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Coupling of chemical reaction with flow and molecular transport

COUPLING OF CHEMICAL REACTION WITH FLOW
AND MOLECULAR TRANSPORT

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Summary. During the last years the interest in the numerical simulation of reacting flows has grown considerably. Numerical methods are available, which allow to couple chemical kinetics with flow and molecular transport. However, the use of detailed physical and chemical models, involving more than 100 chemical species, and thus more than 100 species conservation equations, is restricted to very simple flow configurations like one-dimensional systems or two-dimensional systems with very simple geometries, and models are required, which simplify chemistry without sacrificing accuracy.

In many chemically reacting flows chemical processes occur with time scales differing by many orders of magnitude (e.g., 10^{-10} s to 1 s in combustion processes), whereas the time scales of flow, molecular transport, and turbulence usually cover a much smaller range of time scales. Based on local time scale analyses it is possible to decouple the fast (and thus not rate limiting) chemical processes. In this way the chemistry can be described in terms of a small number of governing reaction progress variables, and computations of complex reacting flow problems become possible. Examples for calculations with detailed and simplified chemistry are shown for various reacting flows, such as hypersonic reacting flows or combustion processes.

Keywords: numerical simulation, flow and molecular transport, chemical reactions, combustion processes

AMS classification: 76K05, 76V05

1. INTRODUCTION

During the last years the interest in the numerical simulation of reacting flows has grown considerably in a variety of different applications such as for example combustion processes [1, 2], hypersonic flows [3], and chemistry in the atmosphere [4]. Some of the approaches use very detailed descriptions of the underlying physical and chemical processes, thus forcing a restriction to very simple flow configurations like one- or two dimensional systems with simple geometries. Other approaches, which are typical for industrial applications, handle very complex, i.e. realistic three-dimensional

flow geometries, but, on the other hand, usually over-simplify the governing physical and chemical processes (e.g., by using one-step chemistry). Thus, methods are needed, which simplify the description of the physical and chemical processes without sacrificing accuracy, but nevertheless allowing the mathematical models to be applied in realistic computations of three-dimensional reacting flows of practical interest.

The development of simplified descriptions of chemical reaction systems, e.g., for the simulation of complex combustion processes has been an intensive object of research, and a variety of different approaches can be found in the literature (see, e.g., [5, 6, 7, 8] for references considering combustion processes). The main motivation for the use of reduced mechanisms is the fact that due to the complexity of the combustion processes usually encountered in practical applications, methods have to be found, which describe the chemical reaction by only a small number of species, while still retaining the essential dynamics of the system. Recently we developed a method, the method of intrinsic low-dimensional manifolds (ILDM) [9], which provides a simplification of the chemical kinetics starting from a detailed reaction mechanism. The method is based on the dynamic systems theory. Besides the detailed reaction mechanism, the only input to the scheme is the desired number of degrees of freedom (i.e., the number of reaction progress variables). Sample calculations for a perfectly stirred reactor [10], laminar flames [11, 12], turbulent flames [13, 14], and hypersonic flows [16] have shown that the method yields good results, and is able to describe the coupling of chemical reaction with physical processes like mixing or molecular transport.

2. MATHEMATICAL MODEL

2.1. Governing equations of reacting flows. Mathematical simulation of chemically reacting multi-component compressible flows is performed by solving the corresponding system of conservation equations for mass, momentum, energy, and species masses (Navier-Stokes equations) which may be written as [17, 18]:

$$(1) \qquad \frac{\partial \varrho}{\partial t} + \text{div} \left(\varrho \vec{v} \right) = 0$$

$$(2) \qquad \frac{\partial \varrho \vec{v}}{\partial t} + \text{div} \left(\varrho \vec{v} \otimes \vec{v} + \bar{\bar{p}} \right) = \varrho \vec{g}$$

$$(3) \qquad \frac{\partial \varrho u}{\partial t} + \text{div} \left(\varrho u \vec{v} + \vec{q} \right) + \bar{\bar{p}} : \text{grad} \, \vec{v} = \omega_h$$

$$(4) \qquad \frac{\partial \varrho_i}{\partial t} + \text{div} \left(\varrho_i \vec{v} + \varrho_i \vec{V_i} \right) = \omega_i M_i \qquad i = 1, 2, \ldots, n_s$$

together with the equation of state

$$(5) \qquad p = p \left[h, \varrho_1, \varrho_2, \ldots, \varrho_{n_s} \right],$$

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where in most cases the equation of state is given by the ideal gas law

$$(6) \qquad p = \frac{\varrho}{\overline{M}} RT.$$

In these equations t denotes the time, ϱ the density, $\vec{v}$ the velocity vector, p the pressure, $\overline{\overline{p}}$ the pressure tensor, $\vec{g}$ the gravitational acceleration, u the specific internal energy, $\vec{q}$ the heat flux density, ω_h a source term for energy (e.g., due to radiation), n_s the number of species, ϱ_i the partial density of species i, M_i the molar mass of species i, $\overline{M}$ the mean molar mass of the mixture, T the temperature, R the universal gas constant, $\vec{V}_i$ the diffusion velocity of species i relative to the center of mass, and ω_i the molar rate of formation of species i. $\otimes$ denotes the dyadic product of two vectors and : the two-fold contraction of two tensors.

