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A Detailed Chemistry Approximation for Turbulent Combustion Models Based on the Probability Density Function

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Abstract

In this paper based on a stochastic chemistry approximation for the chemical source term in the PDF transport equation, further optimizations and approximation have been implemented. The motivation of this approach is to speed up the algorithm. The algorithm presented was applied to a PSR model. Moreover, numerical performance of this new algorithm was investigated in a more complex system. The non-premixed combustion of an n-heptane fuel stream injected into hot air was chosen as a test case. The numerical error caused by the splitting procedure was studied. From this study a suitable time step was chosen to benchmark the new stochastic chemistry approximation against the standard deterministic DASSL. It was found that, depending on the required accuracy, the new stochastic approach clearly outperforms the deterministic method for the case studied.

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1. Introduction

Turbulent combustion is ubiquitous in today's technology. For example, gas turbines, diesel engines and spark-ignition engines make use of it. An important problem of combustion technology in general is its detrimental impact on the environment through unwanted emissions of combustion products and by-products. Industry employs numerical modelling of these processes to achieve a better understanding in order to reduce combustion emissions. Although good progress in the development of such numerical models has been made over the last decades there are still open problems. One modelling approach that has been proved to be quite successful is based on the probability density (PDF) transport equation of the physical quantities of interest [13, 2]. The numerical method for solving the PDF transport equation employs a Monte Carlo technique combined with an operator splitting approach. The Monte Carlo technique is based on a stochastic particle-mesh method. The numerical accuracy of this method has been thoroughly investigated in [16]. However, using Monte Carlo method, the computational cost for the chemistry step is very high. In the chemistry step the chemical species and the temperature are advanced in time which means for each stochastic particle a system of ordinary differential equations (ODE) has to be solved numerically. This system of ODE is usually stiff and special solvers are required to obtain the numerical solution [3, 4, 5]. For large chemical models the number of chemical species can be quite large and the computational time required to solve the system of ODE for each particle is prohibitive. Only in very special cases can full chemistry models be used. For example, if statistical spatial homogeneity is assumed, even large chemical mechanisms, which are necessary to predict the formation and oxidation of soot, can be dealt with [1]). If the full PDF equation has to be solved then it is necessary to reduce the number of scalar quantities. There are different strategies to do this. For instance, sometimes it is sufficient to model combustion by one or a set of global reaction expressions [9]. In many cases a reduced chemical mechanism can be used. These chemical mechanisms are obtained from detailed chemical mechanisms by choosing steady state species and invoking the partial equilibrium assumptions [12]. They are either integrated directly or, in most cases, they are tabulated. The reduction procedure usually leads to numerically very expensive expressions and real computational speed advantage is only achieved if a tabulation procedure is used [2]. A similar strategy is to reduce the number of scalar variables by using the ILDM technique [10]. Here the fast and slow variables of the chemical reaction system are identified by an eigenvalue decomposition of the linearized chemical source term. From this analysis a table can be constructed that allows one to compute all fast quantities as functions of the slow variables [11, 14]. More recently Pope has developed a tabulation strategy [14] which uses skeleton mechanisms and does not introduce limits on time scales. In this technique the table is created along with the simulation. The precision is controlled using the eigenvalues of the chemical source term. Most of the techniques described above have been combined with a neural network to speed up data retrieval and reduce storage requirements. However, all different tabulation procedures have in common that they are restricted to a quite small number of independent variables.

The limit is mainly due to two reasons. One reason is that the memory that is required grows non-linearly with the number of variables. Second, the data retrieval can become time consuming and not very accurate.

