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A stochastic approach to solve the particle size distribution function of soot particles in laminar premixed flames

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Abstract

In this paper we introduce an efficient stochastic approach to solve the population balance equation which describes the formation and oxidation of soot particles in a laminar premixed flame. The approach is based on a stochastic particle system representing the ensemble of soot particles. The different processes contributing to the formation and oxidation of soot particles are treated in probabilistic manner. The stochastic algorithm, which makes use of a very efficient majorant kernel and the method of fictitious jumps resolves the entire soot particle distribution (PSDF) without introducing additional closure assumptions. A fuel rich laminar premixed flame of acetylene is computed using a detailed kinetic soot model. Solutions are obtained for both, the stochastic approach and the method of moments combined with a modified version of the code Premix which is part of the CHEMKIN package. In this manner, for the first time, the accuracy of the method of moments in a real flame is investigated. It is found that the accuracy for the first moment is excellent (5% error), and mean error for rest of the moments is within 25%. Also the effect of the oxidation of the smallest particles (burnout) has been quantified but was not prominent in the flame investigated. The time evolution of computed size distributions as well as integral values are compared to experimental measurements and the agreement was found to be satisfactory. The results show that the PSDF of soot particles is bimodal. Finally, the efficiency of the method is studied.

Contents

Introduction

When modelling the formation of soot in flames, one is interested in the spatial and temporal evolution of the size distribution of the soot particles. Hence the problem of solving the population balance of soot particles has to be studied [1]. For this purpose we have to model the mechanisms of particle formation, growth and oxidation [2] and we need to solve the corresponding population balance equation. Several approaches have been developed to find a solution to the latter problem. Frenklach et al. applied the method of moments [3, 4], which is based on the fact that the solution of the population balance equation is equivalent to the solution of an infinite set of equations for the moments of the size distribution. The method of moments is computationally very efficient and it provides integral quantities such as mean number density and volume fraction that are normally available from measurements. The information of the exact shape of the size distribution is however lost and approximations (interpolation schemes) have to be made to close the system of equations for the moments, which are introduced by coagulation and surface reactions. The knowledge of the shape of the size distribution might however be desired in some cases, in particular in the light of recent findings that ultra-fine particles might be responsible for effects of diesel exhaust on human health [5].
Numerical methods that approximate the size distribution rather than its moments include discrete sectional [6, 7], stochastic [8, 9] and Galerkin methods [10]. Hitherto, only the sectional method and the Galerkin method have been applied to model the soot PSDF. In Ref. [11], a two-dimensional laminar diffusion flames is simulated with a sectional method, and in [12] a Galerkin method has been employed to model a one-dimensional premixed laminar flame. While these methods deal with the size distribution at different levels of resolution, they require by far more computational time than the method of moments. Both approaches, however, have the drawbacks that there is no information about the history of single particles and that the treatment of higher dimensional size distributions to account for several internal variables is not straight forward and are likely to be of very high numerical complexity.
The **purpose of this paper** is to present an alternative approach to solve the population balance of soot particles, that removes some of these limitations. The new method is based on a stochastic description of the particle ensemble. All processes of soot formation and oxidation are treated probabilistically using Monte-Carlo techniques. The method makes use of the new concept of fictitious jumps employing a majorant kernel and hence is much more efficient than previously used Monte-Carlo methods [13, 14]. Another important property of this algorithm is the fact that there exists a mathematical prove that the stochastic particle system converges to the exact solution of the population balance equation. Furthermore, the modelling of higher dimensional distributions is straightforward and the sizes and the age of particles is known explicitly.
The new stochastic particle method is coupled to a detailed kinetic soot model to simulate soot formation and oxidation in laminar premixed flames. The detailed kinetic soot model used was developed by Frenklach et al. [4, 15, 16] and Mauss et al. [17, 18] in fuel rich laminar premixed and counterflow flames but has also been

used to model soot formation and oxidation in more complex systems such as 2D laminar and turbulent non-premixed flames [19, 20], diesel engines [21, 22] and gas turbines [23, 24]. In this study, we focus on two different issues. The accuracy of the method of moments is assessed and numerically computed PSDFs is compared to measured PSDFs. In particular, the oxidation of the smallest particles, which leads to an unclosed term in the method of moments, is investigated and the associated error is quantified. This is of importance in diesel engines and gas turbines where the number of emitted particles is determined by oxidation and burnout. Finally, some remarks on the efficiency of the stochastic method are made. It is however not the intention of this study to thoroughly assess and compare the stochastic method to other numerical methods. Details of this new algorithm will be published elsewhere [25].