The transport terms $\overline{\overline{p}}$, $\vec{V}_i$ and $\vec{q}$, which are needed to close the system, can be derived from the kinetic theory of gases. Using Fourier's law of heat conduction, Newton's law of friction, Fick's law of diffusion, and the law of thermal diffusion, we obtain (neglecting bulk viscosity, the Dufour-effect and pressure diffusion) [17, 18]

$$(7) \qquad \overline{\overline{p}} = p\overline{\overline{E}} - \mu \left\{ (\operatorname{grad} \vec{v}) + (\operatorname{grad} \vec{v})^T - \frac{2}{3} (\operatorname{div} \vec{v}) \overline{\overline{E}} \right\}$$

$$(8) \qquad \vec{j}_i = \varrho_i \vec{V}_i = -\varrho \frac{w_i}{x_i} D_i^D \operatorname{grad} x_i - D_i^T \operatorname{grad}(\ln T)$$

$$(9) \qquad \vec{q} = \sum_{i=1}^{n_s} h_i \vec{j}_i - \lambda \operatorname{grad} T$$

where $\overline{\overline{E}}$ denotes the unit tensor, μ the mean dynamic viscosity of the mixture, x_i the mole fraction of the species i, D_i^D the coefficient for diffusion of component i into the mixture, D_i^T the coefficient of thermal diffusion, $\vec{j}_i$ the diffusion flux density, h_i the specific enthalpy of species i, and λ the heat conductivity of the mixture. A detailed discussion of the chemical and physical aspects of these equations can be found in [17, 18].

For the numerical solution of the partial differential equation system a set of boundary conditions has to be specified. These boundary conditions stem from the physical processes at the boundaries of the domain, and they have to account for effects like heterogeneous reactions or phase transitions (see, e.g., [19]). From a mathematical point of view the boundary conditions can be highly non-linear and complicate the numerical solution of the partial differential equation system considerably.

For the following analysis it is important to note that the dynamic behavior of a chemically reacting flow is governed by the system of conservation equations (1–5),

namely the conservation of mass, momentum, energy, and species masses [17, 18], which describe the time- and space-dependent development of all the variables (e.g., mass fractions, specific enthalpy, density, temperature and velocity field). These equations can be rewritten to yield equations for the scalar field of a reacting flow, which is described by the state vector $\underline{\psi} = (h, p, \varphi_1, \varphi_2, \ldots, \varphi_{n_s})^T$. Here, a formal separation into physical processes Ξ and chemical production terms F shall be made. We obtain

$$
\begin{aligned}
\frac{\partial h}{\partial t} &= F_h + \Xi_h \\
\frac{\partial p}{\partial t} &= F_p + \Xi_p \\
\frac{\partial \varphi_i}{\partial t} &= F_{\varphi_i} + \Xi_{\varphi_i} \qquad i = 1, 2, \ldots, n_s
\end{aligned}
$$

(10)

or in vector formulation

(11)
$$
\frac{\partial \underline{\psi}}{\partial t} = \underline{F} + \underline{\Xi}
$$

with $\underline{F} = (F_h, F_p, F_{\varphi_1}, F_{\varphi_1}, \ldots, F_{\varphi_{n_s}})^T$ and $\underline{\Xi} = (\Xi_h, \Xi_p, \Xi_{\varphi_1}, \Xi_{\varphi_1}, \ldots, \Xi_{\varphi_{n_s}})^T$, and
(12)

$$
\begin{aligned}
F_h &= 0, & \Xi_h &= \frac{f_p}{\varrho} - \vec{v}\,\mathrm{grad}\,h - \frac{1}{\varrho}\,\mathrm{div}\,\vec{q} - \frac{1}{\varrho}\bar{\bar{p}} : \mathrm{grad}\,\vec{v} + \frac{1}{\varrho}\,\mathrm{div}\,p\vec{v} + \frac{\omega_h}{\varrho} \\
F_p &= 0, & \Xi_p &= f_p \\
F_{\varphi_i} &= \omega_i/\varrho, & \Xi_{\varphi_i} &= -\frac{1}{\varrho M_i}\,\mathrm{div}\,\vec{j_i} - \vec{v}\,\mathrm{grad}\,\varphi_i \qquad i = 1, 2, \ldots, n_s
\end{aligned}
$$

where t = time, h = specific enthalpy, p = pressure, ϱ = density, $\vec{v}$ = velocity vector, $\bar{\bar{p}}$ = pressure tensor, $\vec{q}$ = heat flux density, ω_h = source term for energy (e.g., radiation), n_s = number of species, φ_i = specific mole number of species i ($\varphi_i = w_i/M_i$), w_i = mass fraction of species i, M_i = molar mass of species i, $\vec{j_i}$ = diffusion flux density of species i, ω_i = molar rate of formation of species i. This choice of the dependent variables is quite arbitrary. Other formulations, like conservative, could be used, too. The term f_p describes the time behavior of the pressure, which shall not be written down explicitly in this paper (in many cases, like, e.g., in laminar flame calculations, the pressure is assumed to be constant, i.e. $f_p = 0$). Furthermore, note that the terms Ξ are complicated functions of the scalars, the velocity field, and the first and second spatial derivatives.

