Weierstraß–Institut
für Angewandte Analysis und Stochastik

An efficient stochastic chemistry approximation for the PDF transport equation

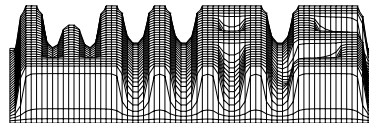## Markus Kraft[1], Wolfgang Wagner[2]

[1] Department of Chemical Engineering
     University of Cambridge
     Pembroke Street
     Cambridge CB2 3RA, UK
     E-Mail: markus_kraft@cheng.cam.ac.uk

[2] Weierstrass Institute for
     Applied Analysis and Stochastics
     Mohrenstrasse 39
     D-10117 Berlin, Germany
     E-Mail: wagner@wias-berlin.de

Abstract

In this paper we present an efficient algorithm for the numerical treatment of the PDF transport equation. Using the partially stirred plug flow model in conjunction with the IEM mixing model we construct a numerical scheme that is based on a time splitting technique and a stochastic chemistry approximation. For this purpose a particle/sub-particle system is introduced. The dynamics of this particle system is determined by a mixing step and a chemistry step. The chemistry step is solved by a jump process where forward and reverse reactions are combined. Various numerical experiments are carried out to study convergence with respect to particle number and sub-particle number. In case of a linear reaction, the comparison between analytical solution and numerical approximation of the third moment reveals that the systematic error is inversely proportional to the number of particles and sub-particles, respectively. The performance of the algorithm is evaluated by studying the combustion of a premixed stoichiometric mixture of n-heptane and air. The stochastic chemistry algorithm is compared with a deterministic approach using the ODE solver DASSL and it is found, for the examples studied, that the stochastic algorithm is more efficient than the deterministic approach.

Contents

1. Introduction

The numerical modelling of complex turbulent flows is an important issue in many engineering applications. The modelling of combustion by-products in internal combustion engines or other combustion devices but also the prediction of material properties during particle synthesis require a detailed description of the underlying chemistry and of the interaction between turbulent mixing and chemical reactions. In cases where chemical time scales and turbulent time scales are of the same order of magnitude the probability density function (PDF) approach has been used successfully in many cases [20, 2].

The PDF transport equation is usually solved by combining a particle method, which approximates the distribution function, with an operator splitting technique, which separates different physical processes [23]. The numerical expense of this approach makes it necessary to reduce [19] or tabulate the chemistry [18, 21]. Both methods suffer from various difficulties when large chemical mechanisms are involved. In some applications the full PDF transport equation may be simplified by assuming spatial homogeneity. Models which are based on this assumption are often called partially stirred reactor models. Such partially stirred models have been used, for example, in [7] to study combustion of methane, in [6, 5] to model the formation of NOx and in [22, 14] to model a stationary combustion device and an internal combustion engine. An overview on this sort of models can be found in [12]. All mentioned PDF models have in common that they are solved by a combined Monte Carlo particle method and a splitting approach. Due to the spatial homogeneity much fewer particles are required and therefore large chemical mechanisms, which are necessary, e.g., for detailed soot modelling, are feasible [1].

In this paper we consider the simple partially stirred plug flow model (PaSPFR), where only two physical processes remain - chemical reaction and mixing. So far the chemistry step for this model has been treated by some deterministic ODE-solver (for example see [3, 4, 9]). Here we propose an alternative algorithm that uses some stochastic chemistry approximation, which was developed in [15]. Our motivation is the idea that, on the one hand, a less accurate chemistry approximation may be sufficient in the context of a Monte Carlo particle method, and, on the other hand, it will make the whole algorithm much faster. This would make it possible to use the algorithm as a tool in the general spatially inhomogeneous situation, providing an alternative to reducing or tabulating large chemical mechanisms.

Consider the **PDF transport equation**

$$\frac{\partial}{\partial t} f(t, \psi) - \sum_{k=1}^{S+1} \frac{\partial}{\partial \psi_k} \Big(\big[R_k(\psi) + C\, M_k(f(t), \psi) \big] f(t, \psi) \Big) = 0 \,, \qquad t \geq 0 \,, \qquad (1.1)$$

with initial condition

$$f(0, \psi) = f_0(\psi) \,. \qquad (1.2)$$

The components of the vector ψ correspond to the mass fractions $Y_1, \dots, Y_S$ of several chemical species and to temperature T.

The terms M_k represent the **mixing properties** of the system. We use the well known IEM or LMSE model (see [10]), with the definition

$$M_k(g, \psi) = \psi_k - \int \ldots \int x_k \, g(x) \, dx_1 \ldots dx_{S+1} , \qquad k = 1, \ldots, S+1 , \qquad (1.3)$$

for any function g.

The terms R_k describe the **reaction mechanism** of the system, which consists of a number I of elementary chemical reactions,

$$(\nu_{\alpha,1}, \ldots, \nu_{\alpha,S}) \longleftrightarrow (\nu^*_{\alpha,1}, \ldots, \nu^*_{\alpha,S}), \qquad \alpha = 1, \ldots, I . \qquad (1.4)$$
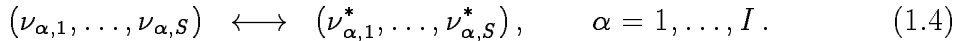
The stoichiometric coefficients $\nu_{\alpha,i}$ and $\nu^*_{\alpha,i}$ of the species i in reaction α are non-negative integer values. The specific definitions are (cf. [17, formula (2); Ch. II, formulas (49), (52), (58)], [11])

$$R_i(\psi) = -\frac{W_i}{\varrho} \dot{\omega}_i , \qquad i = 1, \ldots, S ,$$

and (cf. [17, formula (15)])

$$R_{S+1}(\psi) = \frac{1}{c_p \, \varrho} \sum_{k=1}^{S} h_k \, W_k \, \dot{\omega}_k ,$$

with the chemical production rate of the i-th species

$$\dot{\omega}_i = \sum_{\alpha=1}^{I} (\nu^*_{\alpha,i} - \nu_{\alpha,i}) \, q_\alpha$$

and the rate of progress of the α-th reaction

$$q_\alpha = [M_\alpha] \left(K_{\alpha,f} \prod_{k=1}^{S} [X_k]^{\nu_{\alpha,k}} - K_{\alpha,r} \prod_{k=1}^{S} [X_k]^{\nu^*_{\alpha,k}} \right) .$$

Here $[X]$ and W denote the vectors of the molar concentrations and the molecular weights of the species, respectively. Moreover, ϱ denotes the mass density, h is the vector of specific enthalpies, and c_p is the mean specific heat capacity. The numbers $K_{\alpha,f}$ and $K_{\alpha,r}$ are the forward and reverse rate constants for the α-th reaction, which are assumed to have the following Arrhenius temperature dependence,

$$\begin{aligned} K_{\alpha,f} &= A_{\alpha,f} \, T^{\beta_{\alpha,f}} \, \exp(-E_{\alpha,f}/RT) , \\ K_{\alpha,r} &= A_{\alpha,r} \, T^{\beta_{\alpha,r}} \, \exp(-E_{\alpha,r}/RT) , \end{aligned} \qquad (1.5)$$

where $A_{\alpha,f}, A_{\alpha,r}$ are pre-exponential factors, $\beta_{\alpha,f}, \beta_{\alpha,r}$ are temperature exponents and $E_{\alpha,f}, E_{\alpha,r}$ are activation energies. The factor $[M_\alpha] = \sum_{k=1}^{S} B_{\alpha,k} [X_k]$ takes into account that, in some reactions, a "third body" is required for the reaction to proceed. If no third body is needed, then $[M_\alpha] = 1$.

