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# A New Method for the Automatic Elimination of Reactions from Large Mechanisms

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#### Abstract

In this paper a new explicit algorithm for the numerical solution of homogeneous gas-phase combustion systems is proposed, which is shown to outperform conventional solvers by more than two orders of magnitude for moderate accuracy and large systems. Further speedup is achieved by identifying and removing irrelevant reactions from the mechanism whilst retaining all species. We show that in terms of computational efficiency this brings about another factor of at least five at an acceptable loss of precision. Due to its immediate relationship to stochastic direct simulation, our new (deterministic) algorithm can also be used as an easily applicable tool for the reaction flow analysis of mechanisms. Another characteristic of our method is that reactions in partial equilibrium are effectively removed from the mechanism, which can be regarded as an automatic separation of the fast from the slow timescales. The new algorithm and its usefulness for the elimination of reactions is investigated numerically for a mechanism which models the combustion of n-decane at constant pressure and contains 1218 species and 4825 reversible reactions. Further advantages of our method are its exceptional simplicity of implementation and negligible start-up costs, both of which can be attributed to the explicit nature of the algorithm. These properties suggest as typical application large operator-splitting problems requiring moderate accuracy, such as PDF transport models for example.

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## 1 Introduction

Despite the still ongoing exponential growth of cheaply available computational power, detailed numerical simulations of combustion processes coupled to fluid dynamics remain out of reach. Therefore, the simplification of large reaction mechanisms still has to be considered a necessity.

Previously, several reduction techniques have been developed (see [8] for a short review and a comparison). For instance, the intrinsic low-dimensional manifold (ILDM, [12, 11]) method exploits the fact that chemical timescales cover several orders of magnitude by decoupling the fast processes from the reaction system. However, this involves the tabulation of large amounts of data related to concentration manifolds. Alternatively, a reduction can be achieved by computational singular perturbation (CSP, see [7] and references therein), which determines the eigenvalues of the Jacobi matrix of the source term and identifies the species which are most closely related to them. Another method uses lifetime analysis [9, 13]. In the lifetime analysis approach the steady-state species are detected and then the quasi steady-state assumption (QSSA) is invoked in order to reduce the set of ordinary differential equations governing the time evolution of the system. Though all mentioned approaches have been proven to be very successful at least for some applications, they are usually rather complicated and/or require sometimes extensive preprocessing efforts. In addition, in-depth understanding of and experience with the considered mechanisms may be necessary, which means that a successful reduction using such a technique could only be performed by specialists. The simplest form of model reduction is the elimination of reactions [1]. Dropping reactions from a mechanism reduces the computational cost by decreasing the number of terms needed to evaluate the chemical source terms. Further speedup can be obtained by removing species which occur only in eliminated reactions. The main issue of all reduction techniques is clearly to optimize the ratio between the computational speedup and the loss in numerical precision and/or information about the system.

Direct simulation approaches can provide deeper insight into the reaction flow analysis of mechanisms [19]. In [16], a stochastic method is used for the exploration of the structure and the dynamics of a complex mechanism, in particular the identification of predominant reaction paths.

The purpose of this paper is to present a new explicit algorithm, capable of solving large combustion systems more efficiently for moderate precision than conventional solver packages. Since our method is directly based on the reactions contained in a mechanism, rather than on solving the reaction rate equations as a system of ordinary differential equations, it can easily be applied as tool for the analysis of fluxes. We then introduce an extremely simple way of classifying reactions into "relevant" and "irrelevant" ones and reduce the underlying mechanism by dropping the irrelevant reactions. Our approach is substantially less complicated than conventional ones and requires no detailed knowledge of the involved chemical and physical processes whatsoever. Nonetheless, it can result in significant computational benefit, as we show in our numerical experiments involving a homogeneous gas-phase mechanism for the combustion of n-decane [3], which contains 1218 species and 4825 reversible reactions.