This paper is organized as follows. First the model describing gas phase chemistry and the formation and oxidation of soot particles is briefly presented. Then the new algorithm for solving the the dynamics of the soot particles is introduced. The next section contains the specification of the simulated flame and describes how the stochastic model is coupled to a one-dimensional flame code. Finally, different case studies are presented and discussed in detail. These case studies address the accuracy of the method of moments, the rôle of the oxidation as a source of computational error, and the comparison of measured and simulated PSDFs.

1 Modelling

The soot particle size distribution is described by the following equation:

$$\frac{\partial}{\partial t}N(t,k) = R(t)\delta^*_{in} + G(t,k) + W(t,k), \tag{1}$$

with the initial condition

$$N(0,k) = N_0(k) \geq 0, \tag{2}$$

where $N(t,k)$ is the number density of particles of size k at time t, $R(t)$ the rate of particle inception, δ^*_{in} is the size of the incepted particles, $G(t,k)$ is the rate of coagulation and $W(t,k)$ the rate of surface reactions. The following section presents the physical models for the terms on the right hand side of eq. (1) followed by a description of the method of moments and the new stochastic particle algorithm.

1.1 Soot Formation, Growth and Oxidation

The modelling of the gas phase chemistry and the formation and oxidation of soot particles is taken from Frenklach et al. [4, 15, 16]. The gas phase mechanism [15, 16] describes the oxidation of the fuel and the formation of polycyclic hydrocarbons (PAHs). Soot particles are formed by particle inception, which in this study is modelled as dimerization of two pyrene molecules:

$$R(t) = \frac{1}{2}\beta_{pyrene}N_{pyrene}N_{pyrene}, \tag{3}$$

where β_{pyrene} is the coagulation kernel of two pyrene molecules and N_{pyrene} the number concentration of pyrene. Soot particles grow in size by coagulation, which is described by Smoluchowski's [26] equation:

$$G(t,k) = \frac{1}{2}\sum_{j=1}^{k-1}\beta(t,k-j,j)N(t,k-j)N(t,j) - \sum_{j=1}^{\infty}\beta(t,k,j)N(t,k)N(t,j), \quad (4)$$

where $\beta(t,k,j)$ is the coagulation kernel. Soot particles interact with the gas phase by surface reactions. Surface reactions include surface growth by acetylene, condensation of PAHs, i.e. pyrene, on to the soot's surface and oxidation of particles by molecular oxygen and hydroxyl radicals. They are described by the following equation:

$$W(t,k) = \sum_{l=1}^{4}\left[w^l(t,k-\delta k)N(t,k-\delta k) - w^l(t,k)N(t,k)\right], \quad (5)$$

where $w^l(t,k)$ is the rate of surface process l acting on particles of size k and δk the change in mass induced by the process, e.g. condensation, $l=1$, $\delta k = 16$; surface growth, $l=2$, $\delta k = 2$; oxidation by O_2, $l=3$, $\delta k = -2$; oxidation by OH, $l=4$, $\delta k = -1$. The rates $w^l(t,k)$ are modelled as reported by Frenklach et al. [4, 16]. Condensation is modelled as coagulation of a pyrene molecule and a soot particle [17, 16]. Surface growth is assumed to occur due to addition of acetylene to a radical site on the soot's surface, i.e. the hydrogen abstraction acetylene addition (HACA) mechanism is used. Surface oxidation is considered as reactions of O_2 with surface radicals and reactions of OH with the surface of the particles.

1.2 The Method of Moments and the New Stochastic Particle Algorithm

As mentioned in the introduction one aim of this paper is to compare the results of the well established method of moments with a new stochastic particle algorithm which solves equation (1), In the method of moments eq. (1) is transformed into equations for the moments of the soot PSDF, where the moments are defined as:

$$M_r = \sum_{i=1}^{\infty} i^r N_i. \quad (6)$$

However, the rates of the moments can not be obtained in closed form and have to be approximated. Fractional moments, that appear in the rate terms, have to be calculated by interpolating between the integer-order moments and a double interpolation scheme has to be introduced to close the coagulation rate term. Furthermore, since the number density of the smallest size class is not known, the oxidation rates for the $0th$ moment, i.e. the burnout of small soot particles, can not be taken into account explicitly. For technical details refer to [4].

Instead of solving the equations for the moments, the ensemble of soot particles can be approximated by a stochastic particle system. The different processes of particle inception, coagulation, and surface growth determine the dynamics of this stochastic particle system. In the following we describe the direct simulation Monte Carlo algorithm to demonstrate how a stochastic algorithm works. Then the actual new algorithm is stated in algorithmic language.