All of the methods described above have in common that for each stochastic particle they attempt to solve the chemistry in a deterministic way. This means that the trajectory of a stochastic particle evolves deterministically according to the chemical source term. Other processes like mixing are normally solved in such a way that their trajectories are intrinsically stochastic. This applies to all particle interaction models, e.g. the CURL model just to name one representative of this model class. Consequently, although we compute the trajectories of each particle deterministically we do not make use of it because we are really interested in the PDF as a whole or functionals of the PDF such as the mean and variance. In order to include many species as variables for the PDF transport equation to describe emissions appropriately, we want to introduce a new and alternative method to compute the chemical source term in the PDF transport equation. In our former work an improved stochastic approximation was developed [8], and it was employed to replace the deterministic chemistry step in premixed system using PaSPFR model [7]. However, there is no optimization used fully in these two papers. The **aim** of this paper is twofold. Firstly, based on the stochastic approximation, further optimizations and approximations were implemented to speed up the algorithm, without influencing the precision. To achieve this the stochastic reactor model PSR which contains only the operation for chemical reaction is used. We studied the premixed combustion of n-heptane using a detailed chemical mechanism with 106 chemical species and 808 reversible reactions. Secondly, the numerical performance studying the non-premixed combustion system was investigated. For this purpose the stochastic reactor model PaSPFR which contains operations for mixing and chemical reaction was used. In a first step the error caused by the operator splitting was investigated using deterministic chemistry. This has two purposes, one is to ensure the error caused by the operator splitting is smaller than the error caused by the stochastic particle approximation, and another is to choose the maximum splitting time step in order to achieve a fair comparison between the stochastic and deterministic solution method. Then the new approximation of the chemistry was compared with the deterministic chemistry step which was computed using DASSL [3].

2. The algorithm

We state a Monte Carlo algorithm to obtain a solution for the PaSPFR model given by the following PDF equation,

$$\frac{\partial}{\partial t}f(t,\psi) - \sum_{k=1}^{S+1} \frac{\partial}{\partial \psi_k} \left(\left[R_k(\psi) + C M_k(f(t,\psi),\psi) \right] f(t,\psi) \right) = 0, \qquad (2.1)$$

where $t \ge 0$, with initial condition

$$f(0,\psi) = f_0(\psi).$$
 (2.2)

The components of the vector ψ correspond to the mass fractions Y_1, \ldots, Y_S of several chemical species and to temperature T. The terms M_k represent the **mixing mechanism** of the system. We use the well known IEM or LMSE model (see [6]). The terms R_k describe the **chemical source terms** given by the detailed reaction mechanism with I elementary chemical reactions,

 $(\nu_{\alpha,1},\ldots,\nu_{\alpha,S}) \longleftrightarrow (\nu_{\alpha,1}^*,\ldots,\nu_{\alpha,S}^*), \qquad \alpha = 1,\ldots,I.$ (2.3)

The stoichiometric coefficients $\nu_{\alpha,i}$ and $\nu_{\alpha,i}^*$ of the species *i* in reaction α are non-negative integer values.

In order to generate trajectories of the stochastic process, one introduces a **system** of weighted particles

$$(w^{(i)}, \Psi^{(i)}(t))$$
 $i = 1, \dots, N$ (2.4)

where

$$\sum_{i=1}^{N} w^{(i)} = 1.$$
 (2.5)

Its time evolution is determined by

$$\frac{d}{dt}\Psi_k^{(i)}(t) = -R_k(\Psi^{(i)}(t)) - C\left[\Psi_k^{(i)}(t) - \sum_{j=1}^N w^{(j)}\Psi_k^{(j)}(t)\right],$$
(2.6)

where k = 1, ..., S+1, and $\Psi^{(i)}(0)$, i = 1, ..., N, are independent random variables and distributed according to f_0 . In general the system (2.6) is high-dimensional. Therefore, a **splitting approach** on a time interval $[s, s + \Delta t]$ is applied, in order to decouple the effects of reaction and mixing. The **reaction step** is

$$\frac{d}{dt}\,\tilde{\Psi}_{k}^{(i)}(t) = -R_{k}(\tilde{\Psi}^{(i)}(t))\,,\qquad t \ge s\,,\qquad \tilde{\Psi}_{k}^{(i)}(s) = \Psi_{k}^{(i)}(s)\,,\qquad(2.7)$$

and the **mixing step** is

$$\Psi^{(i)}(s + \Delta t) =$$

$$e^{-C\Delta t} \tilde{\Psi}^{(i)}(s + \Delta t) + \left[1 - e^{-C\Delta t}\right] \sum_{j=1}^{N} w^{(j)} \tilde{\Psi}^{(j)}(s + \Delta t) .$$
(2.8)

This leads to the following **algorithm**.

0. Determine the state of the system of particles (2.4) at time 0 according to the initial density f_0 .

- 1. Given the state of the system at time s, each particle is moved according to the reaction step (2.7).
- 2. Given the system $\tilde{\Psi}^{(1)}(s + \Delta t), \ldots, \tilde{\Psi}^{(N)}(s + \Delta t)$, each particle is moved according to mixing step (2.8).
- 3. If time exceeds termination time then STOP. Otherwise go to Step 1.