2.2. Dynamical behavior of chemical reaction systems.
In chemically reacting flows the different processes (flow, molecular transport and chemical reactions) usually occur with time scales differing by orders of magnitude. Typical time-scales

of chemical reactions (e.g., in combustion systems) cover a range of 10^{-10} to 1 s, and in most cases this range of the chemical time scales is much larger than the range of the physical time scales (e.g., diffusion). The fast chemical time scales are usually responsible for fast equilibration processes (reactions in partial equilibrium, species in steady state). These fast time scales can be decoupled, yielding a simplified kinetic scheme, where the thermochemical state of the fluid is represented by a small number (N) of variables—typically less than five—which we denote by $\underline{\theta} = \{\theta_1, \theta_2, \ldots, \theta_N\}$. These variables may correspond to species mass fractions, though they need not. Then, by assumption, the density $\varrho(\underline{\theta})$, the temperature $T(\underline{\theta})$, and the mass fraction of the species i, $w_i(\underline{\theta})$ are known functions of $\underline{\theta}$.

In order to demonstrate how the time scales can be decoupled, let us consider a simple homogeneous reaction system for the moment.

A chemical reaction system with n_s different species is completely determined by $n = 2 + n_s$ variables, namely specific enthalpy h, pressure p and species mass fractions w_i. These n variables build up an n-dimensional state space, in which chemical reaction takes place.

Chemical reaction corresponds to a movement along a trajectory in this state space, which (for a closed, homogeneous, adiabatic, isobaric system) is governed by the equation system

(13)
$$\frac{\partial}{\partial t}\underline{\psi} = \underline{F}\left(\underline{\psi}\right)$$

with $\underline{\psi} = (h, P, \varphi_1, \varphi_2, \ldots, \varphi_{n_s})^T$ and $\underline{F}(\psi) = (0, 0, \omega_1/\varrho, \omega_2/\varrho, \ldots, \omega_{n_s}/\varrho)^T$. In these equations ϱ denotes the density, ω_i the molar rate of formation of species i, and φ_i the specific mole number of the species i, which is defined by $\varphi_i = w_i/M_i$, where M_i is the molar mass of the species i.

If we restrict to given values of enthalpy and pressure, which are assumed to be constant in this case, chemical reaction is confined to the n_s-dimensional composition space. Furthermore, if we make use of the fact that there are n_e elements in the reaction system, which are conserved in chemical reactions, the chemical reaction is confined to a movement in an ($n_r = n_s - n_e$)-dimensional reaction space.

Starting at given initial conditions, the chemical reaction system evolves until (for $t \to \infty$) it reaches the equilibrium value. This equilibrium is a function of h, p, and the specific element mole numbers χ_j ($\chi_j = w_j/M_j$, where w_j is the mass fraction and M_j the molar mass of element j) only and, thus, a point in the reaction space and an ($n_e - 1$) dimensional manifold in composition space ($n_e - 1$ because of the constraint that the mass fractions sum to one), and an ($2 + n_e - 1$)-dimensional manifold in state space.
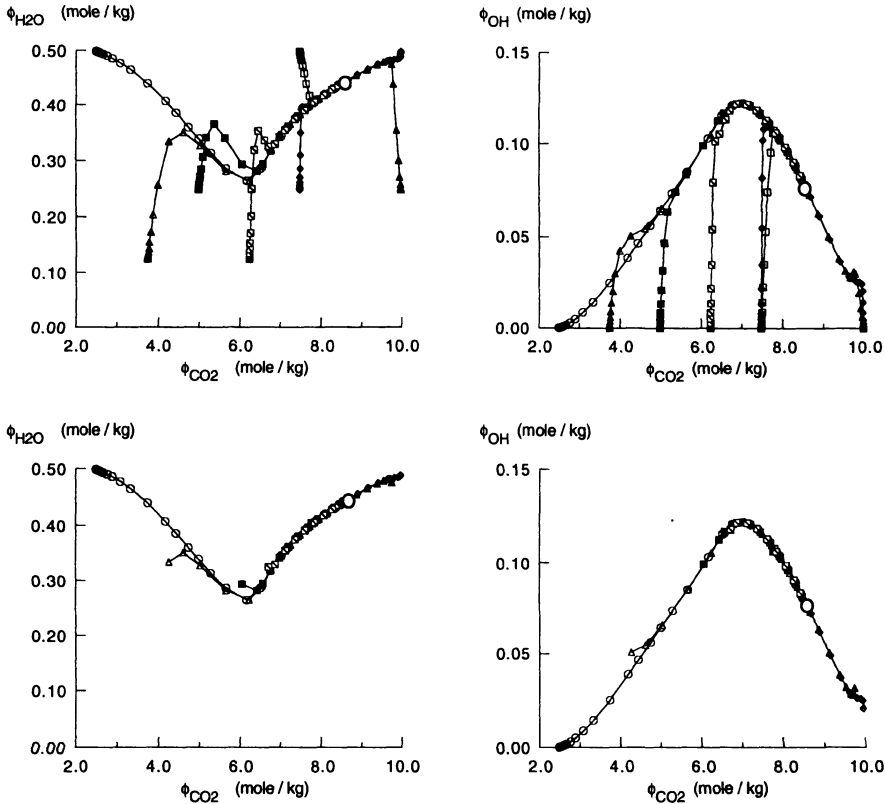
Fig. 1. Trajectories of the chemical reaction for a $CO - H_2$-air system, o denotes the equilibrium; projection into the CO_2-H_2O- and the CO_2-OH- planes. Upper part: complete reaction process, lower part: trajectories after a relaxation time of $100\,\mu s$.