The rates of the different events, i.e. particle inception, coagulation, condensation, surface growth, oxidation by O_2 and oxidation by OH, are calculated corresponding to the detailed soot model as mentioned above. Using these rates the size of the individual time steps or the waiting time is determined according to an exponentially distributed random variable [8]. Next, one of the possible events is chosen probalistically relative to their rates. Depending on which of the events has been selected, the appropriate number of particles needed to perform this event is chosen according to the particles' individual rates. For coagulation e.g. two particles of size i and j are selected in line with the coagulation kernel $\beta(t, i, j)$. Once a step is performed the state of the particle system is updated and a new time step is determined. For oxidation by O_2 e.g. a particle of size i is removed from the system and another particle of size $i - 2$ is added. This cycle of steps is repeated until the final simulation time is reached.
The system of stochastic particles in the algorithm does however not represent the full ensemble of soot particles. Thus one stochastic particle represents a certain number of soot particles depending on a numerical parameter N, which must be specified for each calculation. The choice of this numerical parameter N is determined by a tradeoff between accuracy and computational time needed for one simulation. As mentioned before a property of the algorithm is that it converges to the solution of the master equation for the parameter N approaching infinity [13]. Therefore if we choose N in such a way that specifically chosen functionals of the solution, like the fifth moment for example, do not change with increasing N we know that we are sufficiently close to the solution of eq. (1). To enhance the performance of the algorithm as compared to a direct Monte-Carlo simulation [8], the concept of majorant kernels and fictitious jumps presented in [13] is used. In this concept the actual coagulation kernel is replaced by a majorant kernel, which always exceeds the real kernel. An efficient majorant kernel for coagulation in the free molecular regime [14] is applied here. Using these concepts the computational time increases approximately linearly with the number of stochastic particles N, whereas it is proportional to N^2 using a straightforward treatment of coagulation.
The new simulation algorithm reads as follows:

1. Generate the initial particle system.

2. Wait an exponential distributed time step τ with parameter $\hat{\rho}(p)$, which is the sum of all rates at that time.

3. Select which event to perform based on its probability calculated from rate of the event.

4. If
   (a) particle inception is selected go to step .
   (b) coagulation is selected go to step 6.
   (c) condensation is selected go to step 7.
   (d) surface growth is selected go to step 8.
   (e) oxidation by O_2 is selected go to step 9.
   (f) oxidation by OH is selected go to step 10.
5. Perform a particle inception step, i.e.
   (a) Add a cluster of size 32 to the system and go to step 11.
6. Perform a coagulation step.
   (a) Generate particles i and j according to their probabilities given by the majorant kernel.
   (b) If the selected coagulation event is not fictitious add particle $i + j$ to the system and remove particles i and j. Otherwise nothing changes. Go to step 11.
7. Perform a condensation step.
   (a) Select a particle i according to the condensation rate.
   (b) Replace particle i by particle $i + 16$ and go to step 11.
8. Perform a surface growth step.
   (a) Select a particle i according to the surface growth rate.
   (b) Replace particle i by particle $i + 2$ go to step 11.
9. Perform an oxidation by O_2 step.
   (a) Select a particle i according to the O_2-oxidation rate.
   (b) Replace particle i by particle $i - 2$ and go to step 11.
10. Perform an oxidation by OH step
    (a) Select a particle i according to the surface growth rate.
    (b) Replace particle i by particle $i - 1$ and go to step 11.
11. Update the particle system and go to step 2.

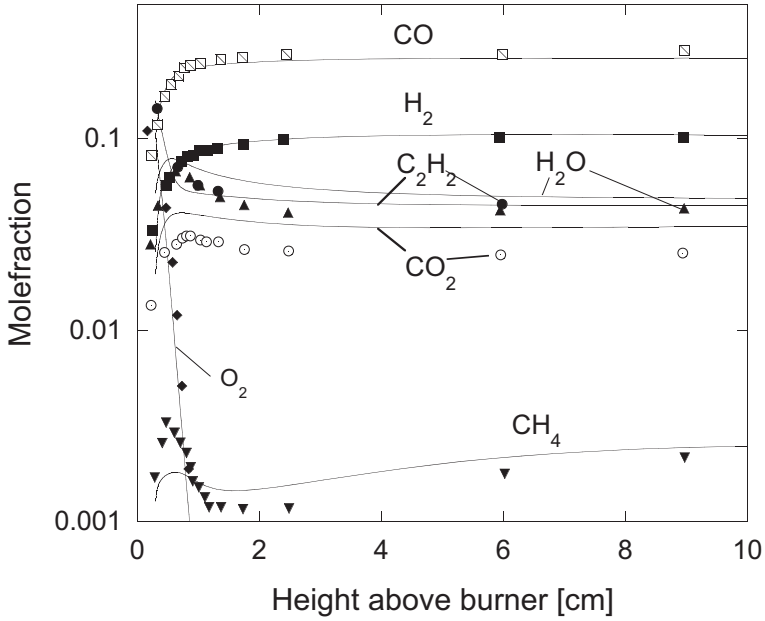

Figure 1: *Comparison of measured [27, 28, 29, 30] and simulated mole fractions of major species.*