The paper is organized as follows. In **Section 2** we discuss the stochastic process corresponding to the solution of equation (1.1). In **Section 3** we describe the algorithm for solving equation (1.1), which is based on some particle approximation and on a splitting technique. In **Section 4** we introduce the stochastic chemistry approximation procedure. **Section 5** is devoted to numerical experiments. First we consider the simple case of a linear reaction term, where an analytic solution of equation (1.1) is available. In this case we study the order of convergence of the algorithm with respect to various numerical parameters. Our second example is combustion of n-heptane. This test case is of practical relevance, since n-heptane is part of the reference fuel for internal combustion engines such as spark-ignition, diesel, and gas turbine engines. Here we study convergence properties of the PDF algorithm with stochastic chemistry approximation. The computational times for the new algorithm are compared with those for the PDF algorithm with deterministic chemistry approximation using the code DASSL [3] for solving systems of differential/algebraic equations. Finally some conclusion are drawn in **Section 6**.

2. The stochastic process

The stochastic process $\Psi(t)$ corresponding to the solution $f(t)$ of equation (1.1) is determined by the system of ordinary differential equations

$$\frac{d}{dt}\,\Psi_k(t) = -R_k(\Psi(t)) - C\left[\Psi_k(t) - E\,\Psi_k(t)\right], \qquad k = 1, \ldots, S+1. \tag{2.1}$$

The initial state $\Psi(0)$ is distributed according to f_0 (cf. (1.2)). Note that, according to (1.3),

$$M_k(f(t), \Psi(t)) = \Psi_k(t) - E\,\Psi_k(t),$$

where E denotes mathematical expectation. As an illustration, we consider several special cases.

The initial state is the only source of stochasticity of the process $\Psi(t)$. Thus, in the case of a **"double-delta" initial condition**, i.e.

$$f_0(\psi) = \alpha_1\,\delta_{\bar{\psi}^{(1)}}(\psi) + \alpha_2\,\delta_{\bar{\psi}^{(2)}}(\psi), \tag{2.2}$$

there are only two different trajectories $\psi^{(1)}(t)$ and $\psi^{(2)}(t)$. The expectation in (2.1) can be explicitly calculated so that the trajectories are determined by two deterministic equations

$$\frac{d}{dt}\,\psi_k^{(1)}(t) = -R_k(\psi^{(1)}(t)) - C\,\alpha_2\,[\psi_k^{(1)}(t) - \psi_k^{(2)}(t)] \tag{2.3}$$

and

$$\frac{d}{dt}\,\psi_k^{(2)}(t) = -R_k(\psi^{(2)}(t)) - C\,\alpha_1\,[\psi_k^{(2)}(t) - \psi_k^{(1)}(t)], \tag{2.4}$$

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with initial conditions

$$\psi^{(1)}(t) = \bar{\psi}^{(1)}, \qquad \psi^{(2)}(t) = \bar{\psi}^{(2)}. \tag{2.5}$$

The solution is of the form

$$f(t, \psi) = \alpha_1 \, \delta_{\psi^{(1)}(t)}(\psi) + \alpha_2 \, \delta_{\psi^{(2)}(t)}(\psi).$$

In particular, if f_0 is one delta-function, then the process is **deterministic** and the only trajectory is determined as the solution of

$$\frac{d}{dt}\psi_k(t) = -R_k(\psi(t)), \qquad \psi(0) = \bar{\psi}.$$

Remark 2.1 *The function*

$$x(t) = e^{At}\left[x_0 + \int_0^t e^{-As}h(s)ds\right] \tag{2.6}$$

solves the initial value problem

$$\frac{d}{dt}x(t) = Ax(t) + h(t), \qquad x(0) = x_0.$$

In case of constant h and non-degenerate A, solution (2.6) takes the form

$$x(t) = e^{At}x_0 + (e^{At} - I)A^{-1}h. \tag{2.7}$$

Remark 2.2 *Consider a random vector ξ with density p_ξ, and a non-degenerate matrix A. Then the random vector $\eta = A\xi + b$ has the density*

$$p_\eta(x) = |\det A^{-1}| p_\xi(A^{-1}(x - b)). \tag{2.8}$$

In case of a **linear reaction term**, (2.1) implies

$$\frac{d}{dt}E\Psi_k(t) = -R_k(E\Psi(t)). \tag{2.9}$$

This equation can be solved explicitly. Denoting its solution by $g(t)$, equation (2.1) takes the form

$$\frac{d}{dt}\Psi_k(t) = -R_k(\Psi(t)) - C\left[\Psi_k(t) - g_k(t)\right], \tag{2.10}$$

which can also be solved explicitly. In particular, if the reaction is determined by some matrix R, one obtains from (2.9)

$$g(t) = E\Psi(t) = e^{-Rt}E\Psi(0)$$

and from (2.10), using (2.6),

$$\Psi(t) = e^{-Rt}e^{-Ct}\left[\Psi(0) + C\int_0^t e^{Rs}e^{Cs}g(s)ds\right] \tag{2.11}$$

$$= e^{-Rt}e^{-Ct}\left[\Psi(0) + (e^{Ct} - 1)E\Psi(0)\right] = e^{-Rt}\left[e^{-Ct}\Psi(0) + (1 - e^{-Ct})E\Psi(0)\right].$$

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Note that

$$E\Psi_k(0) = \int x_k f_0(x)\,dx\ .$$

In the **one-dimensional case** applying (2.8) to (2.11) allows us to express $f(t,\psi)$ through f_0. One obtains

$$
\begin{aligned}
f(t,\psi) &= e^{(R+C)t}\,f_0\Big(e^{(R+C)t}[\psi - e^{-Rt}(1 - e^{-Ct})E\Psi(0)]\Big)\\
&= e^{(R+C)t}\,f_0\Big(e^{(R+C)t}\psi + (1 - e^{Ct})E\Psi(0)\Big),
\end{aligned}
\tag{2.12}
$$

with

$$E\Psi(0) = \int x\, f_0(x)\,dx\ . \tag{2.13}$$

Note that, with the notations

$$R = k\ ,\qquad C = \frac{C_\Phi}{2\tau}\ , \tag{2.14}$$

representation (2.12), (2.13) coincides with formulas (14)-(15) in [13].