Figure 1 shows sample trajectories of chemical reactions in a $CO - H_2$-air combustion system [20] in the phase space. Plotted are projections into the CO_2-H_2O- and the CO_2-OH- planes. Different initial conditions were chosen. It can be seen that the trajectories always end at the equilibrium value, which is denoted by the large circle. Those plots can reveal insight into the dynamics of the chemical reaction. In the case of the CO_2-H_2O- plane the first phase of the reaction corresponds to an increase of H_2 whereas the amount of CO_2 remains almost constant. This, e.g., means that the hydrogen is consumed prior to the carbon monoxide. Now, in the simplest models for diffusion flames, the assumption "mixed equals burnt" is used. This means that, instead of taking into account the detailed kinetics, the dynamics of the reaction system is completely neglected and the system is approximated by its equilibrium value. This is a valid simplification, provided that the chemistry (i.e. the

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time needed to approach the equilibrium value) is fast compared to the time scales of mixing, flow, etc.

However, in the example described above (Fig. 1) the equilibration time is about 10 ms and, thus, the simple "mixed equals burnt" assumption does not hold if, e.g., the time scales of molecular mixing or turbulence are of the order of 1 ms. In this case the dynamics of the reaction system has to be taken into account, but (in this specific case) fortunately not all the dynamics but only the processes occurring with time scales longer than, say, 0.1 ms.

Figure 1 furthermore shows a plot of the trajectories where the first $100\,\mu$s have been omitted. It can be seen that the dynamics is simplified considerably. Within $100\,\mu$s all the trajectories have almost merged to a single line (one-dimensional manifold) in the state space. Thus, the state of the whole system can be described by one variable only. The reason for this behavior is that fast relaxation processes (reactions in partial equilibrium, species in steady state) govern the chemical reaction and provide equations which relate the different species concentrations. Summarizing it can be seen that after 10 ms the system can be approximated by its equilibrium value (depending on h, p, and χ_j), and after $100\,\mu$s it can be approximated using one additional reaction progress variable which determines the dynamics of the system, namely the movement along the one-dimensional manifold in state space. If even smaller time scales have to be considered, the chemistry has to be described by additional reaction progress variables.

The idea of the method presented here is now: 1. To identify the low-dimensional manifolds describing the slow processes. 2. To extract the dynamics within those manifolds. 3. To couple this simplified chemical model with other processes like flow or molecular transport.

2.3. Mathematical simplification of chemical kinetics.
The mathematical model is described in detail elsewhere [9, 10]. Here only the basic ideas shall be outlined. For a reaction system governed by the n-dimensional equation system (13) local eigenvector analyses of the Jacobians $F_\psi(\underline{\psi})$ ($J_{ij} = \partial F_i/\partial \psi_j$) reveal that there are n eigenvalues (i.e. time scales) associated with n eigenvectors (characteristic directions). Typically there are $n_e + 2$ zero eigenvalues which correspond to conserved quantities (h, p, χ_j). Furthermore, there are some positive or moderately negative eigenvalues and (at least in many reacting flow systems) many negative eigenvalues large in magnitude. Those large negative eigenvalues correspond to fast relaxation processes, namely reactions in partial equilibrium or species in steady state. Of course these eigenvalues (i.e. fast relaxation processes) depend on the regime, i.e. they are defined locally in the state space. If we want to identify the slow manifolds, we simply have to determine the points in state space, where the fast processes are in
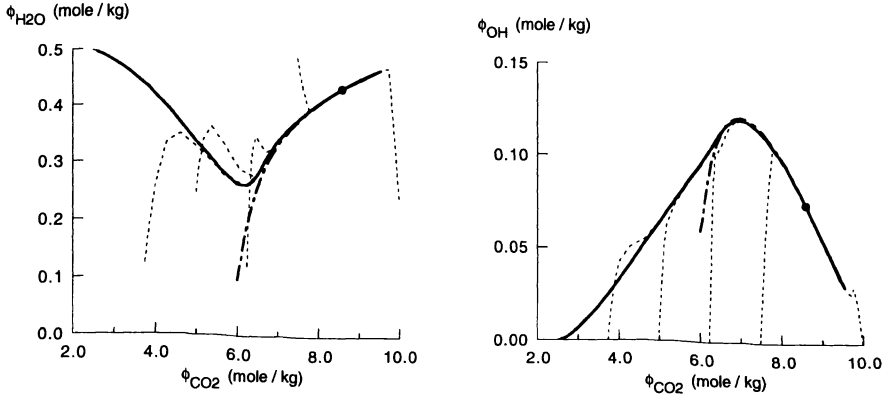
Fig. 2. Low-dimensional manifolds and trajectories of the chemical reaction for a $CO - H_2$-air system [20]; projection into the CO_2-H_2O- and the CO_2-OH- planes. Thin lines: trajectories, ———: intrinsic one-dimensional manifold, — - —: one-dimensional manifold obtained from steady state and partial equilibrium assumptions, • equilibrium value (0-dimensional manifold)

local equilibrium. This means that the low-dimensional manifolds are composed of those points where the rate in direction of the n_f eigenvectors which correspond to large negative eigenvalues, vanish. In this case these n_f conditions define an $m = (n_r - n_f)$-dimensional manifold in reaction space according to:

$$(14) \qquad \tilde{V}_f \left(F_\psi(\underline{\psi}) \right)' F(\underline{\psi}) = 0,$$

where $\tilde{V}_f$ denotes the $n_f \times n$ matrix of left eigenvectors with corresponding smallest real part of the eigenvalue. (In order to avoid problems stemming from degenerate or complex eigenvalues, this equation system can be re-formulated in terms of Schur vectors [9]). The manifolds, which are defined by (14) can be computed numerically [9, 10]. Here only results for the CO-H_2-air system shall be shown.