1.3 Simulation Details

A $C_2H_2/O_2/Ar$ laminar premixed flame was simulated ($p = 0.12\,atm$, $v = 20.4\,cm/s$, C/O = 1.1, Ar = 55% mole fraction, $T_{max} = 1992\,K$). For this flame measurements of species concentration, temperature, mean number density, soot volume fraction as well as relative size distributions of soot particles at several heights above the burner were available from literature [27, 28, 29, 30] .
A modified version of the Premix code [31, 32], including equations for the moments of the PSDF [17] was applied. Both, the model parameters of the soot model and the gas phase mechanism are taken from Ref. [16]. With this code a steady state solution of the coupled transport equation for chemical species and the first six moments of the PSDF was obtained. The temperature profile was taken from the experimental measurements. Gas phase species and the moments of the PSDF were coupled through particle inception and surface reactions. The temperature, velocity and species profiles obtained from this steady-state solution were subsequently used to simulate soot formation in a Lagrangian manner. In other words a system of ODEs describing the time evolution of the first six moments of the PSDF was solved using the computer code LSODE. The Stochastic particle system was solved using the algorithm described in the previous section. In both cases the source terms were taken from the computed premix profiles by transforming the spatial coordinate into a time coordinate using the known velocity.

The different simulations performed in this study are divided in two cases summarized as follow.

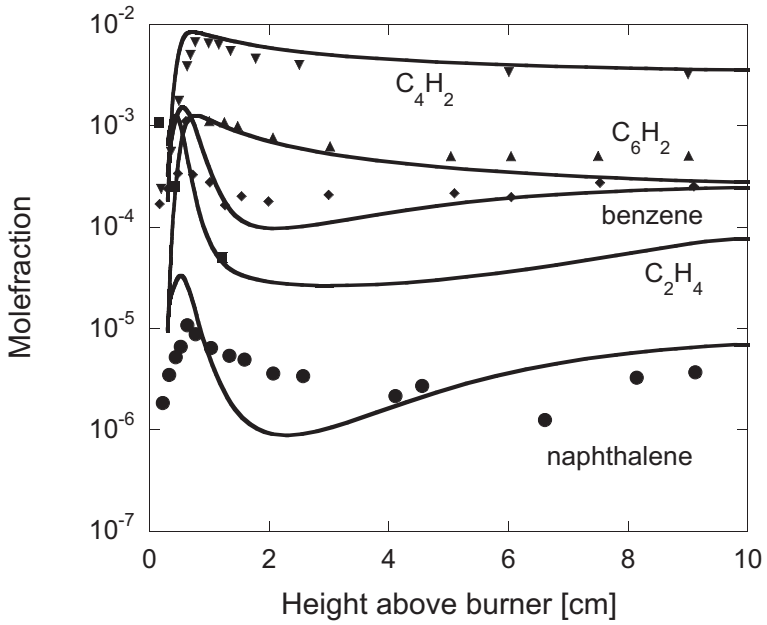

Figure 2: *Comparison of measured [27, 28, 29, 30] and simulated mole fractions of minor species.*

Case 1: **Oxidation switched off**. Aim of this numerical study was to assess the numerical error introduced by the interpolation scheme that is used by the method of moments. In order to avoid the error caused by the closure of the oxidation term in the method of moments the oxidation was switched off in both models.

Case 2: **Oxidation switched on**. In this study the aim was to compare both methods with experimental data and to quantify the numerical error introduced by the oxidation closure. Again two cases were considered:
Case 2(a): Oxidation (burnout) of the smallest particles ($i = 32$) not taken into account.
Case 2(b): Including oxidation (burnout) of smallest particles. This case corresponds to the full soot model, which is described in section 1.1.

2 Results

Starting point of the numerical studies was the simulation of the low-pressure $C_2H_2/O_2/Ar$ flame with the modified Premix code using a measured temperature profile. In **Figure 1** the mole fractions of the major species are displayed. The flame is located approximately 0.5 cm away from the burner. In **Figure 2** the mole fraction of minor species as well as the aromatic compounds benzene and naphtalene are shown. For all species good agreement between measurements and simulation is found. From these profiles the source terms for the following studies are calculated.