   Moments

$$m_k(t) = \int x^k f(t,x)\,dx = E\Psi(t)^k\ ,\qquad k = 1, 2, \ldots\ ,$$

are derived directly from (2.11). One obtains, for example,

$$m_1(t) = e^{-Rt}E\Psi(0) = e^{-Rt}m_1(0)\ ,$$

$$
\begin{aligned}
m_2(t) &= e^{-2Rt}\left[e^{-2Ct}m_2(0) + 2e^{-Ct}(1 - e^{-Ct})m_1(0)^2 + (1 - e^{-Ct})^2 m_1(0)^2\right]\\
&= e^{-2Rt}\left[e^{-2Ct}m_2(0) + (1 - e^{-2Ct})m_1(0)^2\right]
\end{aligned}
$$

and

$$
\begin{aligned}
m_3(t) &= e^{-3Rt}\Big[e^{-3Ct}m_3(0) + 3e^{-2Ct}(1 - e^{-Ct})m_2(0)m_1(0)\\
&\qquad + 3e^{-Ct}(1 - e^{-Ct})^2 m_1(0)^3 + (1 - e^{-Ct})^3 m_1(0)^3\Big]\\
&= e^{-3Rt}\Big[e^{-3Ct}m_3(0) + 3e^{-2Ct}(1 - e^{-Ct})m_2(0)m_1(0)\\
&\qquad + (1 + 2e^{-Ct})(1 - e^{-Ct})^2 m_1(0)^3\Big].
\end{aligned}
\tag{2.15}
$$

3. The algorithm

In order to generate trajectories of the stochastic process, the expectation in (2.1) has to be approximated. One introduces a **system of particles**

$$\Psi^{(1)}(t), \ldots, \Psi^{(N)}(t) \tag{3.1}$$

determined by

$$\frac{d}{dt} \Psi_k^{(i)}(t) = -R_k(\Psi^{(i)}(t)) - C \left[\Psi_k^{(i)}(t) - \frac{1}{N} \sum_{j=1}^{N} \Psi_k^{(j)}(t) \right], \quad k = 1, \ldots, S+1, \tag{3.2}$$

where $\Psi^{(i)}(0)$, $i = 1, \ldots, N$, are independent and distributed according to f_0. In general the system (3.2) 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

$$\frac{d}{dt} \tilde{\Psi}_k^{(i)}(t) = -R_k(\tilde{\Psi}^{(i)}(t)), \qquad t \geq s, \qquad \tilde{\Psi}_k^{(i)}(s) = \Psi_k^{(i)}(s), \tag{3.3}$$

and the **mixing step** is

$$\frac{d}{dt} \Psi^{(i)}(t) = -C \left[\Psi^{(i)}(t) - \frac{1}{N} \sum_{j=1}^{N} \Psi^{(j)}(t) \right], \quad t \geq s, \quad \Psi^{(i)}(s) = \tilde{\Psi}^{(i)}(s + \Delta t). \tag{3.4}$$

One obtains from (3.4) that

$$\frac{d}{dt} \frac{1}{N} \sum_{i=1}^{N} \Psi^{(i)}(t) = 0,$$

and thus

$$\frac{d}{dt} \Psi^{(i)}(t) = -C \left[\Psi^{(i)}(t) - \frac{1}{N} \sum_{j=1}^{N} \tilde{\Psi}^{(j)}(s + \Delta t) \right],$$

which can be solved explicitly. Using (2.7) with $A = -C\,I$, one obtains

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

so that

$$\Psi^{(i)}(s + \Delta t) = e^{-C\Delta t} \tilde{\Psi}^{(i)}(s + \Delta t) + \left[1 - e^{-C\Delta t}\right] \frac{1}{N} \sum_{j=1}^{N} \tilde{\Psi}^{(j)}(s + \Delta t). \tag{3.5}$$

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This leads to the following **algorithm**.

0. Determine the state of the system of particles (3.1) 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 (3.3).

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 (3.5).

3. If time exceeds termination time then STOP. Otherwise go to Step 1 .

Remark 3.1 *Note that the same algorithm is obtained when the splitting approach is applied directly to (2.1), and the particle approximation (3.1) is applied later. The reaction step is*

$$\frac{d}{dt}\,\tilde{\Psi}_k(t) = -R_k(\tilde{\Psi}(t))\,, \qquad t \geq s\,, \qquad \tilde{\Psi}_k(s) = \Psi_k(s)\,,$$

and the mixing step is

$$\frac{d}{dt}\,\Psi(t) = -C\left[\Psi(t) - E\Psi(t)\right]\,, \qquad t \geq s\,, \qquad \Psi(s) = \tilde{\Psi}(s + \Delta t)\,. \qquad (3.6)$$

One obtains from (3.6) that

$$\frac{d}{dt}\,E\Psi(t) = 0\,,$$

and thus

$$\frac{d}{dt}\,\Psi(t) = -C\left[\Psi(t) - E\tilde{\Psi}(s + \Delta t)\right]\,,$$

which can be solved explicitly. Using (2.7) with $A = -C\,I$, one obtains

$$\Psi(t) \quad = \quad e^{-C(t-s)}\Psi(s) + \left[1 - e^{-C(t-s)}\right]E\Psi(s)\,,$$

so that

$$\Psi(s + \Delta t) \quad = \quad e^{-C\Delta t}\tilde{\Psi}(s + \Delta t) + \left[1 - e^{-C\Delta t}\right]E\tilde{\Psi}(s + \Delta t)\,.$$

It remains to apply the particle approximation in order to obtain (3.5).

Functionals with respect to $f(t,\psi)$ are approximated using empirical averages over the system (3.1), i.e.

$$\int g(\psi)\,f(t,\psi)\,d\psi \quad \sim \quad \frac{1}{N}\sum_{i=1}^{N} g(\Psi^{(i)}(t))\,, \qquad (3.7)$$

for appropriate functions g .

There are two sources of systematic error - the parameter N of the particle approximation, and the splitting parameter Δt .

Example 3.2 *In case of a double-delta initial condition (2.2), there is no need in introducing a system of particles (3.1), or even in the splitting procedure. Simply the deterministic system (2.3)-(2.5) has to be solved. However, splitting allows one to apply standard routines to the chemistry step. One obtains from (2.3)-(2.5),*

$$\frac{d}{dt}\tilde{\psi}_k^{(i)}(t) = -R_k(\tilde{\psi}^{(i)}(t))\,,\qquad t \geq s\,,\qquad \tilde{\psi}_k^{(i)}(s) = \bar{\psi}_k^{(i)}\,,\qquad i = 1,2\,,$$

and

$$\frac{d}{dt}\psi^{(1)}(t) = -C\,\alpha_2\,[\psi^{(1)}(t) - \psi^{(2)}(t)]\,,\quad \frac{d}{dt}\psi^{(2)}(t) = -C\,\alpha_1\,[\psi^{(2)}(t) - \psi^{(1)}(t)]\,,$$
$$t \geq s\,,\qquad \psi^{(i)}(s) = \tilde{\psi}^{(i)}(s + \Delta t)\,,\qquad i = 1,2\,,$$

instead of (3.3) and (3.4).

Example 3.3 *In case of a linear reaction term, one obtains from (3.3), using (2.11) with $C = 0$,*

$$\tilde{\Psi}^{(i)}(\Delta t) = e^{-R\,\Delta t}\,\Psi^{(i)}(0)\,.$$

Thus, (3.5) takes the form

$$\begin{aligned}
\Psi^{(i)}(\Delta t) &= e^{-C\Delta t}\,\tilde{\Psi}^{(i)}(\Delta t) + \left[1 - e^{-C\Delta t}\right]\frac{1}{N}\sum_{j=1}^{N}\tilde{\Psi}^{(j)}(\Delta t)\\[2mm]
&= e^{-(C+R)\Delta t}\,\Psi^{(i)}(0) + e^{-R\Delta t}\left[1 - e^{-C\Delta t}\right]\frac{1}{N}\sum_{j=1}^{N}\Psi^{(j)}(0)\,.
\end{aligned}$$

Compared to (2.11), there is only the approximation of the expectation. In particular, first moments have no systematic error.

