ILDM Reduction of Reaction Mechanisms for the Oxidation of Large Hydrocarbons

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Abstract

The assumption of intrinsic low-dimensional manifolds (ILDM) leads to a rigorous simplification of the complexity of chemical reaction systems and is a promising approach to describe reactive flows in a rather easy way. The paper describes a new feature of the implementation of this approach, namely the use of different dimensions of the ILDM in one calculation. Two application examples are shown: Decane oxidation in a spatially homogeneous reactor and in laminar flat flame. Three-dimensional ILDM prove to be sufficient to describe chemical reaction in these systems.

1. Introduction

Detailed reaction mechanism developed to describe the oxidation (flame propagation and NO formation) of hydrocarbon fuels include about 50-100 species and over 1000 reactions. The complexity of chemical processes leads to strong non-linearity and due to different time scales to stiffness of the Navier-Stokes equations describing reacting flows. Therefore, detailed mechanisms cannot be used for the simulation of complex systems like engines or turbines.

Thus, it is necessary to use drastically reduced mechanism to get results in reasonable times. The ILDM (Intrinsic Low-Dimensional Manifold) method is a method to reduce detailed mechanism.

2. Determination of Intrinsic Low-Dimensional Manifolds

A homogenous reacting mixture is described by an ordinary differential equation system

$$\dot{x} = S(x) \text{ with a state vector } x = (T, \rho, w_1, ..., w_n).$$

The time scales of this system are the inverse values of the negative eigenvalues λ_i of the Jacobi matrix of $S(x)$. With block-diagonalization $J(x)$ can be written as

$$J(x) = E(x)\Lambda(x)\tilde{E}(x) = (E_s E_f)\begin{pmatrix} \Lambda_s & \\ & \Lambda_f \end{pmatrix}\begin{pmatrix} \tilde{E}_s \\ \tilde{E}_f \end{pmatrix},$$

where $\tilde{E}(x) = \begin{pmatrix} \tilde{E}_s \\ \tilde{E}_f \end{pmatrix}$ and $E(x) = (E_s E_f)$ are the left and the right eigenspaces.

The ILDM assumption is to assume $\tilde{E}_f(x)S(x) = 0$ [1]. This means that the relaxation of the time scales is very fast and the system is relaxed onto the manifold. Thus, the chemical system can be described by a small number of progress variables. To close the algebraic equation and to specify a single point on the manifold, the parameter equations $P(x,c) = 0$ are specified. The temperature or the enthalpy, the pressure, the mixture fraction and the reaction progress variables (CO_2, H_2O and O_2) are normally used as parameters to specify a single point on the low dimensional manifold.

3. Implementation in a CFD Code

In non-homogenous systems diffusion effects can move a state away from the manifold. However, the fast chemical time scales are by several orders faster than the time scales of the diffusion effects. Thus, the fast chemical time scales drive the system back onto the manifold. Therefore, even in non-homogenous systems the whole chemical system can be described by a few progress variables. The Navier-Stokes equations need to be solved for these variables in a CFD code. The other physical and chemical properties depend on the parameter set of the progress variables and can be read out of the ILDM table. Sometimes the boundary conditions of the system are not on the manifold. In this case, too, the fast chemical time scales will move the system fastly onto the ILDM. Thus, this boundary condition should be projected onto the ILDM in the CFD code.

Here, a simple interface is used to couple the ILDM software with a CFD code [2,]. The ILDM code needs the parameter set (enthalpy, pressure, mixture fraction, and reaction progress variables) as input and delivers as output the corresponding properties (e. g., reaction rate of the progress variables).

4. ILDM Tables Using Different Numbers of Reaction Progress Variables

When using three reaction progress variables (CO_2, H_2O, O_2), ILDM points can often be found only for a few O_2 mass fractions when CO_2 and H_2O mass fractions are both near the equilibrium value. The same behaviour can be found when using two reaction progress variables under high-pressure conditions. Thus, in some cases not all of the ILDM points that are necessary for the interpolation can be found when using a coarse tabulation grid.

A possible solution of this problem is to switch in these cases to a lower-dimensional ILDM. Using different numbers of reaction progress variables in a CFD code would lead to the problem that a different number of conservation equations must be solved in the CFD code. In addition it is difficult to find simple global rules when to use the lower dimensional ILDM and when not.

A method has been developed to overcome this problem. The basic idea is: When using an ILDM with two progress variables instead of an ILDM with three progress variables, an auxiliary additional progress variable is added. Thus, within the CFD code always the same number of reaction progress variables can be used.

For this model, the first and second reaction progress variable should be the same independent of the number of progress variables used (e.g. CO_2, H_2O, (O_2)). If possible, three progress variables should be used. However, it should be tested if the ILDM point generated with three progress variables is near the ILDM with two progress variables. In this case, it is possibile to use ILDM with two progress variables.