Figure 2 shows plots of trajectories together with computed one-dimensional manifolds. The intrinsic low-dimensional manifold (ILDM) is obtained using the analysis outlined above. The other low-dimensional manifold has been obtained by explicitly specifying partial equilibrium or steady state conditions. Whereas the ILDM describes the system well in large parts of the domain, the other manifold fails if the system is far from equilibrium. The reason for this behavior is that the specified assumptions are only valid near equilibrium. At lower temperatures (smaller amount of CO_2) the reaction mechanism changes and the partial equilibrium and steady state assumptions valid near equilibrium can no longer be used in this part of the state space.
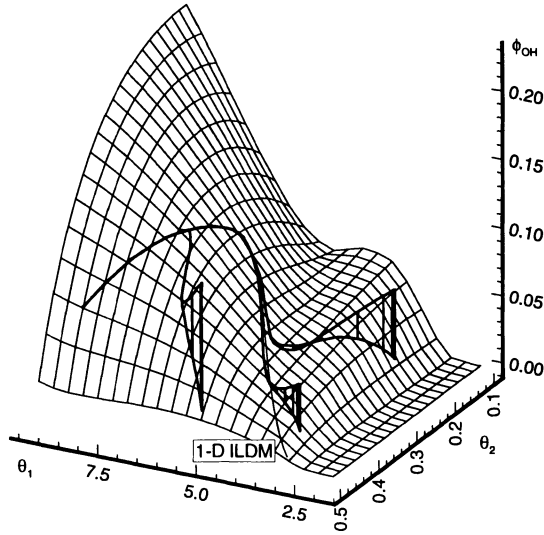
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Fig. 3. Trajectories and one- and two-dimensional manifolds of the CO-H_2-air system, specific mole numbers of OH, units of mole/kg [20]

Figure 3 shows a two-dimensional manifold for OH-radicals together with trajectories with different initial conditions, which have been calculated using detailed chemistry. Plotted are the specific mole numbers of OH versus the reaction progress variables, which are $\theta_1 = \varphi_{CO_2}$ and $\theta_2 = \varphi_{H_2O}$ in this example. Additionally the vertical projections onto the manifold and vertical bars, which denote equidistant time steps of $10\,\mu s$, are plotted. If, e.g. 10 vertical bars lie between the initial value and the point, where the trajectory and its projection merge, it means that the trajectory has relaxed to the manifold within $100\,\mu s$. Furthermore, the improvement with respect to the one-dimensional manifold can be seen. First the trajectories approach the two-dimensional manifold. Then they bundle around the one-dimensional manifold (line). A three-dimensional manifold would improve the results further.

After the ILDM has been identified, the chemical reaction system governed by the n-dimensional system of conservation equations (13) can be described by a lower (N) dimensional equation system describing the dynamics within the N-dimensional manifold.

$$(15) \qquad \frac{\partial}{\partial t}\underline{\theta} = \underline{S}(\underline{\theta}),$$

where $\underline{\theta}$ is the vector of reaction progress variables and $\underline{S}(\underline{\theta})$ is the rate of change of the reaction progress variables. The reaction progress variables can be chosen quite arbitrarily [9, 10] and the rate of change can be computed explicitly from the chemical reaction rates $\underline{F}(\underline{\psi})$.

2.4. Coupling of the simplified chemical kinetics with physical processes.

Above it has been shown that the method of constructing intrinsic low-dimensional manifolds in composition space can be used to simplify chemical kinetics and thus, the solution of the chemical rate equations. However, most interesting reacting flow problems involve the coupling of chemical kinetics with other processes like flow and molecular transport. These physical processes can be viewed as disturbances of the chemical reaction system (which indeed may be very large).

The basic assumption of manifold methods for the reduction of chemical kinetics is that the state ψ is (at any time and at any point in the flow) close to an attracting low-dimensional manifold (of dimension N). Then the dynamics of the reactive system can be approximated by assuming that the state is confined to these N-dimensional manifolds and is thus a function of N variables only, which describe the dynamics within the manifold.
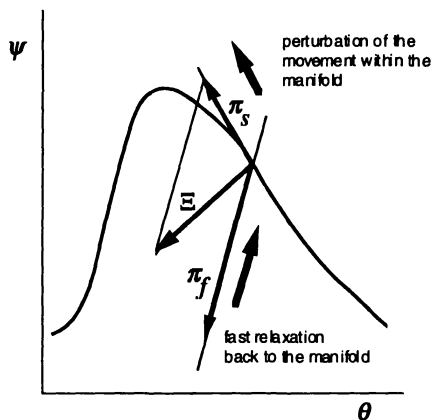

Fig. 4. Schematical illustration of a perturbation of the chemistry by some physical process.