4. Stochastic chemistry approximation

The reaction step (3.3) is treated by the following stochastic algorithm, which has been introduced and studied with respect to its convergence properties in [15] (see also [16] concerning a simplified version of the algorithm). Consider a stochastic system

$$x = \left(N_1^{(n)}(t), \ldots, N_S^{(n)}(t), T^{(n)}(t)\right)\,,\qquad t \geq 0\,,$$

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

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Step 0

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

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

according to the initial conditions of the differential equation (3.3). Note that

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

plays the role of an approximation parameter, which can be interpreted as the number of "sub-particles".

Step 1

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

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

where (cf. (1.4), (1.5))

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

$$Q_{\alpha,f}(x) = \gamma(x)^{1-\sum_{j=1}^{S}\nu_{\alpha,j}}\, M_\alpha(x)\, K_{\alpha,f}(x_{S+1}) \prod_{j=1}^{S} \prod_{i=0}^{\nu_{\alpha,j}-1} (x_j - i)^+\,, \qquad (4.1)$$

$$Q_{\alpha,r}(x) = \gamma(x)^{1-\sum_{j=1}^{S}\nu_{\alpha,j}^*}\, M_\alpha(x)\, K_{\alpha,r}(x_{S+1}) \prod_{j=1}^{S} \prod_{i=0}^{\nu_{\alpha,j}^*-1} (x_j - i)^+\,, \qquad (4.2)$$

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

and

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

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**

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

Step 3

Finally, the process jumps into the state

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

where

$$J_{\alpha,f}(x) = (x_1 - \nu_{\alpha,1} + \nu^*_{\alpha,1}, \ldots, x_S - \nu_{\alpha,S} + \nu^*_{\alpha,S}, x_{S+1} + \Delta T_{\alpha,f}(x)) \tag{4.3}$$

and

$$J_{\alpha,r}(x) = (x_1 - \nu^*_{\alpha,1} + \nu_{\alpha,1}, \ldots, x_S - \nu^*_{\alpha,S} + \nu_{\alpha,S}, x_{S+1} + \Delta T_{\alpha,r}(x)). \tag{4.4}$$

The temperature step is defined as

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

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

Then the procedure returns to Step 1.

Remark 4.1 *The second products in (4.1), (4.2) assure that a reaction may only occur if the mole numbers of the corresponding particles in the system are big enough (cf. (4.3), (4.4)). Note that by definition $a^+ = a$ if $a > 0$ and $a^+ = 0$ otherwise. Thus these products are zero if $x_j < \nu_{\alpha,j}$ (or $x_j < \nu^*_{\alpha,j}$, respectively) for some $j = 1, \ldots, S$. They are defined to be 1 in the case $\nu_{\alpha,j} = 0$ or $\nu^*_{\alpha,j} = 0$, respectively.*

The basic theoretical result concerning this algorithm is that

$$\lim_{n \to \infty} \frac{N_k^{(n)}(t)}{\sum_j N_j^{(n)}(t)} = X_k(s+t), \qquad k = 1, \ldots, S, \qquad t \geq 0,$$

and

$$\lim_{n \to \infty} T^{(n)}(t) = T(s+t), \qquad t \geq 0.$$

Note that

$$Y_k(t) = \frac{W_k\,X_k(t)}{\sum_j W_j\,X_j(t)}, \qquad X_k(t) = \frac{Y_k(t)/W_k}{\sum_j Y_j(t)/W_j}.$$

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5. Numerical experiments

We consider two examples. In the simple case of a **linear reaction term** the analytic solution of the PDF transport equation is known (cf. (2.12)). In this test case we study the order of convergence with respect to different numerical parameters. The second example is the **combustion of a stoichiometric n-heptane air mixture**. This test case is of practical relevance, since n-heptane is part of the reference fuel for internal combustion engines such as spark-ignition, diesel, and gas turbine engines. Here we use two initial conditions which represent different combustion situations - a high temperature regime and a low temperature regime. In both cases convergence of the algorithm with stochastic chemistry approximation is shown. The computational times are compared with those for the PDF algorithm with deterministic chemistry approximation using the code DASSL [3] for solving systems of differential/algebraic equations. DASSL has been applied successfully to combustion problems as part of the software package SENKIN [17]. All simulations have been carried out on a Compaq AlphaServer GS80 733MHz at the Weierstrass Institute in Berlin.

5.1. Linear reaction term

We consider the linear first order reaction

$$A \xrightarrow{k} \text{Products} ,$$

with uniform initial distribution

$$f(\psi, 0) = \chi_{[0,1]}(\psi) .$$

The reaction rate and mixing time are set to $k = 1s^{-1}$ and $\tau = 0.5s$, respectively, and the constant is $C_\Phi = 2$ (cf. (2.14)). Calculations are performed in the time interval $[0, 5]s$. We investigate the convergence behaviour studying the quantity

$$m_3(t) = \int_0^1 \psi^3 f(\psi, t) d\psi .$$

The time evolution of this quantity can be obtained directly from the analytic solution (2.15). At time $t = 0s$ the initial value of m_3 is 0.25. At $t = 1.5s$ the third moment has decayed to a value of 0.0013921, which reduces to 3.82×10^{-8} at the end of the simulation interval $t = 5.0s$.

The approximate solution is calculated at some observation points (t_i), which are integer multiples of the splitting time step Δt. A number L of independent runs of the particle ensemble is used to construct confidence bands with width $c_{stat}(t_i)$. The product $L \times N = 131072 = 2^{17}$ is kept fixed, in order to get confidence bands of roughly the same width for different calculations. The error $c_{tot}(t_i)$ is the difference between the empirical third moment and the analytic third moment (cf. (3.7)). In general the measured quantities depend on the number of repetitions L,

the number of particles N, the number of sub-particles n used for the stochastic chemistry approximation, and on the time step Δt.

First we note that in this simple example there is no error with respect to the **splitting step** Δt, at least for $N, n \to \infty$ (cf. Example 3.3).

Results concerning the error with respect to the **particle number** N are displayed in **Table 1**. Here the algorithm with deterministic chemistry approximation is used. These results suggest an order N^{-1} in this particular situation (see **Figure 1**). Note that the systematic error reaches the level of the stochastic fluctuations for $N = 64$ at $t = 0.5$ and for $N = 128$ at $t = 5.0$. Thus, the choice $N = 100$ is appropriate for our next study.