To couple the gasphase species with the soot particle surface reactions we solve the

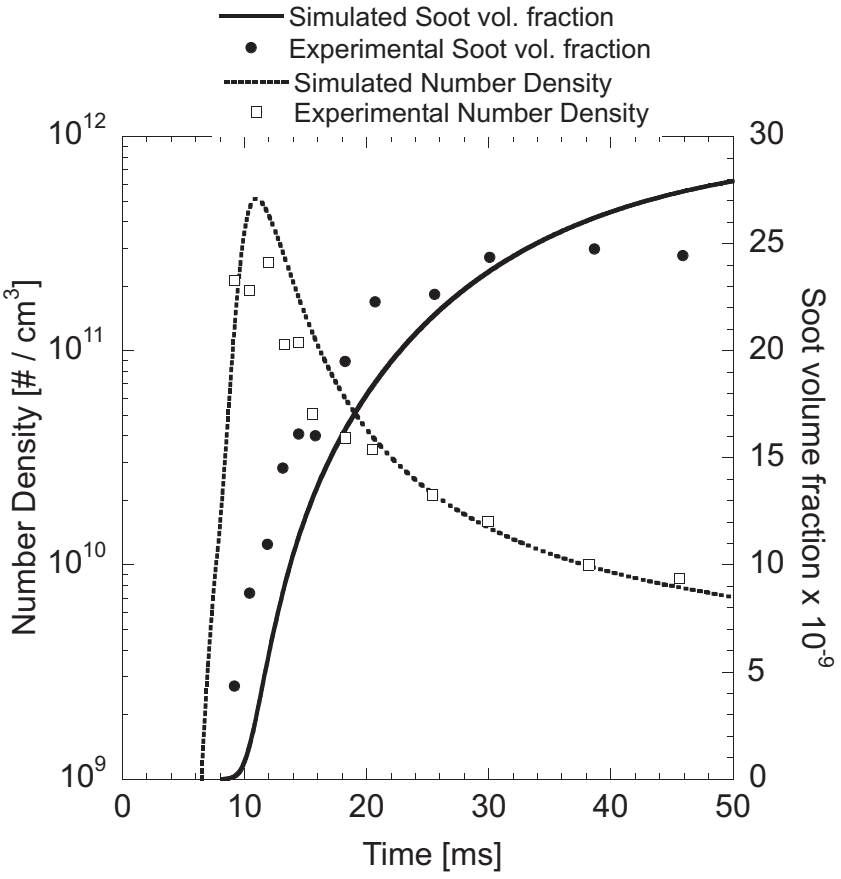

Figure 3: *Comparison of measured and simulated number densities and soot volume fractions. The simulated values were obtained using the code Premix augmented with the transport equations for the first six moments of the soot PSDF. The experimental values were taken from [27, 28, 29, 30].*

full one-dimensional transport equation for the first six moments of the PSDF as described by Mauss et al. [17, 16]. In **Figure 3** the computed number density and soot volume fraction are compared with the experimental measurements. Good agreement was found for soot volume fraction whereas the maximum value of number density is overpredicted by a factor of two. The agreement between measured and computed values is however excellent at larger heights above burner. The discrepancy in number density can be explained by the fact that particles smaller than $d = 1nm$ could not be measured in the experiment whereas the smallest particles in the model have a diameter of around $d = 0.87nm$.

In order to assess the error caused by the interpolation between moments of the PSDF to approximate fractional moments we perform simulations where the oxidation of the soot particles is switched off. This is to insure to study the same model with the stochastic algorithm as with the method of moments. Frenklach and Harris [3] found in their study good agreement between the method of moments and a dis-

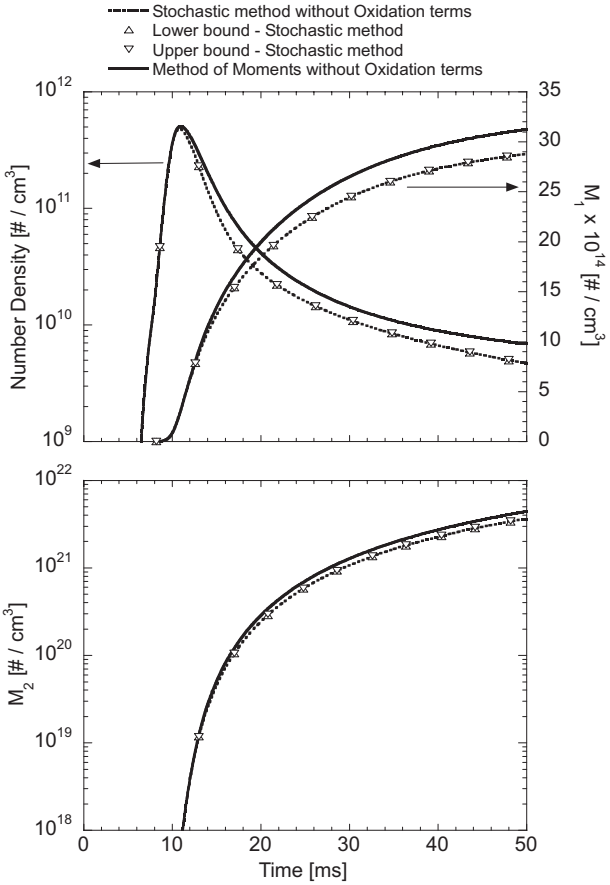

Figure 4: *Comparison of first three moments with the Method of moments and the Stochastic approach as a function of time. Oxidation has been switched off in order to asses the error caused by the interpolation of the fractional moments.*