In this implementation the species concentrations and other physical properties are determined by an ILDM with two progress variables. The reaction rates of the first and second progress variable are determined by ILDM with two progress variables, as well. However, the reaction rate of the third progress variable must be modelled:

$$\dot{w}_3^{relax} = -k * (w_3 - x_{O_2}^{ILDM})$$

where w_3 is the value of the third progress variable and $x_{O_2}^{ILDM}$ the mass fraction of O_2 on the ILDM with two progress variables. It consists of two terms: The first term describes the reaction parallel to the ILDM. It is given by the detailed mechanism and the species

concentration of the ILDM using two progress variables. The second part is the fast reaction onto the ILDM. This term must be modelled using some chemical considerations. The assumption for this term is: k is a time scale that describes how fast the relaxation onto the ILDM with two progress variables happens. In theory, k is the time scale for the relaxation of O_2. Tests in homogenous systems show that the exact value of k is not important. For practical use, it is only important that k is chosen larger than the time scales of the physical processes to ensure that the systems always relaxes onto the ILDM with two progress variables. If k is chosen too large, additional stiffness is added to the ILDM system. That may cause an increase of time needed for the solution of the conservation equations in the CFD code, but the result is not significantly changed.

5. Simulation of Homogeneous Reaction Systems with ILDM

The model described above was successfully implemented in several homogenous systems and for different fuels. Results for one example (decane oxidation, where decane is used as model fuel for kerosine) are shown in Fig. 1.
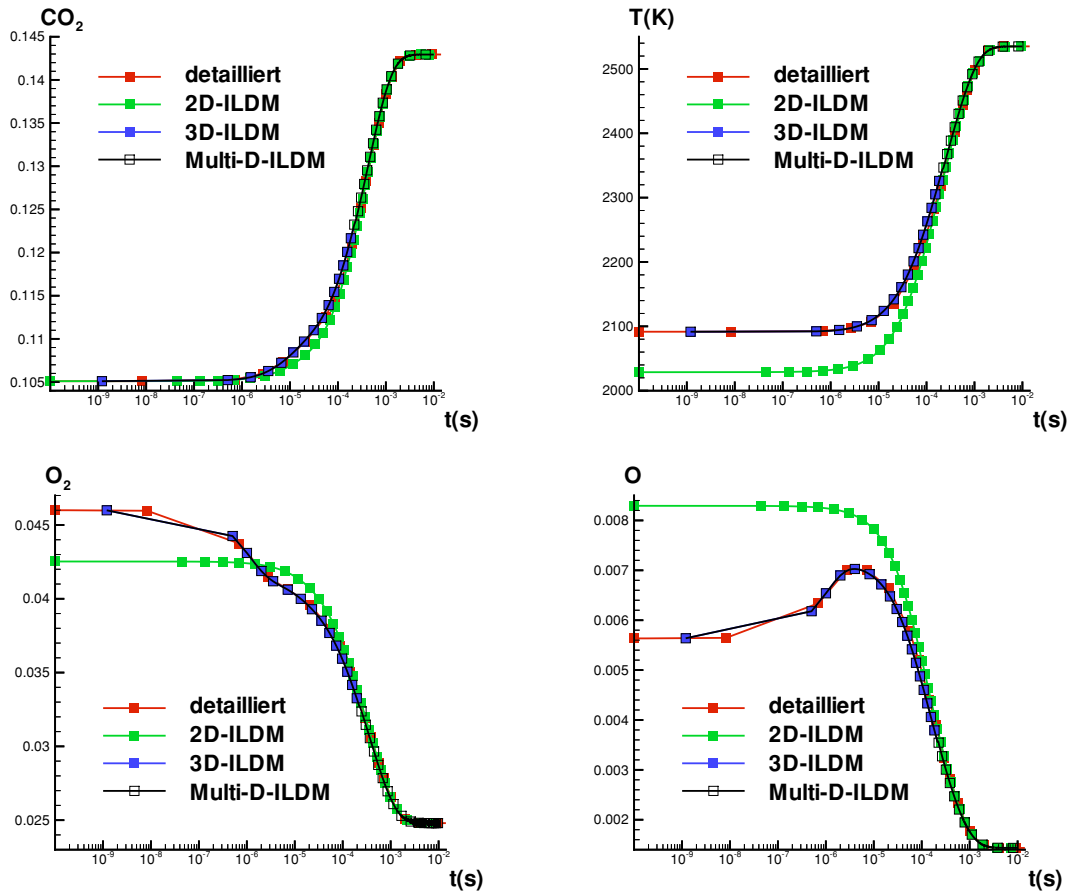

Fig. 1: Homogenous decane system, using a detailed mechanism, ILDM with 2 or 3 progress variables and ILDM with a variable dimension

6. Simulation of Laminar Flames with ILDM

A free premixed laminar flame was simulated with the ILDM method in order to investigate the influence of the number of reaction progress variables used. In addition the the

implementation of the software modul and the developed models like multi-dimensional ILDMs can be testet under more realistic conditions than in homogenous systems.

Again, decane was used as model fuel for kerosine. Free premixed laminar flames are a good test case because they are one-dimensional problems. Therefore, a direct comparison between simulations using detailed and reduced mechanism is possible. Due to large gradients in the flame front physical transport processes are very important. Thus in laminar flames the coupling between reduced mechanism and physical transport processes can be investigated.