Table 1: *Computational study for varying* N

N	$c_{stat}(0.5) \times 10^4$	$c_{tot}(0.5) \times 10^4$	$c_{stat}(5.0) \times 10^8$	$c_{tot}(5.0) \times 10^8$
1	5.735	240.40	0.079	3.8132
2	5.393	120.24	0.074	1.9081
4	5.048	60.217	0.0684	0.9567
8	4.793	30.00	0.0642	0.4776
16	4.644	14.95	0.0617	0.2389
32	4.639	7.622	0.0615	0.1227
64	4.612	3.878	0.0609	0.0632
128	4.624	2.041	0.0610	0.0341
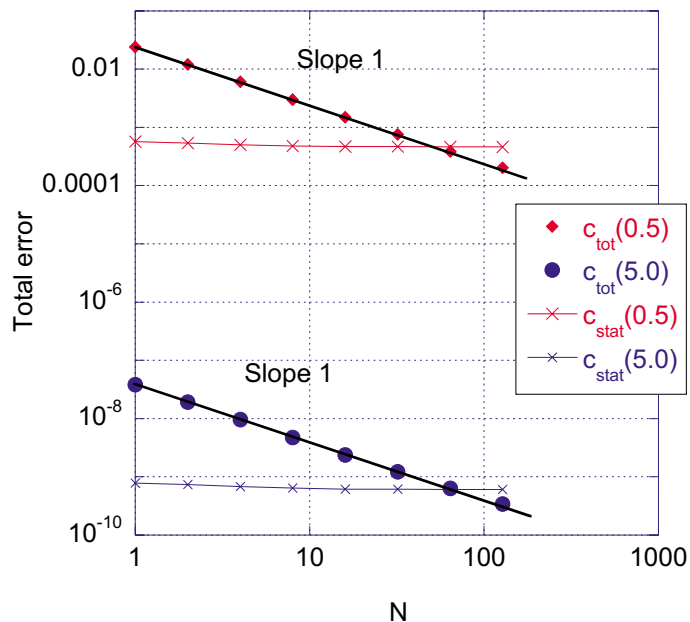
Figure 1: *Order of convergence for Table 1*

Next we study the error with respect to the **number of sub-particles** n. Here the algorithm with stochastic chemistry approximation is used. The other parameters are $\Delta t = 0.1$ and $N = 100$. Results are displayed in **Table 2**. These results suggest an order n^{-1} in this particular situation (see **Figure 2**). Note that at time $t = 0.5$ the choice $n = 320$ is sufficient to reach the level of the N-error. For $t = 5.0$ one needs many more particles ($n = 16384$) in order to reach the level of the N-error. This is due to the very low concentration, which also explains the behaviour of the error for small n, where the smallest possible resolution is much to big. Figure 2 shows this behaviour. Up to the point where n is small enough to resolve m_3 the order of convergence is n^{-3} due to the third power in m_3. Then one can observe the order n^{-1} as it is expected from $t = 0.5$.

Table 2: *Computational study for varying n*

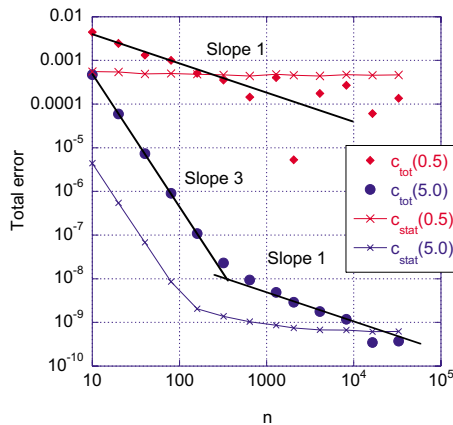| n	$c_{stat}(0.5) \times 10^4$	$c_{tot}(0.5) \times 10^4$	$c_{stat}(5.0) \times 10^8$	$c_{tot}(5.0) \times 10^8$
10	5.578	44.63	441.1	47446
20	5.453	24.43	53.99	5960.8
40	4.879	13.33	6.85	741.21
80	5.002	9.958	0.863	90.34
160	4.821	5.084	0.204	10.845
320	4.657	3.552	0.138	2.30
640	4.409	1.460	0.105	0.942
1280	4.808	4.054	0.086	0.491
2048	4.599	0.053	0.075	0.291
4096	4.410	1.763	0.067	0.178
8192	4.748	2.677	0.066	0.119
16384	4.560	0.608	0.062	0.034
32768	4.641	1.366	0.062	0.037

Figure 2: *Order of convergence for Table 2*

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5.2.   Combustion of n-heptane

In this example we study the combustion of n-heptane. The combustion chemistry is modelled by a reaction mechanism containing 107 chemical species and 808 reversible reactions [8]. At time $t = 0s$ we consider a homogeneous diluted mixture of n-heptane, oxygen and nitrogen. The initial conditions for the concentrations are deterministic, with

$$X_{n-C_7H_{16}}(0) = 0.0187 \,, \quad X_{O_2}(0) = 0.2061 \,, \quad X_{N_2}(0) = 0.7752 \,,$$

and the concentration of the other 104 species being zero. The pressure is constant at $p = 1.0133 \times 10^6$ PA. We consider two different **random initial conditions for the temperature**. For the current simulations the numerical parameters are chosen to be $L = 4$ (number of repetitions), $N = 100$ (number of particles), and $\Delta t = 4.0 \times 10^{-6}$ (splitting time step). The simulation time interval is $[0, 2.0 \times 10^{-4}]s$. Tests have been carried out to certify that the splitting error and the error in N are small enough.

5.2.1.   High temperature regime

First we consider the case when temperature at time zero is distributed uniformly on the interval $[1300, 1700]\, K$. **Figure 3** shows the confidence band for the temperature curve produced by the algorithm with deterministic chemistry approximation, in comparison with the temperature curve corresponding to the deterministic initial condition $T(0) = 1500\, K$.

Figure 4 and **Figure 5** show average temperature curves for the algorithm with stochastic chemistry, in comparison with the average curve and confidence bands for the algorithm with deterministic chemistry. While the curves for stochastic chemistry and $n = 10^4$ are still outside the confidence band at the end of the time interval, they completely fit the reference average curve for $n = 10^5$.

A similar comparison is performed for the concentrations of the species n-heptane in **Figure 6**, CO_2 in **Figure 7**, CO in **Figure 8**, and OH in **Figure 9**. For most of these species, the results for $n = 10^4$ are already satisfactory, i.e. are inside the reference confidence band for the algorithm with deterministic chemistry. However, for CO one needs $n = 10^5$ sub-particles.

A comparison of the CPU-time for different methods is given in **Table 3**. These results show that even with $n = 10^5$ sub-particles the algorithm with stochastic chemistry is faster than the algorithm with deterministic chemistry. In cases where a lower of sub-particles is sufficient, the algorithm with stochastic chemistry is much faster reaching a gain factor of 20 for $n = 10^4$.

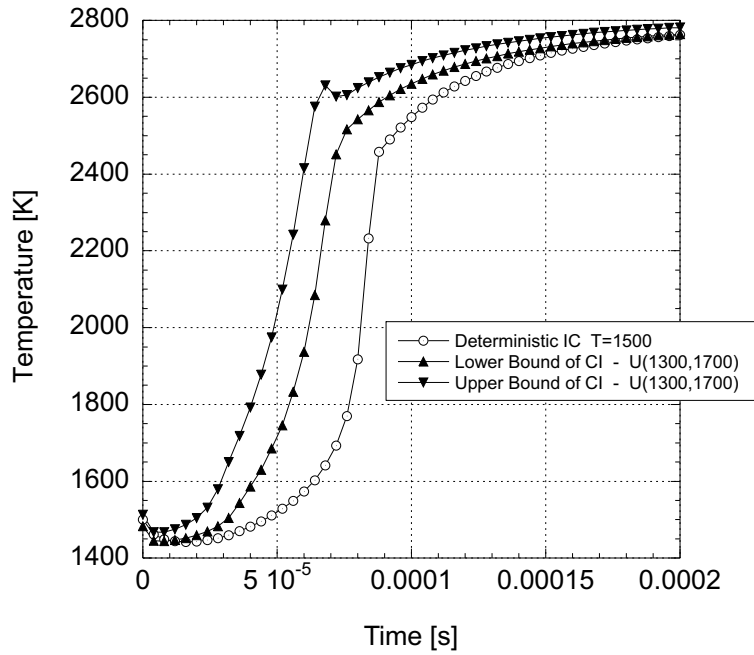**Figure 3:** *Temperature evolution for deterministic and stochastic initial conditions in the high temperature regime.*