This paper is structured as follows. In the next section, we specify the model under consideration and state the equations to be solved. Thereafter, the new algorithm is briefly motivated and explained. Then, in the central part of the text, we elaborate on numerical experiments performed with the new algorithm exploring some of its properties followed by a more detailed investigation of its potential for the elimination of reactions. Finally, we draw some conclusions and indicate directions of future work.

#### 2 The model

Consider a mechanism consisting of I elementary reversible homogeneous gas-phase reactions involving S different species. We only look at combined forward/reverse reactions, which are denoted by

$$(\nu_{\alpha 1}, \dots, \nu_{\alpha S}) \quad \longleftrightarrow \quad (\nu_{\alpha 1}^*, \dots, \nu_{\alpha S}^*) \qquad ; \alpha = 1, 2, \dots, I,$$

where the stoichiometric coefficients  $\nu_{\alpha j}$  and  $\nu^*_{\alpha j}$  are non-negative integers.

**Example**: Consider the single reaction

$$H_2O + O \iff 2OH$$

involving three species. In the notation of (2.1) this would be written as

$$(1,1,0) \quad \longleftrightarrow \quad (0,0,2).$$

The time evolution of the molar concentrations  $[X_i]$  of the species is described by the reaction rate equations (cf. [10])

$$\frac{d[X_i]}{dt} = \sum_{\alpha=1}^{I} (\nu_{\alpha i}^* - \nu_{\alpha i}) \Big( \sum_{j=1}^{S} B_{\alpha j}[X_j] \Big) \Big( k_{\alpha, f} \prod_{j=1}^{S} [X_j]^{\nu_{\alpha j}} - k_{\alpha, r} \prod_{j=1}^{S} [X_j]^{\nu_{\alpha j}^*} \Big)$$
(2.2)

with i = 1, 2, ..., S. The right hand side is simply the molar production rate which is written here as a summation of the rate of progress variables for all reactions involving the *i*-th species.  $k_{\alpha,f}$  and  $k_{\alpha,r}$  denote the forward and reverse reaction rate constants for reaction  $\alpha$  and  $B_{\alpha j}$  accounts for third-body reactions. This notation essentially agrees with the one used in CHEMKIN [4].

The time evolution of the temperature is governed by (cf. [10])

$$\frac{dT}{dt} = -\frac{1}{c_p \varrho} \sum_{j=1}^{S} h_j W_j \dot{\omega}_j, \qquad (2.3)$$

where  $c_p$  denotes the mean specific heat capacity at constant pressure,  $\rho$  the mass density,  $h_j$  the specific enthalpy and  $W_j$  the molecular weight of the *j*-th species.  $\dot{\omega}_j$ denotes the molar production rate of the species, which is given by the right hand side of Eqn. 2.2.

### 3 The deterministic chemistry algorithm

Our algorithm is directly motivated by stochastic modelling techniques studied previously for instance in [2] or [6, 5]. In a stochastic approach, single reaction events are considered to occur probabilistically at a *rate* (number of events per unit time), which is given by the reaction rate function (cf. [6] or [5])

$$Q_{\alpha}(x) = (N_A V)^{1 - \sum_{j=1}^{S} \nu_{\alpha j}} k_{\alpha} \prod_{j=1}^{S} \prod_{i=1}^{\nu_{\alpha j}} (x_j - i + 1), \qquad (3.1)$$

where  $x_j$  denotes the number of atoms/molecules of species j. The normalization factor  $N_A V = \frac{RT}{p} \sum_{j=1}^{S} x_j$  ensures that Q has the correct physical dimension (s<sup>-1</sup>). Note also that  $Q_{\alpha}(x)$  is always non-negative.