In terms of the ILDM-approach all physical processes do the same: they move the state either within the low-dimensional manifolds or off the manifold. The consequences for the chemical reaction system can be explained by means of a simple diagram (Fig. 4). Let us assume that we are at a point ψ_0 on the manifold and that there is some perturbation Ξ. The perturbation can be decomposed into its components in the local eigenvector basis, i.e. into two parts—one part, describing the rate of change in the slow subspace and one describing the rate of change in the fast subspace. Now let us assume that the time-scale of the perturbation is of the order of the time scales of the slow movement within the manifold, i.e. much smaller than those of the fast relaxing time scales. The components of the perturbation in the

direction of the fast subspace will have a minor effect on the chemical reaction system, because chemistry (fast equilibration processes) relaxes the perturbation back to the manifold. The components of the perturbation in the slow subspace instead, will directly couple with the time scales of the chemical reaction and thus move the state within the manifold. That means if we project the perturbation locally onto the slow subspace, we can account for the interaction of the physical processes with the slow time scales, whereas we neglect all processes which perturb the chemistry, but are "equilibrated" by the chemistry within a very short time (of the order of the fast time scales). Using these ideas, we can formulate a projection operator P, which depends on the local characteristics of the manifold and which projects a physical perturbation $\underline{\Xi}(\underline{\psi})$ onto a perturbation $\underline{\Gamma}(\underline{\theta})$ within the manifold (see [10]). This means that all we have to know in order to solve the coupled problem are the rates of change of the parameters $\underline{S}(\underline{\theta})$, the state space $\underline{\psi}(\underline{\theta})$ and the local projection matrices $P(\underline{\theta})$ as functions of the parameters $\underline{\theta}$.

In this way, the $(2 + n_s)$-dimensional equation system (11) is transformed into an equation system of much lower dimension (N) for the variables $\underline{\theta} = (\theta_1, \theta_2, \ldots, \theta_N)^T$. The simplification of the detailed reaction mechanism yields $\underline{\psi}(\underline{\theta})$, which is the equation of the low-dimensional manifold, $\underline{S}$, and, in addition, provides information, how to project the physical processes $\underline{\Xi}$ onto the manifold.

The method described above will work and yield good approximations as long as the time scales of the perturbations are slow compared with the fast relaxing time scales which had been decoupled by the construction of the intrinsic low-dimensional manifold.

2.5. Reduced equations for reacting flow calculations. The dynamic behavior of a chemically reacting flow is governed by the system of conservation equations, which, above, had been rewritten to yield equations for the scalar field of a reacting flow (11), which is described by the state vector $\underline{\psi} = (h, p, \varphi_1, \varphi_2, \ldots, \varphi_{n_s})^T$.

(16)
$$\frac{\partial \underline{\psi}}{\partial t} = \underline{F} + \underline{\Xi}$$

It can be shown that convection always leads to movements within the manifold [20]. Thus, the only physical perturbation, which tends to move the system off the manifold in the equations above, is molecular transport.

Let the reacting system be described by the $(2 + n_e + n_c)$ parameters h, p, $\chi_1, \ldots, \chi_{n_e}$, and $\underline{\tau}_c = (\tau_{c,1}, \ldots, \tau_{c,n_c})^T$ of the reduced scheme, where χ_j denote the n_e specific element mole numbers ($\chi_j = w_j/M_j$), w_j the mass fraction of element j, M_j the molar mass of element j, n_e the number of elements in the reaction system,

and $\tau_{c,i}$ the reaction progress variables. Then the state $\underline{\psi}$ is a known function of these parameters $\underline{\tau} = (h, p, \chi_1, \ldots, \chi_{n_e}, \tau_{c,1}, \ldots, \tau_{c,n_c})^T$.

Using the results of [10] it can be shown [11] that the governing equations (10) can be rewritten as

(17)
$$\frac{\partial h}{\partial t} = \Xi_h$$
$$\frac{\partial p}{\partial t} = \Xi_p$$
$$\frac{\partial \chi_i}{\partial t} = \mu_i^T \underline{\Xi}_\varphi \qquad i = 1, 2, \ldots, n_e$$
$$\frac{\partial \underline{\tau}_c}{\partial t} = \underline{S} + Z\Xi,$$

where $\underline{\Xi}_\varphi = (\Xi_{\varphi_1}, \Xi_{\varphi_2}, \ldots, \Xi_{\varphi_{n_s}})^T$, $\mu_i^T = (\mu_{i,1}, \mu_{i,2}, \ldots, \mu_{i,n_s})^T$ are the element vectors with $\mu_{i,j}$ denoting the number of elements i in species j, $\underline{S}$ are rates of production of the reaction progress variables and Z is an $n_c \times (n_s + 2)$ projection matrix. $\underline{S}$ and Z are functions of the parameters $\underline{\tau}$, which are calculated in the mechanism reduction and tabulated.

Thus, we have equations for $2 + n_e + n_c$ dependent variables $\underline{\tau}$, namely for the enthalpy, for the pressure, for each of the specific element mole numbers, and for each of the reaction progress variables. The implementation of the reduced mechanism is now very simple: At each point in the flow, the initial values of the dependent variables are known. Then we know the rates $\underline{S}$ of the reaction progress variables and the thermochemical state $\underline{\psi}$ of the system, which are stored during the tabulation of the manifold. From this we can compute the physical processes $\underline{\Xi}$, and, using tabulated values for the projection matrix Z, calculate the total rates of change of the reduced variables. It shall be noted that the calculation can be further simplified by rewriting the molecular transport terms in terms of gradients of the variables of the reduced scheme (this can be done very easily, because the the state $\underline{\psi}$ of the system is a known function of the variables of the reduced scheme). In this case the molecular transport coefficients can be calculated during the mechanism reduction and do not need to be evaluated during the reacting flow calculation.

Some complications can arise in the computations due to the fact that initial or boundary values might not correspond to states on the manifolds. A detailed discussion of this problem cannot be given here, however, there are methods to solve it [21].