2.1. The chemistry step

The chemistry step (2.7) is usually solved by integrating the system of ODE for each particle numerically to obtain the trajectories for each particle. The **new approach** in this paper is to approximate the trajectory by a stochastic process. For this purpose each particle is represented in the form

$$\Psi = \left(N_1^{(n)}(t), \dots, N_S^{(n)}(t), T^{(n)}(t) \right),$$

where $N_j^{(n)}(t) \ge 0$ denotes the approximate mole number (Unit = mole) of species $j = 1, \ldots, S$, and $T^{(n)}(t) > 0$ denotes the approximate temperature at time t. The number of sub-particles

$$n = \sum_{j=1}^{S} N_j^{(n)}(0)$$

plays the role of an approximation parameter. The right choice of this approximation parameter is a priori not clear and needs to be determined in numerical studies.

Step 0

The **initial state** of the system is determined as

$$N_j^{(n)}(0) = n X_j(s), \qquad j = 1, \dots, S, \qquad T^{(n)}(0) = T(s),$$

according to the initial conditions of the differential equation (2.7).

Step 1

Given the state x at time t, the process remains there for a random waiting time τ such that

$$\operatorname{Prob}(\tau \ge u) = \exp(-u\,\pi(x))\,, \qquad u \ge 0\,,$$

where

$$\pi(x) = \sum_{\alpha=1}^{I} |Q_{\alpha,f}(x) - Q_{\alpha,r}(x)|,$$

and $Q_{\alpha,f}$ and $Q_{\alpha,r}$ are, respectively, the forward and reverse reaction rates of reaction α . The procedure stops when time $t + \tau$ exceeds the splitting step Δt .

Step 2

At the moment $t + \tau$, a particular reaction is chosen according to the **reaction** probabilities

$$P_{\alpha}(x) = \frac{|Q_{\alpha,f}(x) - Q_{\alpha,r}(x)|}{\pi(x)}, \qquad \alpha = 1, \dots, I$$

Step 3

Finally, the process jumps into the state

$$J_{\alpha}(x) = \begin{cases} J_{\alpha,f}(x), & \text{if } Q_{\alpha,f}(x) \ge Q_{\alpha,r}(x), \\ J_{\alpha,r}(x), & \text{otherwise}, \end{cases}$$

where

$$J_{\alpha,f}(x) = (x_1 - \nu_{\alpha,1} + \nu_{\alpha,1}^*, \dots, x_S - \nu_{\alpha,S} + \nu_{\alpha,S}^*, x_{S+1} + \Delta T_{\alpha,f}(x))$$

and

$$J_{\alpha,r}(x) = (x_1 - \nu_{\alpha,1}^* + \nu_{\alpha,1}, \dots, x_S - \nu_{\alpha,S}^* + \nu_{\alpha,S}, x_{S+1} + \Delta T_{\alpha,r}(x)),$$

The temperature step is defined as

$$\Delta T_{\alpha,f}(x) = -\frac{\sum_{k=1}^{S} H_k(x_{S+1}) \left[\nu_{\alpha,k}^* - \nu_{\alpha,k}\right]}{\sum_{k=1}^{S} Cp_k(x_{S+1}) x_k},$$
$$\Delta T_{\alpha,r}(x) = -\frac{\sum_{k=1}^{S} H_k(x_{S+1}) \left[\nu_{\alpha,k} - \nu_{\alpha,k}^*\right]}{\sum_{k=1}^{S} Cp_k(x_{S+1}) x_k}.$$

where

$$Cp$$
 - specific heat
 H - enthalpy

Then the procedure returns to Step 1.

2.2. Approximations and optimizations

By analyzing the CPU time distribution, it is shown that more than 90% of the CPU time is required for updating P_{α} (in table 1). So it is crucial to approximate or optimize these procedures to save the CPU time without influencing precision.

According to the chemistry approximation, Q_{ii} is calculated by

$$Q_{ii} = \gamma(x)^{1 - \sum_{j=1}^{S} \nu_{ii,j}} M_{\alpha}(x) \qquad \underbrace{k_{ii}(x_{S+1})}_{reaction \ rate \ constant} \qquad \underbrace{\prod_{j=1}^{S} \prod_{i=0}^{\nu_{ii,j}-1} (x_j - i)^+}_{product},$$
$$ii = 1, ..., 2I \quad (2.9)$$

Procedure	CPU Time(%)	
Update k, Cp and H	56	
Update products	16	
Update reaction rates	27	
others	1	

Table 1: the original CPU Time Distribution.