A stochastic simulation procedure proceeds by choosing in each step a reaction  $\alpha$  according to the probability  $Q_{\alpha} / \sum_{\beta=1}^{I} Q_{\beta}$  and performing the chosen reaction. Then, the time is advanced by an exponentially distributed waiting time, whose mean value (expectation) is given by  $1 / \sum_{\beta} Q_{\beta}$ . Repeating this until a given stopping time is reached yields an approximation of the time evolution of the system (for details, see [2, 6]). This model can be extended to allow for variable temperature: After each reaction event the temperature is changed by an amount  $\Delta T$  given by

$$\Delta T_{\alpha} = -\frac{\sum_{j=1}^{S} H_j(T)(\nu_{\alpha j}^* - \nu_{\alpha j})}{\sum_{j=1}^{S} C_j(T) x_j},$$
(3.2)

where  $H_j(T)$  denotes the enthalpy and  $C_j(T)$  the heat capacity of the *j*-th species. For a derivation of this equation and its relationship to Eqn. 2.3 see [5].

This stochastic prescription can be turned into a deterministic one by using the following principle. On average, after a large number of steps N, the  $\alpha$ -th reaction will have occurred approximately  $NQ_{\alpha}/\sum_{\beta}Q_{\beta}$  times, assuming constant rates, which is reasonable for sufficiently small time steps. Therefore, we accumulate the probabilities  $Q_{\alpha}/\sum_{\beta}Q_{\beta}$  until they surpass unity, and whenever this is the case, the corresponding reaction is performed.

Another central aspect of our method is not to treat each forward and each backward reaction separately but to look at the combined reversible reactions with (possibly negative) rates  $R_{\alpha}(x) = Q_{\alpha,f}(x) - Q_{\alpha,r}(x)$ . Here,  $Q_{\alpha,f}$  and  $Q_{\alpha,r}$  denote the forward and reverse rates, each given by Eqn. 3.1 with forward/reverse rate constants  $k_{\alpha,f}$ and  $k_{\alpha,r}$  respectively. The underlying idea is to perform either forward or reverse reactions according to the sign of the rates. The temperature variable is then treated as follows. If a reaction  $\alpha$  is performed in the forward direction then the temperature is changed by an amount  $+\Delta T_{\alpha}$  (see Eqn. 3.2), otherwise by  $-\Delta T_{\alpha}$ .

A noteworthy advantage of this method is that compared to conventional direct simulation techniques fewer events occur because forward and reverse reaction steps can compensate such that they are not actually performed, thereby saving computational effort. Or in a more physical interpretation, reactions in partial equilibrium are effectively dropped from the mechanism. This essentially means that the separation of the fast from the slow timescales is achieved automatically, so that after the fast processes have reached partial equilibrium, the system evolves within the slow manifold.

The species  $x_j$  and therefore the rates  $R_{\alpha}(x)$  depend on the total initial particle number n, which plays the role of a control parameter of the numerical error. In the limit  $n \to \infty$ , the exact solution of Eqns. 2.2 and 2.3 would be recovered [6]. In the context of conventional solution of ordinary differential equations, the particle number n corresponds to the absolute error tolerance ATOL via ATOL = 1/n. There exists no analogue of the relative error tolerance RTOL, which can also be interpreted as RTOL = 0.

This description results in the following algorithm.

- 1. Fix the particle number n, a stopping time  $t_{\text{stop}} > 0$ , set the species  $x_j$  and the temperature T equal to their initial values and set the changes  $\Delta P_{\alpha} = 0$ .
- 2. Wait a time step  $\Delta t$ , i.e. update  $t \mapsto t + \Delta t$  with  $\Delta t = 1/\sum_{\beta=1}^{I} |R_{\beta}(x)|$ .
- 3. If the stopping time is exceeded  $(t > t_{stop})$  then stop.
- 4. For each  $\alpha = 1, 2, \ldots, I$  update

$$\Delta P_{\alpha} \mapsto \Delta P_{\alpha} + \frac{R_{\alpha}(x)}{\sum_{\beta=1}^{I} |R_{\beta}(x)|}$$

5. If  $|\Delta P_{\alpha}| < 1$  for all  $\alpha = 1, 2, ..., I$  then go ostep 2. Otherwise, choose a reaction index  $\alpha$  such that  $|\Delta P_{\alpha}|$  is maximal. For this reaction  $\alpha$ , if  $\Delta P_{\alpha} \ge 1$  then perform a forward reaction event, i.e. update

$$x_j \mapsto x_j + (\nu_{\alpha j}^* - \nu_{\alpha j})$$
 for all  $j = 1, 2, \dots, S$ 

and update  $\Delta P_{\alpha} \mapsto \Delta P_{\alpha} - 1$ .