Table 3: *Computational times (CT) for varying n with $N = 100$ and $L = 4$ (high temperature regime).*

n	$CT[s]$	CT
DASSL	72960	$21h00m$
1.0×10^5	31254	$8h40m$
1.0×10^4	3567	$59m$
1.0×10^3	550	$9m$

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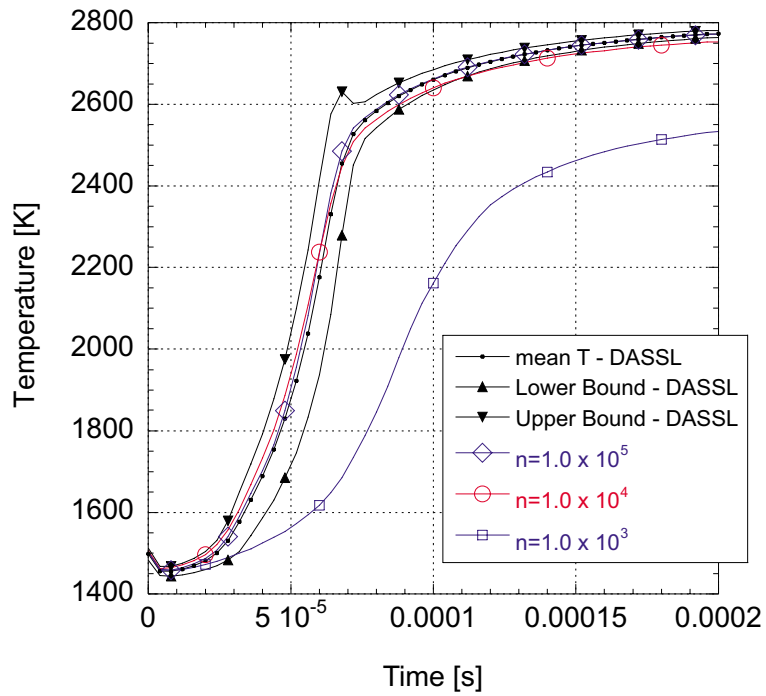
Figure 4: *Temperature evolution for the high temperature regime.*
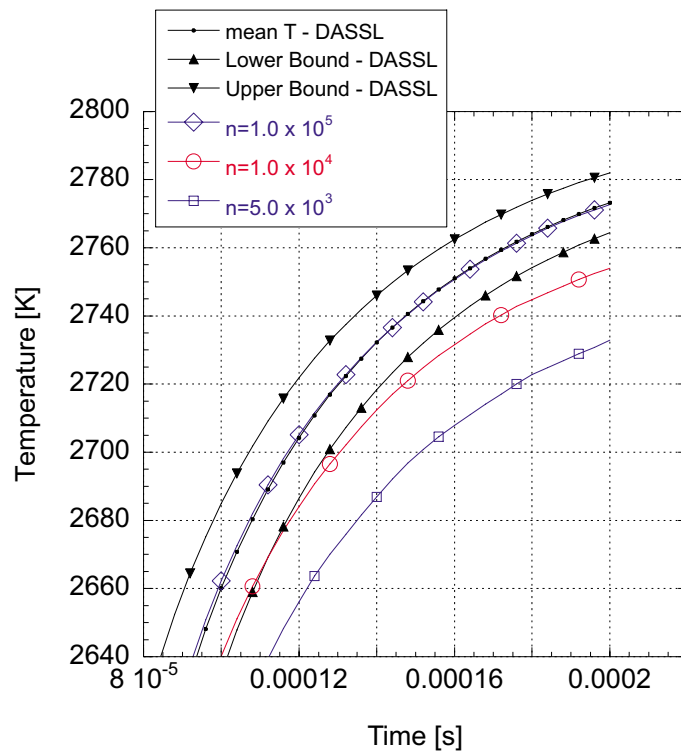
Figure 5: *Close up of the final part of Figure 4.*
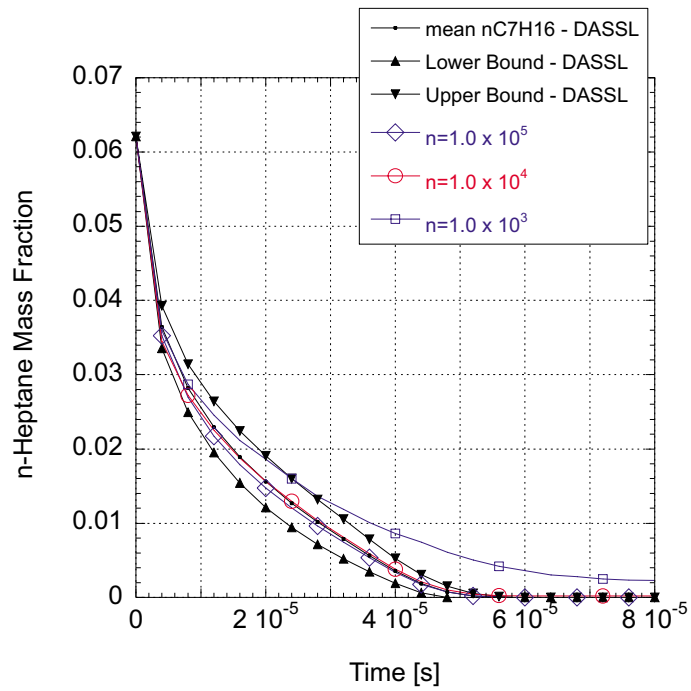
Figure 6: *n-heptane evolution for the high temperature regime.*
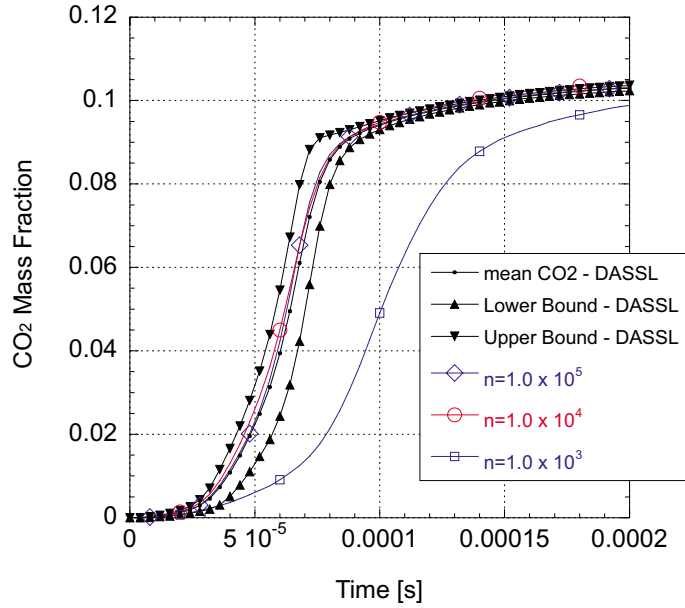
Figure 7: CO_2 *evolution for the high temperature regime.*
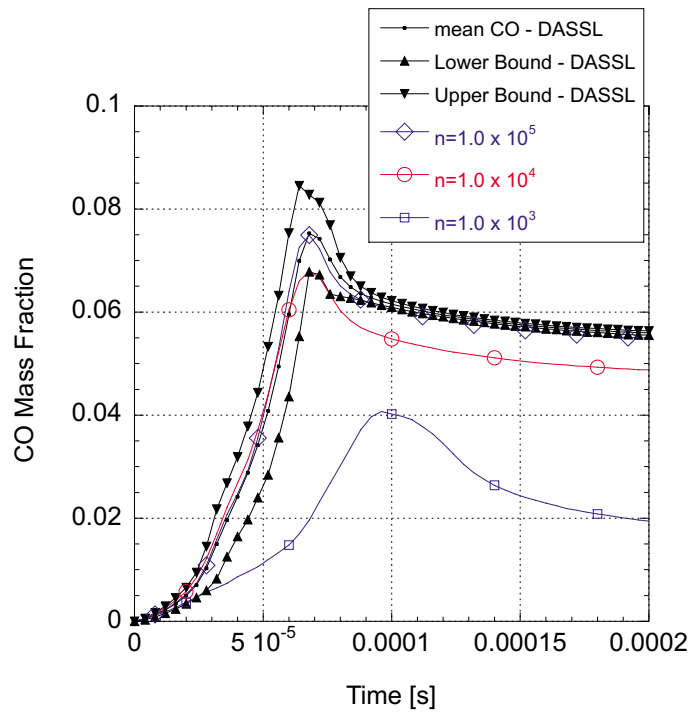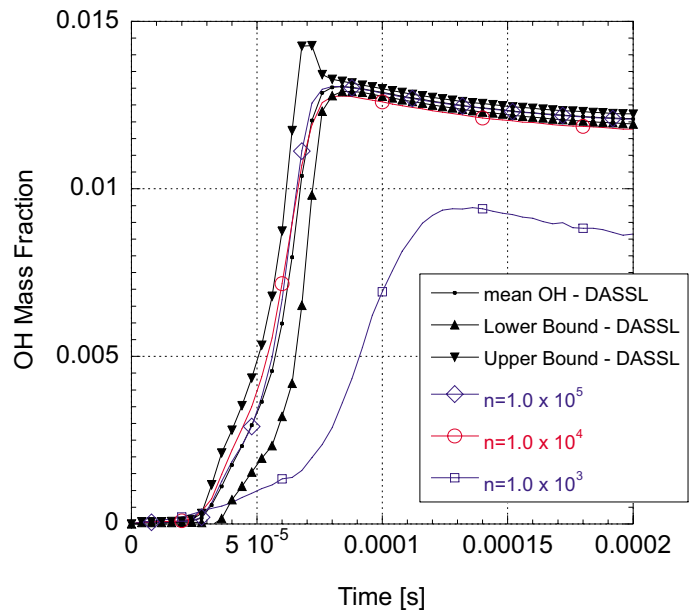
Figure 8: CO *evolution for the high temperature regime.*