 $M_{ii}(x) = \begin{cases} \sum_{k=1}^{S} B_{ii,k} \frac{x_k}{\gamma(x)}, & \text{if third body reaction with some species}, \\ \frac{p}{Rx_{S+1}}, & \text{if third body reaction with all species}, \\ 1, & \text{otherwise}, \end{cases}$

and

$$\gamma(x) = \frac{R x_{S+1}}{p} \sum_{j=1}^{S} x_j \,.$$

So $Q_{ii} = 0$ if $x_j < \nu_{ii,j}$. Furthermore, there is only one reaction performed every event. Based on these theories four optimized and approximate methods are implemented.

Optimization 1

Only the products of those reactions whose educts of species are changed should be updated.

$$\exists \nu_{ii,j} \times \nu_{\alpha,j} > 0, j = 1 \dots s \begin{cases} prod^{new} : \text{unknown, when } prod^{old} > 0 \\ prod^{new} = 0, \text{ when } prod^{old} = 0 \\ prod^{new} > 0, \text{ when } prod^{old} > 0 \\ prod^{new} > 0, \text{ when } prod^{old} > 0 \\ prod^{new} : \text{ unknown, when } prod^{old} = 0 \\ \exists \nu_{ii,j} \times \nu_{\alpha,j} > 0 \text{ and } \nu_{ii,j} \times \nu_{\alpha,j}^* > 0, j = 1 \dots s \end{cases}$$

otherwise $prod^{new} = prod^{old}$

Where

 α - the reaction which is performed ii - the ii-th reaction, representing every forward and reverse reaction $prod^{new}$ - the product of reaction ii after reaction α is performed $prod^{old}$ - the product of reaction ii before reaction α is performed

Moreover ,the product will be calculated only if $x_j \ge \nu_{ii,j}$.

Optimization 2

The reaction rate will be calculated, only if the product is greater than zero.

$$Q_{ii} \begin{cases} = 0, \text{ when } product = 0 \\ > 0, \text{ when } product > 0 \end{cases}$$

Optimization 3

The reaction rate constant will be updated, only if the product is greater than zero.

Approximation

Because only one reaction is performed every event, temperature is changed slightly, and a number of physical properties, such as specific heat, enthalpy, volume, pressure and reaction rate constant, do not change significantly. And hence the values of C_p , H, V, k are updated only if temperature difference exceeds a given ΔT .

Through these strategies the CPU time to update P_{α} will be decreased intensively. Therefore, the algorithm can be speeded up.

3. A computational study

In this section we study the algorithm given above and compare the performance of the new stochastic chemistry approximation with the standard deterministic chemistry approximation. The deterministic chemistry approximation is obtained by using the code DASSL [3].

3.1. Choice of approximations

Before assessing the above algorithm the premixed combustion of n-heptane in hot air is studied. In Table 2 the flow rate and the composition of the two streams are given. At time =0s all other concentrations are zero and the temperature is 1500K. The pressure is constant at $p = 1.0133 \times 10^5 Pa$. The residence time is chosen to be 0.0002s to ensure that under the current condition full consumption of oxygen can take place. A comparison result of the different approximations is given in Figure 1. In this figure, Ctot stands for the mean of temperature error [K].

From the Figure 1 it is shown that all strategies work very well and in general the temperature errors get big as ΔT increases. When ΔT is equal to 10 in the condition of the number of particles= 1.0×10^4 and ΔT is equal to 1 in the condition of the number of particles= 1.0×10^5 , the new algorithm is about 20 times faster than the original one, without influencing precision.

	Fuel	Air
	\dot{n}_1	\dot{n}_2
	2 mol/min	52 mol/min
X(nC7H16)	1	0
X(N2)	0	0.7900
X(O2)	0	0.2100

 Table 2: Premixed combustion of n-heptane. Initial concentrations.



Figure 1: Comparison of CPU Time [s] and Ctot [K] of (a) repetition=1000, the number of particles= 1.0×10^4 and (b) repetition=100, the number of particles= 1.0×10^5

The new CPU Time Distribution is given in Table 3 when ΔT is equal to 10 and the number of particles is equal to 1.0×10^4 . Comparing Table 1 with Table 3, we can see that the ratio of other procedures increases, and this mean the three most time-consumed procedures have saved the CPU Time.