Else if  $\Delta P_{\alpha} \leq -1$  then perform a reverse reaction event, i.e.

$$x_j \mapsto x_j - (\nu_{\alpha j}^* - \nu_{\alpha j})$$
 for all  $j = 1, 2, \dots, S$ 

and update  $\Delta P_{\alpha} \mapsto \Delta P_{\alpha} + 1$ .

- 6. Let  $\alpha$  be the index of the reaction chosen in the previous step. If reaction  $\alpha$  has been performed in the forward direction then update the temperature according to  $T \mapsto T + \Delta T_{\alpha}$ , otherwise  $T \mapsto T \Delta T_{\alpha}$ , where  $\Delta T_{\alpha}$  is given by Eqn. 3.2.
- 7. Go to step 2.

We emphasize that this algorithm is entirely deterministic, i.e. it does not contain any random element whatsoever. Nonetheless, there exists a close relationship between deterministic and stochastic methods and the scheme presented here can even be generalized to arbitrary systems of ordinary differential equations. Both of these points are explored in some detail in [15] and [14].



Figure 1: Time evolution of some major species for the full n-decane mechanism calculated with the new algorithm at  $n = 10^6$  particles.

### 4 Numerical experiments

We created a FORTRAN program containing the new algorithm as well as the SENKIN [10] and the CHEMKIN [4] packages. All simulations for this paper have been performed on an Intel Pentium III PC at 866 MHz running Microsoft Windows 2000.

In order to assess the accuracy of the solutions produced by our algorithm, we compared them to a high precision run performed with SENKIN using  $ATOL = 10^{-20}$  and  $RTOL = 10^{-8}$ . Since we are only interested in applications requiring moderate accuracy, this run can be taken as the "exact" solution.

For all our numerical experiments, we used an automatically generated mechanism for the combustion of n-decane [3] containing 1218 species and 4825 reversible reactions whose CHEMKIN mechanism file can be obtained from the website www.ensic.unancy.fr/DCPR/Anglais/GCR/softwares.htm. As initial temperature we chose T = 1500 K and the (constant) pressure was set equal to one physical atmosphere ( $p = 1.01325 \times 10^5$  Pa). The initial fuel/air ratio was chosen stoichiometric.

For the quantitative measurement of the overall numerical error of the solutions produced by our algorithm we use an estimate of the average deviation of the approximate from the exact quantity of interest given by

$$c_{\text{tot}} = \frac{1}{M+1} \sum_{j=0}^{M} \left| f(t_j) - \tilde{f}(t_j) \right|, \tag{4.1}$$

where f denotes some function of the exact solution (e.g. the mass density, the temperature or the species mole fractions) and  $\tilde{f}$  the numerical approximation of f. The time interval between the initial time 0 and the stopping time  $t_{\text{stop}}$  is split into



Figure 2: Time evolution of some radicals for the full n-decane mechanism calculated with the new algorithm at  $n = 10^6$  particles and SENKIN for comparison.

M subintervals of equal length via

$$t_j = j \times \frac{t_{\text{stop}}}{M}.$$

#### 4.1 Performance of the new algorithm

For the calculation of the rate functions in our algorithm, we did not employ the routines provided by CHEMKIN. Instead, we improved the standard routines by various optimizations and approximations as follows. The rate constants and normalization factors in Eqn. 3.1 are updated only if the change in the temperature exceeds a certain minimum value:  $|\Delta T| \ge 10^5 \text{ K/n}$ . Furthermore, the rate functions are evaluated fully only if the products of the species particle numbers  $x_j$  in Eqn. 3.1 are non-zero. Most importantly, this means that the rate constants are updated only in the case of non-zero products. The underlying stochastic version of the algorithm presented in this paper, including all mentioned modifications to speed up the evaluation of the rate functions, is examined numerically to quite some extent in [18] (together with a more detailed explanation of the optimizations and approximations but without the application to the reduction of mechanisms).