Figure 9: OH *evolution for the high temperature regime.*

5.2.2. Low temperature regime

Next we consider the case when temperature at time zero is distributed uniformly on the interval $[1200, 1500]\, K$.

Figure 10 shows the average temperature curves for the algorithm with stochastic chemistry, in comparison with the average curve and confidence bands for the algorithm with deterministic chemistry. Results for numbers of sub-particles $n = 10^4$ and $n = 10^5$ are inside the reference confidence band.

A similar comparison is performed for the concentrations of the species n-heptane in **Figure 11**, CO_2 in **Figure 12**, CO in **Figure 13**, and OH in **Figure 14**. For most of these species, satisfactory results are already obtained for $n = 10^4$. However, for OH one needs $n = 10^6$ sub-particles, which is clearly due to the very low concentration.

A comparison of the CPU-time for different methods is given in **Table 4**. These results show that even with $n = 10^6$ sub-particles the algorithm with stochastic chemistry is faster than the algorithm with deterministic chemistry. In cases where a lower of sub-particles is sufficient, the algorithm with stochastic chemistry is much faster reaching a gain factor of 15 (for $n = 10^5$) or even 150 (for $n = 10^4$).

Table 4: *Computational times (CT) for varying n with $N = 100$ and $L = 4$ (low temperature regime)*

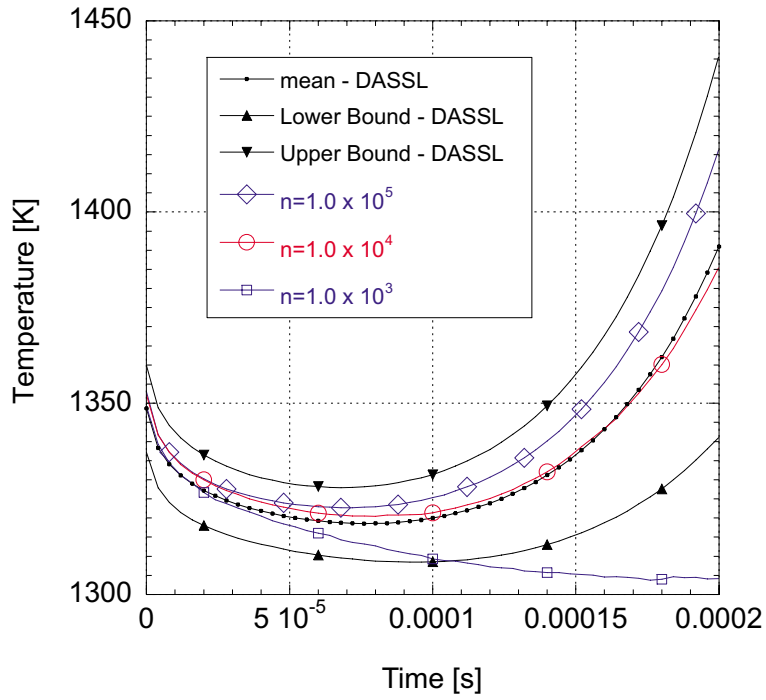| n	$CT[s]$	CT
DASSL	75950	$21h00m$
1.0×10^6	54918	$15h15m$
1.0×10^5	5695	$1h34m$
1.0×10^4	560	$9m$
1.0×10^3	61	$1m$