3. RESULTS

3.1. Simulation of one-dimensional laminar premixed flames. Above it was shown that the reduced kinetics based on intrinsic low-dimensional manifolds can be used to simulate laminar reacting flows. Although reduced mechanisms are of special interest in multi-dimensional problems, simple laminar flat premixed flames shall be considered here. They provide a nice, simple test case for the verification of the model and are usually more sensitive with respect to the reaction mechanism than diffusion flames. The specific example considered here is a syngas (40 Vol. % CO, 30 Vol. % H_2, 30 Vol. % N_2)-air system at $p = 1$ bar, and with a temperature of 290 K in the unburnt gas. The fuel/air ratio is 6/10. The low-dimensional manifold used for this calculation corresponds to the one used in [10] for homogeneous systems. The fact that the same manifold is used, reflects that the method of intrinsic low-dimensional manifolds yields general reduced mechanisms. An adaptation to the specific problem is not necessary. (Furthermore, this reduced mechanism has been used for the simulation of turbulent jet diffusion flames [14, 13], where the mixture fraction was used as an additional tabulation coordinate for the manifold.)
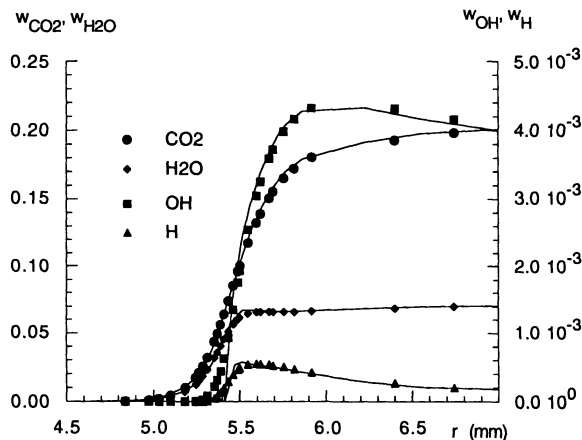

Fig. 5. Calculated structure of a syngas-air flame; points: reduced mechanism, line: detailed mechanism.

The influence of simplified transport models is described elsewhere [11]. Here, for the sake of simplicity, only systems with equal diffusivity shall be considered. In this case a three-dimensional manifold with enthalpy and two reaction progress variables as parameters has been calculated, i.e. the chemistry has been simplified to a two-step reaction scheme. Figure 5 shows profiles of CO_2, H_2O, OH and H in the flame both for reduced and detailed kinetics. Good agreement is obtained in the

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flame front as well as behind the flame front, where the slow equilibration process takes place. Differences are observed at the beginning of the flame front. This is caused by the fact that at the low temperatures ($T < 1000$ K) the decoupled time scales are of the order of the time scales of diffusion and heat conduction. However, if an additional reaction progress variable were used, the results would become much more accurate. The small deviations behind the flame front can be attributed to discretization errors in the numerical simulation (the points reflect directly the mesh used in the computations).

In order to allow a realistic comparison between cpu-times for reduced and detailed chemistry calculations, we performed computations where the initial profiles were assumed as step functions between burnt and unburnt gas composition. Of course, this is an extremely bad initial guess, and it turns out that very small time steps are needed in the detailed chemistry calculations. Surprisingly those problems do not arise, if the reduced mechanism is used. Because 16 partial differential equations have to be solved for detailed chemistry and only 5 if reduced chemistry is used, the reduction of the computational effort can be estimated to be a factor of 6 (due to the small number of equations, there is not yet the quadratic dependence of the cpu-time on the number of equations, which is typical for implicit methods). However, the comparison of the cpu-time shows that the detailed chemistry calculations need 844 cpu-sec on a SiliconGraphics Indigo, and the calculations with the reduced scheme only 86 cpu-sec, which corresponds to a speed-up of a factor of ten. The main reason for this behavior is that much of the stiffness is removed by the mechanism reduction, and large stepsizes are chosen by the integrator. Further research will show, whether explicit methods can lead to a further speed-up of the computation. It is an interesting and promising result that the mechanism generated by the ILDM method does not cause convergence problems in the numerical simulations, which are usually observed, if reduced mechanisms are used [5]. The reason for this behavior is mainly that the fast time scales are really decoupled locally, whereas the global conditions of other reduced mechanisms do not guarantee this.

3.2. Hypersonic flow calculations. The development of new space transportation systems like HERMES has created considerable interest in the simulation of hypersonic flows. The high gas temperatures occurring during re-entry cause the dissociation of oxygen and nitrogen and subsequently the formation of nitric oxide [15]. Besides the information obtainable from windtunnel and free flight measurements numerical methods are gaining more and more importance as an additional tool for the prediction of hypersonic flow fields [22].