However, in most cases no more than two or three progress variables can be used due to increasing computational time. Thus, the agreement between simulations using the detailed mechanism and the ILDM-reduced mechanism is often not as good as in homogenous systems.

The reduced chemistry was implemented in the following way: The CFD code MIXRUN [3] was used to simulate the reative flow. The Navier-Stokes equations are solved for the reaction progress variables (CO_2, H_2O and O_2). The other species concentrations and the temperature are a function of the reaction progress variables and are read out of the ILDM table. Unity Lewis number was assumed. The implementation of an ILDM with varying dimension is used if the ILDm with three progress variables is used.
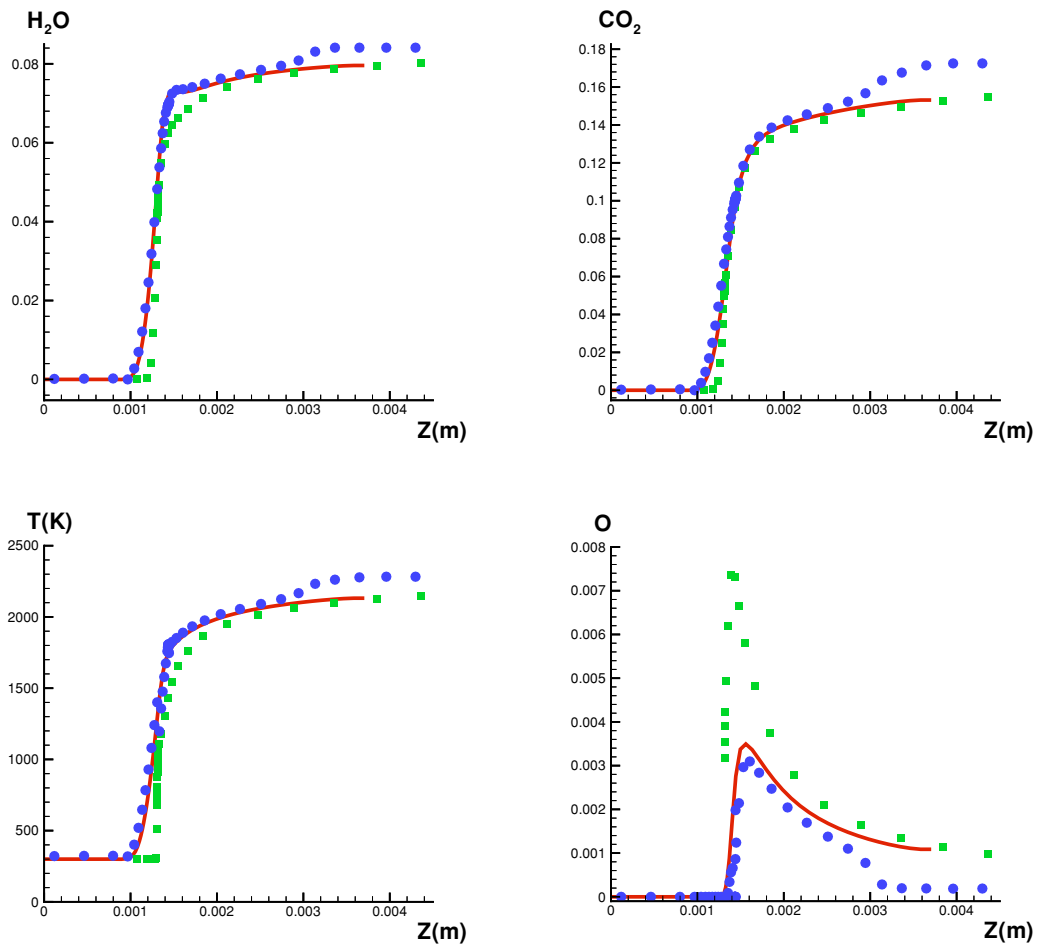

Fig. 2: Free laminar premixed flame, decane/air system with mixture fraction 0.062, 1 bar pressure, simulated with detailed chemistry (lines) and ILDM using 2 (boxes) and 3 (circles) reaction progress variables

The concentration of the progress variables can be predicted well for two or three progress

variables, but the shape of the flame front can be better predicted using three progress variables. The temperature is satisfactorily predicted as well, but the errors for the O atoms are larger using two progress variables. In this case the maximum is overpredicted by a factor of 2-3. Thus at least three reaction progress variables have to been chosen to predict the O atoms correctly in the decane system. Calculations for other stoichiometries have been done with similar results.

7. Literature

[1] U. Maas, S. Pope, Implementation of Simplified Chemical Kinetics Based on Intrinsic Low-Dimensional Manifolds, Proc. Comb. Inst. 24, 108-117 (1993)

[2] C.Correa, H. Niemann, B. Schramm, J. Warnatz: Reaction Mechanism Reduction for Higher Hydrocarbons by the ILDM Method. Proc. Comb. Inst. 28, 1607-1614 (2001)

[3] J. Warnatz: Calculation of the Structure of Laminar Flat Flames I: Flame Velocity of Freely Propagating Ozone Decomposition Flames. Ber. Bunsenges. Phys. Chem. 82, 193-200 (1978)