Figure 10: *Temperature evolution for the low temperature regime.*
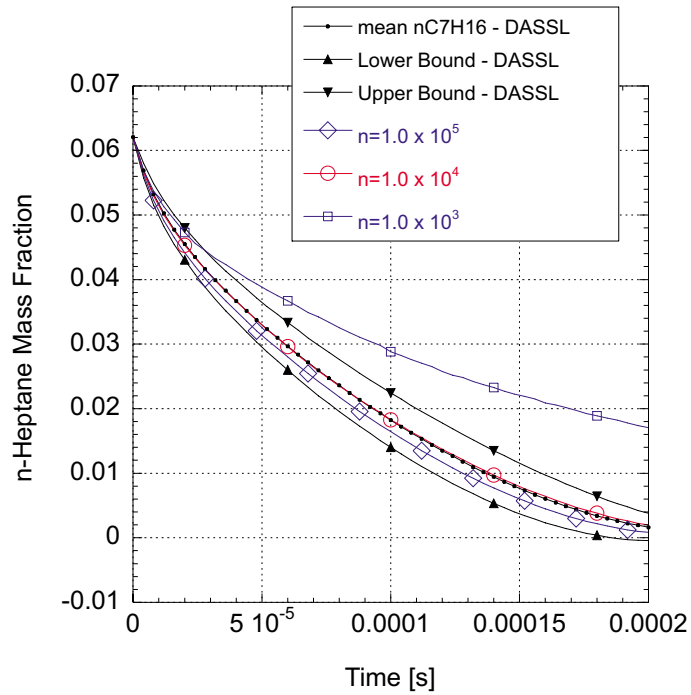

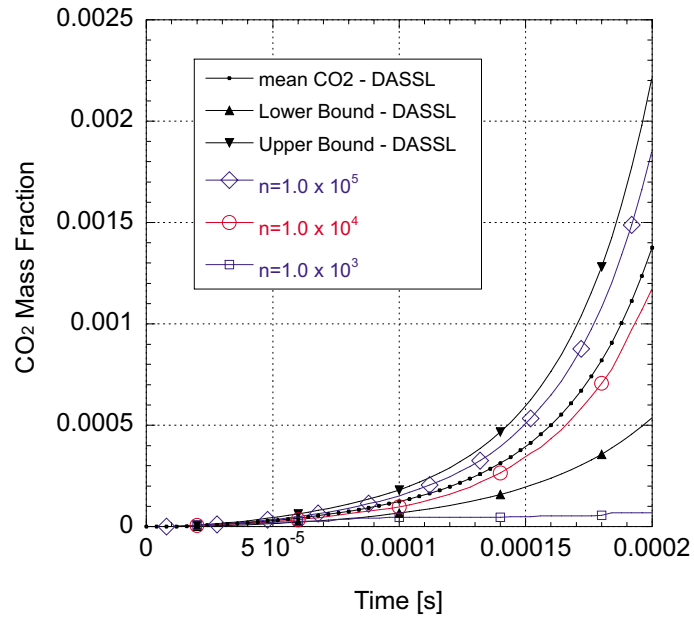**Figure 11:** *n-heptane evolution for the low temperature regime.*

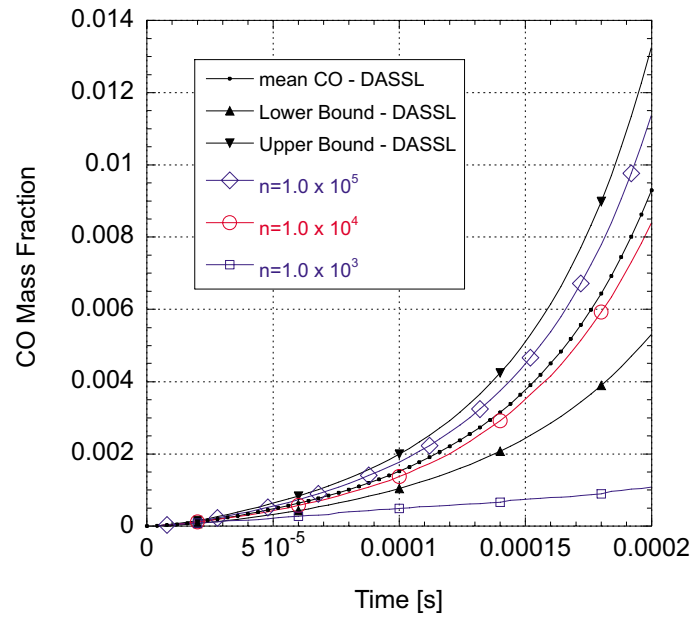**Figure 12:** CO_2 *evolution for the low temperature regime.*

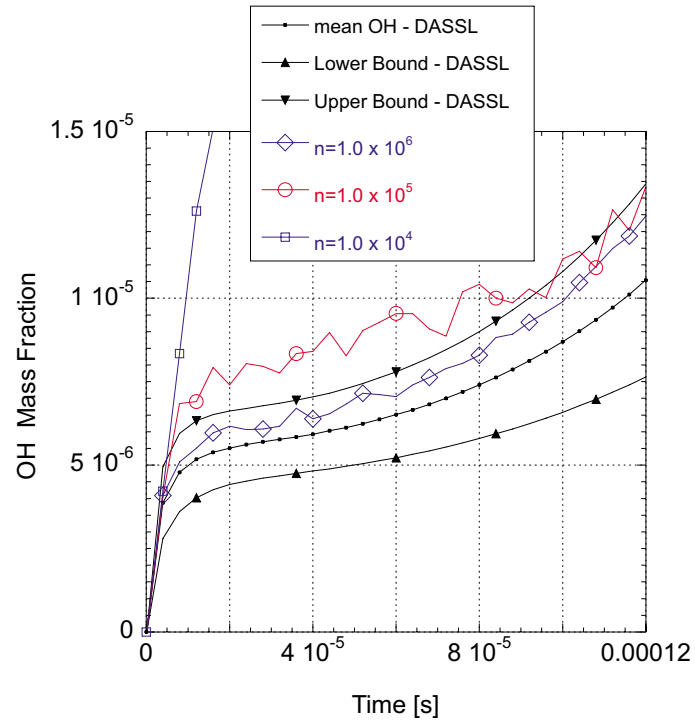**Figure 13:** CO *evolution for the low temperature regime.*

Figure 14: OH *evolution for the low temperature regime.*

6. Concluding remarks

In this paper we presented a new numerical technique which combines a stochastic chemistry approximation with a time splitting approach for the solution of the PDF transport equation as it is used in turbulent combustion. We considered the partially stirred plug flow model (PaSPFR) combined with the IEM mixing model. The algorithm is based on a combined particle/sub-particle system and a splitting scheme for the corresponding stochastic process, which treats chemical reactions and mixing separately. The chemistry step is approximated by a jump process where forward and reverse reactions are combined. The mixing step is solved analytically.

Numerical experiments were carried out to assess the new algorithm. For this purpose a simple case, a linear reaction, and a practically relevant case, the combustion of a premixed stoichiometric mixture of n-heptane and air, were studied. In the simple case the analytic solution of the third moment of the PaSPFR model was used to investigate the numerical properties of the new algorithm. The systematic error of the algorithm was found to be inversely proportional to the numbers of particles and of sub-particles, respectively.

The combustion of n-heptane was studied to investigate the performance of the new algorithm by comparing it with the standard deterministic chemistry algorithm using the code DASSL. Two cases were examined, a complete ignition at elevated temperatures and the degradation of n-heptane in the low temperature regime. In both cases the convergence properties were studied and it was demonstrated that the stochastic chemistry approximation led to a significant gain in computational speed while guaranteeing sufficient accuracy.

Finally we conclude that the stochastic chemistry approximation can be used to accelerate also numerical solution of the inhomogeneous PDF. If further progress is achieved this approach may be an alternative to existing reduction or tabulation strategies which have been employed in conjunction with PDF methods.

Acknowledgments

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