crete approach for simultaneous coagulation, particle inception and surface growth. Limitations in CPU-time made a thorough verification of the model however impossible, i.e. the number of discrete size classes and thus the simulation times were small. A better verification of the method of moments is however possible with the new stochastic approach due to its accuracy and efficiency. Simulations with a large value of the model parameter N and thus a high accuracy can be conducted within reasonable computational time. To investigate the convergence of the stochastic method with respect to model parameter N, N was varied in a range from 10^3 to 10^7 and the systematic error was investigated. Doing so, we could ascertain that the solutions that are used in the following were converged and the error was sufficiently small. **Figure 4** shows a comparison of the moments calculated with the method of moments and the solution obtained with the stochastic approach. Mean moments as well as confidence intervals are given for the stochastic approach. Note that oxidation by O_2 and OH was not taken into account. It can be seen that the method of moments overpredicts the moments and deviation from the solution increases with increasing residence time. In order to quantify the accuracy of the method of mo-

ments, the mean error of the method was computed for the whole computational domain. The mean error of the zeroth and first moments is around 25% and 5% respectively. The mean error increases however for the higher moments, e.g. the error for the second moment is 13% and for the third moment 20%. Thus it can be summarized that, in the case studied here and with this particular formulation of the method of moments [32], the method of moments exhibits reasonable accuracy for all the moment and excellent for the first moment. However, having in mind the efficiency of the method and the uncertainty of the parameters in the soot model, the method of moments is sufficiently accurate.

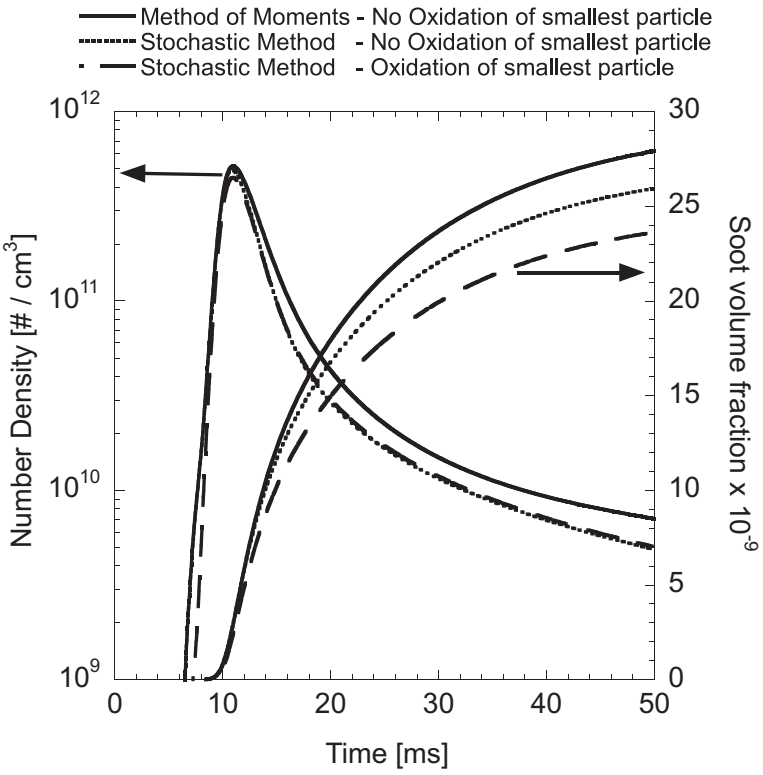

Figure 5: *Comparison of number density and soot volume fraction as a function of residence time obtained with the method of moments and the stochastic approach. Two different oxidation models for the stochastic method are studies.*

As already mentioned, a drawback of the method of moments is that the rates in equation (1) can not be closed properly and approximations have to be used, e.g. the rate of oxidation of the zeroth moment. In the method of moments this rate can not properly be closed since the number density of particles in the smallest size class is not explicitly known. The implementation of the physical models describing formation and oxidation of soot particles into the stochastic approach is straightforward and no assumptions have to be made. Therefore, it was possible to investigate the effect that the oxidation of the smallest particles has on mean number densities and volume fraction. For this purpose, we defined the smallest particle to be of size $i = 32$, i.e. being comprised of 32 carbon-atoms, since this is also the size of

the incepted particles. However, note that the method would also allow for a more complex treatment of burnout of particles. Two simulation cases for the stochastic approach were defined differing in their treatment of the oxidation of smallest particles. The two cases (2(a) and 2(b)) are compared to the results obtained with the method of moments in **Figure 5**. It can be seen that the burnout of the smallest particles reduces the number densities and the volume fraction by about 10%. This is again not critical for the method of moments due to the uncertainties in the oxidation rate constants. Also, this error can be reduced by solving an additional equation for the first size class [3] or by using approximations for the contribution of the oxidation of the smallest particles to the total rates of the moments [17]. The flame investigated is however a fuel rich premixed flame where oxidation is of minor importance. The effect of burnout is expected to be more important when the overall fuel/air ratio is lean as in diesel engines or gas turbines. It is anticipated that the new stochastic approach improves the modelling of burnout of soot particles in these devices.