The comparison of CPU time among different algorithms is given in Table 4. The new algorithm with optimizations and approximations is about 20 times faster than the original chemistry approximation. Consequently, it is proved that the new algorithm is efficient.

3.2. PaSPFR

In this part the non-premixed combustion of n-heptane in hot air is studied. We consider a fuel stream consisting of n-heptane, which is injected into hot air similar to the configuration described in [15]. The data of flow rate and composition of the two streams are as same as those data which are given in table 2, and in table 5 Δ T is given.

Procedure	CPU Time(%)	
Update k, Cp and H	11.4	
Update products	71.3	
Update reaction rates	5.9	
others	11.4	

Table 3: the Optimized CPU Time Distribution.

Table 4: the CPU Time of Different Algorithms.

Algorithm	CPU Time(s)
Original Chemistry Approximation	27
With Optimizations	9.6
With Optimizations and Approximations	1.2

At time t = 0s all other concentrations are zero. The overall mixture is slightly rich. The pressure is constant at $p = 1.0133 \times 10^5 PA$. The temperature is uniformly distributed in the interval [290, 310]K in the fuel stream, and uniformly distributed in the interval [1000, 1400]K in the hot oxidiser stream. In Figure 2(a) the particle count for the empirical marginal PDF of temperature is displayed. Note that cold particles and hot particles carry different weights to represent the different mass flow of the two streams appropriately without having to use a very large particle number. The magnitude of the temperature fluctuations can be considered to be realistic for non-premixed turbulent combustion.

The residence time is chosen to be 0.01s to ensure that under the current condition full consumption of oxygen can take place. The turbulent mixing time is set to the value $\tau = 4.0 \times 10^{-4}s$ which ensures that mixing significantly influences combustion of n-heptane. If there was no chemical reaction present the empirical standard deviation of temperature would decay to less than 25K as displayed in Figure 2(b).

For the current simulations the following numerical parameters are fixed to be L = 30 (number of repetition), N = 100 (number of particles). We chose L = 30 to get an

number of sub-particles	$\Delta T(K)$
1.0×10^3	10
$5.0 imes 10^3$	10
1.0×10^4	10
5.0×10^{4}	2

Table 5: The number of sub-particles and ΔT .

impression of the magnitude of the fluctuations introduced by the particle system while at the same time keeping the overall CPU time manageable. The initial conditions are approximated by 50 particles of weight $w^{(i)} = 2.36 \times 10^{-3}$, i = 1, ..., 50, for the fuel stream, and 50 particles of weight $w^{(i)} = 1.764 \times 10^{-2}$, i = 51, ..., 100, for the hot air stream.



Figure 2: (a) A particle count of the empirical marginal PDF of temperature at time t = 0s. The cold particles carry the weight 2.36×10^{-3} and the hot particles have the weight 1.764×10^{-2} . (b) Decay of the standard deviation for the non-reacting case at a turbulent mixing time $\tau = 4.0 \times 10^{-3}$ s for the simulation time interval.

Although typical for non-premixed turbulent combustion, in this example, we deliberately did not consider fluctuations in the chemical species to isolate the effects of the temperature fluctuations.

3.2.1. The splitting error

We first study the splitting error using the deterministic chemistry approximation DASSL. To this end we performed a calculation with very small time steps to obtain a precise solution for comparison. Then we consider the deviation of solutions obtained by bigger time steps from that precise solution. Also the two error tolerances in DASSL, RTOL and ATOL, were varied in order to maximize the computational speed. The following values were used throughout this study: $RTOL = 1.0 \times 10^{-8}$ and $ATOL = 1.0 \times 10^{-20}$.

For this error analysis the empirical mean temperature was studied. The error in Table 6 is the difference of the mean temperature at the end of the simulation time interval at time t = 0.01s for the run with a small reference time step $\Delta t_{\rm ref} =$

 1.5625×10^{-4} and the empirical mean temperature obtained from runs with $\Delta t = 2^n \Delta t_{\text{ref}}$ n = 2, 3, 4. The reference time step was chosen small enough such that a even smaller time step would reduce the error by less than 5K. It was also found that the computational time grows linearly with the number of splitting steps.

$\Delta t\left[s ight]$	error	
2.5×10^{-3}	1249.5	
1.25×10^{-3}	417.40	
6.25×10^{-4}	26.500	

Table 6: Splitting error of the temperature at time t = 0.01s.

