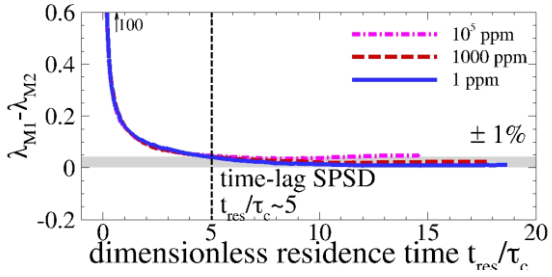

Figure 2. The time-lag for attaining the SPSD.

Currently, in the literature, this time-lag is typically calculated as the time needed to converge within 1% of error in the geometric standard deviation, this method works fine for totally coalescing spheres however, for

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non-coalescing fractal aggregates it is not necessarily the case (see Fig. 1a). This time-lag has studied for aggregates with a constant fractal dimension larger than 2 by assuming that aggregation takes place whether in purely free molecular or purely continuum flow regimes (Vermury & Pratsinis, 1995). In this context, for aggregates generated in purely free molecular regime, these authors reported a time-lag within the 3.2 - 4.3 range.

4. CONCLUSIONS

A new and more robust method for determining the kernel homogeneity is introduced and tested for different coagulation conditions consisting of different initial volume fractions. Homogeneity coefficient evolves in time in a different way depending on the initial volume fraction due to the change of aggregation regime from ballistic to near diffusive. However, this variation cannot be evaluated by conventional methods to determine the homogeneity coefficient found in the literature. The convergence between the homogeneity coefficient derived from the 1st and 2nd moments of the particle size distribution is used as a criterion to determine the time-lag for attaining the SPSD. This time-lag is found to be around t/τ_c = 5 independent on the initial volume fraction.

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