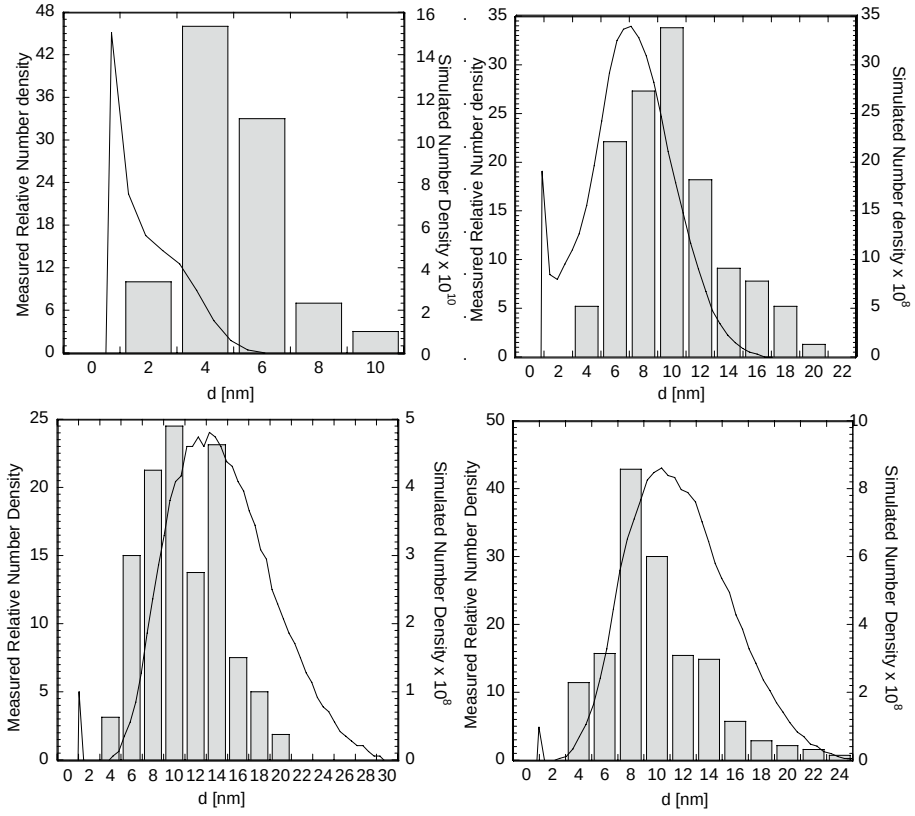

Figure 6: *Comparison of measured (columns) [27, 28, 29, 30] and computed (—) size distributions of soot particles at different heights above the burner.*

Finally, the computed and measured [27, 28, 29, 30] size distributions are compared, see **Figure 6**. The percentage of relative number densities is presented, i.e. the number density of particles of a certain size range collected in bins. The bin size of

the experimental data is $2\,nm$ while the bin size of the simulations is proportional to the square root of the total number of particles. Note that in the experimental study the lower detection limit was reported to be $d = 1\,nm$, and that particles were collected in bins of $2\,nm$ size and are given in percent of the relative number density. Since the smallest particles in the detailed soot model are smaller than $1\,nm$ and in order to obtain a better resolution of the size distribution, we chose the square root of the actual number of particles as the basis of our bin size. Thus the heights of the two distributions are different. Also, note that the scale of the relative number density is changing and thus the distribution should be compared in accordance to changing scales. The shape of the computed PSDF at $x = 14\,mm$ is very different from the measured one. The reason for this might be that the smallest particles in the model are smaller than $1\,nm$. Whether particles of this size should be considered as soot particles or as large PAHs is of course not obvious from this calculation. The agreement between measured and computed PSDFs improves with increasing height above the burner. This gives evidence that the poor agreement at $x = 14\,mm$ actually stems from the different definition of a smallest soot particle.

Figure 7 finally shows the temporal evolution of the size distribution. Note that the logarithm of the number densities is given and that the particles were collected in bins of $0.5\,nm$ size. Initially, the distribution is very narrow due to a peak in particle inception rate. At larger heights above the burner, the distribution broadens since the processes of coagulation and surface growth dominate. The small peak at the small size part of the distribution exists at all heights above burner due to continuous particle inception. However one has to be aware that a simple particle inception model was used, i.e. soot particles are formed exclusively from pyrene. A gap between in the distribution is formed due to the size dependence of coagulation and surface reactions.