The aim of this investigation is to make the splitting error smaller than the statistical error, which gives some measure of the fluctuations. The corresponding curves for the temperature are displayed in Figure 3(a) and the OH mass fraction is displayed in Figure 3(b).



Figure 3: Time evolution of the empirical mean of (a) temperature and (b) OH mass fraction with confidence bounds for thirty repetitions.

From the above study we chose the time step $\Delta t = 4.0 \times 10^{-4}$. Note that, for transient simulations, we also need to have sufficiently many output points.

It is clear from Figure 3 that the empirical means fluctuate strongly for different realizations of the initial conditions. The confidence bounds obtained from thirty repetitions give an impression of the magnitude of fluctuations in temperature and OH mass fraction. These fluctuations motivate the use of the stochastic chemistry approximation.

3.2.2. Comparison of stochastic and deterministic chemistry

We have researched the example of non-premixed combustion. Results for the algorithm with deterministic chemistry and with the stochastic chemistry approximation are presented in Figure 4. Four important quantities are displayed, the empirical mean of temperature (Figure 4(a)), OH mass fraction (Figure 4(b)), n-heptane mass fraction (Figure 4(c)), and methane mass fraction (Figure 4(d)). The stochastic chemistry approximation for the parameter $n = 5.0 \times 10^4$, $n = 10^4$, $n = 5.0 \times 10^3$, and $n = 10^3$ are shown along with the deterministic chemistry approximation. It is observed that for increasing n the stochastic chemistry result approaches the deterministic chemistry result. On the basis of the magnitude of fluctuations shown in Figure 2(b) one can consider the result for $n = 1.0 \times 10^4$ to be sufficiently accurate. For $n = 5.0 \times 10^3$ the most important characteristics of the ignition are captured but especially for temperature the difference between stochastic and deterministic approximation is still too large. The approximation of all other displayed quantities are still in the confidence bounds of the deterministic chemistry. For even smaller n the stochastic chemistry does not capture the ignition at all. This observation is in accordance with the findings in [8]. An explanation for this is that the low concentrations of radicals can not be represented with so few particles. Therefore, there are no active chain branching reactions which would drive ignition.

A comparison of the CPU-time for the different methods is given in Table 7. Other three deterministic chemistry approximations of different tolerance are calculated, lower precision DASSL 1, lower precision DASSL 2 and lowest precision DASSL 3. For lowest precision DASSL 3, it is not able to increase RTOL and ATOL anymore. These results show that with $n = 10^4$ the algorithm with stochastic chemistry is about 170 times faster than the algorithm with deterministic chemistry, while it provides a comparable accuracy. Even if compared with lowest precision DASSL, it is still about 24 times faster. In the case where a lower number of sub-particles $(n = 5. \times 10^3)$ is sufficient, the algorithm with stochastic chemistry reaches a gain factor of more than 300. In general one can say (see [8]) the computational time of the stochastic method is proportional to the number of reaction events taking place which in turn is proportional to the number of sub-particles if the stochastic particle system is close to the converged solution. Consequently, we would expect the quotient of computational time and number of particles to be roughly constant.

4. Conclusion

In this paper based on a stochastic chemistry approximation for the chemical source term in the PDF transport equation, further optimizations and approximation have been implemented. The motivation of this approach is to speed up the algorithm. The algorithm presented was applied to a PSR model. Moreover, numerical performance of this new algorithm was investigated in a more complex system. The non-premixed combustion of an n-heptane fuel stream injected into hot air was



Figure 4: The deterministic chemistry is compared with the stochastic chemistry for three different approximation parameters. The time evolution of the empirical mean of the following quantities is displayed: (a) temperature. (b) OH mass fraction. (c) n-heptane mass fraction. (d) methane mass fraction.

		CPU time		
method	CPU time [s]	of	speed factor	speed factor 2
		single run [s]		
DASSL	434,759	14,492	1	
DASSL 1	111,263	3,709	3.9	
DASSL 2	61, 618	2,054	7.0	
DASSL 3	60,082	2,003	7.2	1
5.0×10^4	11,280	376	38.5	5.3
1.0×10^4	2,506	84	173.5	24.0
5.0×10^{3}	1,298	43	335	46.3
1.0×10^{3}	223	7.4	1,950	269.4

 Table 7: Comparison of computational time of deterministic chemistry and stochastic chemistry approximation.