In this subsection, we consider throughout only the full mechanism containing all reactions (and all species).

Figure 1 depicts the time evolution of a number of major species calculated with the new algorithm at  $n = 10^6$  particles. The SENKIN high precision run is not shown since it would coincide exactly with the plotted curves.

Even for species with a relatively small mole fraction, like the radicals shown in Fig. 2, the solution produced by the new algorithm, again at  $n = 10^6$  particles, is indistinguishable from the SENKIN high precision solution.



Figure 3: Efficiency of the new algorithm compared to SENKIN for the full ndecane mechanism. The error is calculated for the temperature.

In Fig. 3, the efficiency of the new algorithm and of SENKIN are compared. In this graph, the parameter RTOL for SENKIN has been chosen to be zero because of the closest resemblance to our method (as mentioned above). Regarding the efficiency, experiments have shown that using a non-zero RTOL does not make a significant difference. The value of ATOL varies between  $10^{-4}$  and  $10^{0}$ . The number of particles for our algorithm is chosen between  $2 \times 10^{3}$  and  $10^{6}$  as indicated. For moderate precision (here  $c_{\text{tot}} > 10$  K roughly) the new algorithm is more than two orders of magnitude faster than SENKIN. We are aware of the fact that solvers of ordinary differential equations can be optimized in various ways for combustion systems. In particular, for large systems, sparse matrix routines can be applied successfully (see for example [17]). But since SENKIN is wide-spread, it may simplify the comparison to solvers by other authors.

#### 4.2 Exclusion of "irrelevant" reactions

Profiling runs with direct simulation codes show unambiguously that an overwhelming fraction of the computation time is spent with the evaluation of the reaction rate functions (Eqn. 3.1). This motivates on the one hand the modifications mentioned in the previous section and on the other hand the idea of including as few reactions as possible into the mechanism (as proposed in [1]) at an acceptable loss of precision. Our approach to reducing mechanisms therefore distinctly differs from conventional ones like [8] in that all species are retained at all times. Note that we refer to our mechanisms as "full" or "reduced" according to the number of included reactions, even though both the full and the reduced mechanisms (in our terminology) contain all species.

Given the result of a simulation run with a certain number of particles (the "preprocessing run"). We define a reaction  $\alpha$  to be *relevant* if the ratio between the number



Figure 4: Number of included reactions as function of the threshold for different particle numbers.

of events of that reaction and the total number of occurred events is greater than or equal to a given threshold  $\varepsilon$ . The considered ratio of events for every reaction lies by definition between 0 and 1, which implies the same range of reasonable values for  $\varepsilon$ . Evidently, if  $\varepsilon = 0$  then all reactions are relevant and the "reduced" mechanism coincides with the full mechanism. Otherwise, if  $\varepsilon > 0$  computational speed up is achieved by excluding the irrelevant reactions. We emphasize that this definition of relevance is rather naive and does not take into account more non-trivial physical properties of the reactions, like sensitivities (cf. for instance the *level of importance* in [8]).

Not only does the notion of relevance given here depend on the physical initial conditions, but it also depends on the number of particles of the provided simulation run. In Fig. 4, the number of included reactions is plotted against the threshold for different numbers of particles. For  $\varepsilon > 0.1$  all reactions are found to be irrelevant and conversely, the full mechanism is recovered for  $\varepsilon = 0$  only, which means that even at a large number of particles not a single event occurs for a majority of the reactions (up to 3000) - for the chosen initial conditions. We furthermore notice that for threshold values between roughly  $10^{-5}$  and  $10^{-2}$ , the number of included reactions does not depend significantly on the number of particles. Of course, the relevance of a reaction becomes asymptotically (for high numbers of particles) independent of the number of particles, regardless of the threshold.