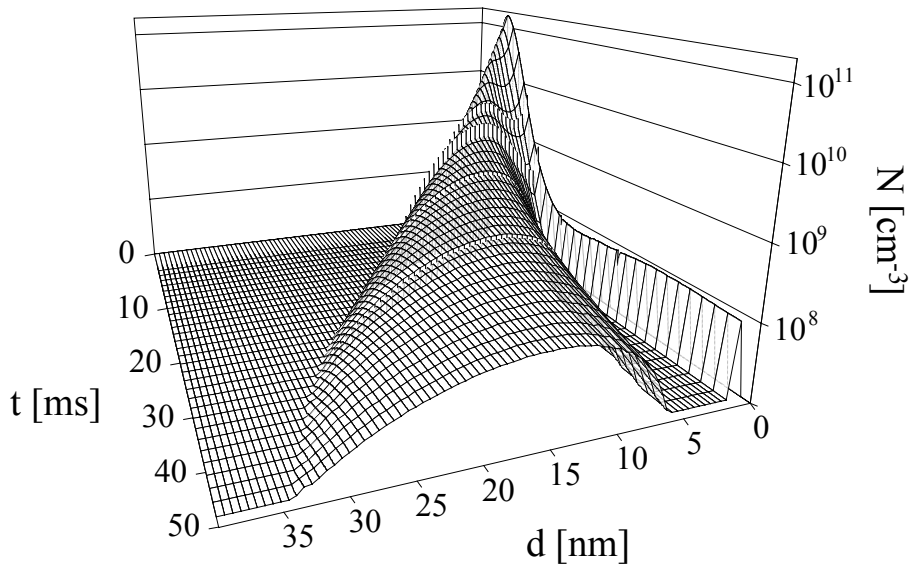

Figure 7: *The temporal evolution of the computed size distribution of soot particles. Presented are the number densities of bins of size 0.5 nm.*

Finally, the efficiency of the stochastic approach was investigated. The method includes two model parameters, which determine the accuracy and thus also the efficiency: the parameter N introduced above and the number of repetitions, i.e. the number of independent runs. Simulations with different values of N were conducted and the accuracy of the solutions were compared to the accurate solution and the solution obtained with the method of moments. It was observed that the error using $N = 10000$ is small and considerably lower than the error resulting from the method of moments. One repetition with $N = 10000$ takes about $70\,s$ on a computer equipped with a Pentium III 1GHz processor. To get a solution with a small confidence intervals, normally 30 repetitions are required but already a fewer number can produce good results. If one is only interested in a very accurate description of the first three moments even a number of $N = 1000$ is sufficient. This reduces the CPU time of one repetition to about $t \approx 8\,s$. The method is thus very efficient although slower than the method of moments. The stochastic method provides on the other hand more detailed information about the particle ensemble and simplifies the use of more complex physical models. It is anticipated that the new approach can further be improved in terms of accuracy and speed by applying variance reduction techniques and adaption in time.

3 Conclusion

A new approach for solving the population balance equation of soot particles in laminar premixed flames is presented. The approach is based on a stochastic particle system representing the ensemble of soot particles. All processes occurring during the formation and oxidation of soot particles are treated probabilistically. The approach is applied to simulate soot formation and oxidation in a laminar premixed $C_2H_2/O_2/Ar$ flame using profiles of temperature and species computed with help of a modified version of the Premix code. A converged, exact solution for the temporal evolution of the PSDF of soot particles was computed for the investigated flame and used to verify the accuracy of the method of moments. While the agreement for higher moments of the PSDF is fair, the accuracy of the first two moments obtained from the method of moments is good. This demonstrates the usefulness of the method of moments for physical model development when only mean quantities such as number density and volume fraction are required. The effect of neglecting the burnout of small particles was investigated. It was shown that the error of not taking this effect into account is small in the studied flame. Neglecting this effect in systems where oxidation of soot particles plays a more important role such as diesel engine and gas turbine combustion may however lead to more significant errors. The computed size distribution was compared to measurements and the agreement was found to be reasonable although a direct comparison was not feasible.
The stochastic approach was found to be very efficient as compared to other methods used in the field of population balance modelling. The method is however superior to others since: a) it is known to converge to the correct solution of the population balance equation, b) the whole size distribution is resolved c) it is very efficient

and d) an expansion to more detailed physical models is straightforward. Future work will include improvements of the efficiency of the algorithm by using variance reduction techniques as well as adaption in time. Also, diffusion and thermodiffusion of soot particles will be included in the model.

4 Acknowledgment

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