DASSL: RTOL= 1.0×10^{-8} and ATOL= 1.0×10^{-20} **DASSL 1:** RTOL= 1.0×10^{-3} and ATOL= 1.0×10^{-9}

DASSL 2: RTOL= 1.0×10^{-2} and ATOL= 1.0×10^{-5}

DASSL 3: RTOL= 0.0 and ATOL= 8.8×10^{-2}

chosen as a test case. The numerical error caused by the splitting procedure was studied. From this study a suitable time step was chosen to benchmark the new stochastic chemistry approximation against the standard deterministic DASSL. It was found that, depending on the required accuracy, the new stochastic approach clearly outperforms the deterministic method for the case studied.

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References

- Balthasar, M., Mauss, F., Knobel, A. & Kraft, M. (2002). Soot formation in turbulent reacting flows - a PDF based approach applied to carbon black production. *Combustion and Flame* 128, 395–409. See http://www.cheng.cam.ac.uk. To appear in *Combustion and Flame*.
- [2] Barlow, R., Bilger, R., Chen, J.-Y., Gokalp, I., Hassel, E., Masri, A. & Peters, N. (1996). Proceedings of the International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames. See http://www.ca.sandia.gov/tdf/Workshop.html.

- [3] Brenan, K. E., Campbell, S. & Petzold, L. (1996). Numerical Solution of Initial-Value Problems in Differential-Algebraic Equations, vol. 14, SIAM, Classics in Applied Mathematics.
- [4] Brown, P. N., Byrne, G. D. & Hindmarsh, A. C. (1989). VODE, A variablecoefficient ODE solver. SIAM J. Sci. Statist. Comput. 10, 1038–1051.
- [5] Deuflhard, P. & Nowak, U. (1987). Extrapolation integrators for quasilinear implicit ODE's. In P. Deuflhard & B. Engquist (Eds), *Large Scale Scientific Computing. Progress in Scientific Computing*, pp. 37–50). Birkhaeuser.
- [6] Dopazo, C. (1975). Probability density function approach for a turbulent axisymmetric heated jet centerline evolution. *Phys. Fluids* 18, 397–410.
- [7] Kraft, M. & Wagner, W. (2002). An efficient stochastic chemistry approximation for the pdf transport equation. *Monte Carlo Methods and Appl.* 8(4), 371– 394.
- [8] Kraft, M. & Wagner, W. (2003). An improved stochastic algorithm for temperature-dependent homogeneous gas phase reactions. *Journal of Computational Physics* 185, 139–157. http://www.wiasberlin.de/publications/preprints/570.html.
- [9] Kraft, M., Klos, T. & Bockhorn, H. (1996). Turbulent diffusion flames: Pdfmodelling and comparison to raman /rayleigh measured pdfs. In H. Neunzert (Ed.), Progress in Industrial Mathematics at ECMI 94, pp. 184–191). Wiley Teubner.
- [10] Maas, U. & Pope, S. (1992). Simplifying chemical kinetics: Intrinsic lowdimensional manifolds in composition space. *Combustion and Flame* 88, 239– 264.
- [11] Nooren, P., Wouters, H., Peeters, T., Roekaerts, D., Maas, U. & Schmidt, D. (1997). Monte Carlo PDF modelling of a turbulent natural-gas diffusion flame. *Combust. Theory Model.* 1, 76–96.
- [12] Peters, N. & Rogg, B. (1993). Reduced Reaction mechanisms for Applications in Combustion Systems, Lecture Notes in Physics 15, Springer Heidelberg.
- [13] Pope, S. B. (1985). PDF methods for turbulent reactive flows. Prog. Energy Combust. Sci. 11, 119–192.
- [14] Pope, S. B. (1997). Computationally efficient implementation of combustion chemistry using in situ adaptive tabulation. *Combust. Theory Model.* 1(1), 41– 63.
- [15] Procaccini, C., Kraft, M., Fey, H., Bockhorn, H., Longwell, J. P., Sarofim, A. & Smith, K. A. (1998). PIC formation during the combustion of simple hydrocarbons in inhomogeneous incineration systems. *Proc. Combust. Inst.* 27, 1275–1281.

[16] Xu, J. & Pope, S. B. (1999). Assessment of numerical accuracy of PDF/Monte Carlo methods for turbulent reacting flows. *Journal of Computational Physics* 152, 192–230.