In Figure 5 the time evolution of the temperature is shown for various numbers of included reactions. In addition, the SENKIN high precision run with all reactions included is shown. This demonstrates that even for as few as 245 reactions (compared to the 4825 of the full mechanism), the temperature (and the ignition time) is predicted rather accurately. For these three curves, the corresponding error values  $c_{tot}$  of the temperature are approximately 14.5 K (245 reactions), 107 K (161 reactions) and 212 K (99 reactions) respectively.



Figure 5: Time evolution of the temperature for different reduced mechanisms at  $n = 10^6$  particles compared to the full mechanism calculated by SENKIN.

Figure 6 depicts the dependance of the total error  $c_{\rm tot}$  of the temperature on the number of included reactions for different numbers of particles. In accordance with Figure 5, we notice that the number of reactions can be decreased from 4825 down to roughly a few hundred (depending on the number of particles) without a significant increase in numerical error. Furthermore, one can deduce that if a relatively large error (e.g.  $c_{\rm tot} \approx 10$  K here) suffices then one can not only work with a low number of reactions ( $\approx 250$ ) but also with a low number of particles ( $n = 10^4$ ).

In Figure 7, the dependance of the relative computation time on the number of included reactions is shown. Or in other words, one can read off by what factor the CPU-time reduces when a certain number of reactions is included. This factor apparently depends only weakly on the number of particles.

Index	Reactions
А	4825
В	732
С	661
D	615
Ε	581
F	530
G	488
Н	428
J	359
Κ	302
$\mathbf{L}$	245
М	161
Ν	99

Table 1: Number of included reaction	ns
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Figure 6: Absolute error  $c_{tot}$  of the temperature as function of the number of included reactions for different particle numbers.

Figure 8 shows the increase in efficiency when removing reactions from the mechanism for  $n = 10^6$  particles. Starting from the point labelled A, which indicates the full mechanism, the number of included reactions is reduced down to 99 for the point labelled N. The complete list of how many reactions are included for each point is given in Table 1. We recognize that the CPU-time can be reduced approximately by a factor of five (cf. Fig. 7) with only negligible loss of precision. In order to attain an intuitive understanding of the magnitude of the error, note that the three curves for the reduced mechanisms in Figure 5 correspond to the points L (245 reactions), M (161 reactions) and N (99 reactions) respectively. The curves for different numbers of particles exhibit similar characteristics.

### 5 Conclusions

We presented a new explicit and deterministic algorithm for the solution of homogeneous gas-phase combustion systems. In a way, it automatically separates fast and slow timescales by no longer performing reactions that have reached partial equilibrium. Also, being motivated by stochastic direct simulation schemes, it is suitable for the straightforward analysis of reaction flow. We have demonstrated the efficiency of the new algorithm by calculating the combustion of n-decane, a mechanism containing 1218 species and 4825 reactions. Even for the full mechanism, our method was shown to be roughly two orders of magnitude faster than SENKIN, for moderate precision. Applying our algorithm to the reduction of mechanisms, we examined the number of included reactions as function of the user-specified threshold. We then studied extensively the effects of the exclusion of reactions on the numerical precision. For this, we have determined the error as function of the number of included reactions, for varying number of particles, which serves as a *priori* error control parameter. Furthermore, we investigated the speedup achieved by the reduction,



Figure 7: Ratio between the CPU-times of the reduced and the full mechanism as function of the number of included reactions for different particle numbers.

which showed the substantial decrease in CPU-time in light of the still rather moderate error. For the considered mechanism, the computation time required by our algorithm could be reduced by a factor of five or more at a negligible loss of precision, which means for this particular case that our method is about 500 times faster than SENKIN.

Obvious future extensions of our work are for instance to reduce the number of species by deleting those which occur only in eliminated reactions, to exploit information gathered by reaction flow analysis and to take into account sensitivities of species and reactions.

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Figure 8: Efficiency of the reduction at  $n = 10^6$  particles. The error is calculated for the temperature. The number of included reactions for each point is provided in Table 1.

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