If the characteristic chemical time scales are much shorter than the time required for a fluid element to pass the body, the flow can be assumed to be in local chemical
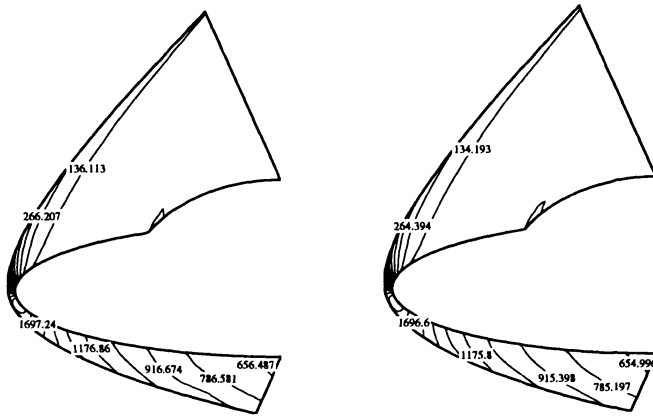
Fig. 6. Contour lines of pressure around a re-entry body (in Pa); left: reduced mechanism, right: detailed chemistry [16].
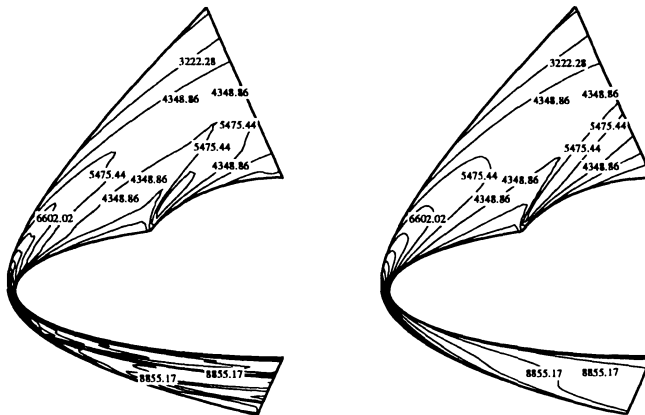

Fig. 7. Contour lines of temperature around the re-entry body (in K); left: reduced mechanism, right: detailed chemistry [16].

equilibrium. But on a typical re-entry trajectory equilibrium gas assumptions do no longer hold for altitudes above 40 km, corresponding to a free stream Mach number of 15. With increasing altitude the decrease of the free stream density and the increase of velocity causes the typical reaction length to be of the same order of magnitude as a typical vehicle length. In this regime non-equilibrium effects have to be taken into account to model the physics and chemistry of the flow correctly [23]. In order to account for finite rate chemistry, for each species in the system (O_2, N_2, O, N and NO) an additional conservation equation has to be introduced to describe the change of concentrations due to chemical reactions, convection and diffusion. A
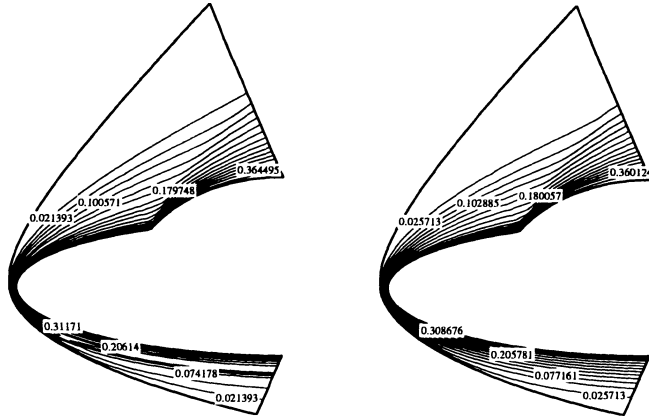
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Fig. 8. Contour lines of nitrogen mass fractions around the re-entry body; left: re-duced mechanism, right: detailed chemistry [16].

detailed reaction scheme consisting of 10 elementary reactions is used to model the non-equilibrium chemistry [23, 24].

We have simulated the re-entry process of a space vehicle both using detailed and reduced chemistry. The used CFD code is a two-dimensional Euler code, developed by Weiland et al. [25, 26]. It is formulated in quasi-conservative Euler equations using a split-matrix method for a proper upwind discretization. The bow shock is fitted using Rankine-Hugeniot relations. A three step Runge-Kutta scheme is applied for the solution of the time dependent Euler equations. Because of the stiffness introduced by the chemistry a point implicit treatment for those terms is used. For more detailed information about the code see [25, 26].

For the reduced equation system a three-dimensional manifold has been calculated with the enthalpy, the density, and one reaction progress variable as parameters. Because the simulation is based on the Euler equations, molecular transport is ne-glected, and the transformation of the equations is simplified considerably. However, the method is not restricted to this choice (as could be seen in the previous sec-tion), and Navier-Stokes simulations are possible, too. The calculated test cases for the simulation of the bow shock of a re-entry vehicle are shown in Figs. 6–8. The freestream conditions are: Mach number 25, angle of attack 30°. The altitude is about 75 km ($T = 205K$, $p = 2.52Pa$) with freestream mole fractions $x_{N_2} = 0.79$ and $x_{O_2} = 0.21$. In the figures the pressure, temperature and the mass fraction of N_2 of the flow field between the shock and the vehicle surface are shown both for detailed and reduced kinetics (see [16] for details). From the figures it can be seen that the agreement between reduced and detailed chemistry is quite good.

4. Conclusions

It has been shown that the method of simplifying chemical kinetics by constructing intrinsic low-dimensional manifolds can be used successfully in the simulation of reacting flows. There is no restriction to simplified transport models, but processes like non-unity Lewis number, differential diffusion or thermal diffusion can be treated by the method very easily. The results are in very good agreement with results from detailed chemistry calculations, which verifies the approach and allows the conclusion that the method can be used in turbulent reacting flow calculations for a reliable description of the chemistry. The computational effort in the reacting flow calculations is reduced considerably. Convergence problems, known from simulations with reduced reaction mechanisms are not observed, but, to the contrary, the method of intrinsic low-dimensional manifolds yields reduced reaction mechanisms, which simplify the numerical integration to a great extent, and might even allow the use of explicit integration methods. It can be estimated that the method can speed up calculations of flows with more complex chemistry (like, e.g. combustion of higher hydrocarbons) by a factor of much more than 1000.

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