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The reactions supporting or opposing the development of explosive modes: Auto-ignition of a homogeneous methane/air mixture

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Abstract

The development of time scales that characterize the initiation of an auto-ignition processes is supported by specific reactions and is opposed by some others. An algorithmic tool which identifies these two sets of reactions is validated on the basis of the auto-ignition of a homogeneous stoichiometric methane/air mixture at 50 bar and 1100 K. It is shown that this process is characterized by two time scales, the fastest of which relates to the generation of the required for ignition radical pool and the temperature increase. This time scale associates mainly to carbon chemistry, except the very last period of its presence where it relates to hydrogen/oxygen-chemistry. The analysis allows for the quantitative assessment of several chemical phenomena that have been associated with the abnormal long ignition delay of methane, such as the formation of C_2H_6 and the relative importance of the formation of CH_2O and CH_3O as means of consumption of CH_3 radicals. The identification of the reactions supporting or opposing the initiation of the auto-ignition is most useful when it is desired to control the ignition process.

Keywords: Auto-ignition; Explosive time scales; Computational singular perturbation

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1. Introduction

There is a growing interest recently on the time scales that characterize ignition. These are time scales that relate to physical mechanisms which tend to move the system away from equilibrium and are referred as *explosive time scales*. The time scales that relate to physical mechanisms which tend to move the system in the opposite direction, that is towards equilibrium, are referred as *dissipative time scales*. Explosive time scales are usually encountered in auto-ignition processes and might also be encountered in flames [1–11].

An explosive time scale is associated with a specific component of the source term in the vector field $\mathbf{g}(\mathbf{y})$ of the dynamical system $d\mathbf{y}/\mathbf{dt} = \mathbf{L}(\mathbf{y}) + \mathbf{g}(\mathbf{y})$ that governs the evolution of the reactive system, where $\mathbf{L}(\mathbf{y})$ is the transport

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operator [12]. The magnitude of this explosive component is indicative of its contribution to the rate of change of the variables, while the time frame in which the occurring changes due to this component are taking place is set by the magnitude of the explosive time scale. Therefore, given a detailed chemical kinetics mechanism, the analysis of an explosive component in the governing equations must include the identification of:

(i) the reactions that contribute to the magnitude of the explosive time scale,
(ii) the reactions that contribute to the magnitude of the component of $\mathbf{g}(\mathbf{y})$ that relates to the explosive time scale, and
(iii) the variables that relate to the explosive time scale.

Clearly, such identifications are most important when it is desired to determine the appropriate means in order to control the reactive process.

Usually, the fastest time scales in a reacting system are dissipative ones, so that the system evolves on a low dimensional surface in phase space, which is known as a *slow invariant manifold* (SIM) [13]. On the SIM, the fast reactions participate in the equilibria that are generated under the action of the fast time scales so that the system evolves according to the *reduced system*, which is free of the fast time scales. When sufficiently far from the boundaries of the SIM, the characteristic time scales of the reduced system are the slow ones of the original system [14]; among them the explosive ones. Therefore, the investigation for the origin of the explosive time scales must follow a multi-scale analysis. For that purpose, the classical asymptotic methods can be employed in order first to construct the SIM and the reduced system and then to analyze the slow dynamics. This approach has been widely employed and lead to the acquisition of significant physical understandings, e.g. [15,16]. However, the difficulties in constructing reliable reduced chemical kinetics mechanisms and the strong dependence of these mechanisms on the operating conditions of interest (e.g., range of pressure, temperature and stoichiometry), limit severely this approach for the investigation of the explosive components.

The development of algorithmic methodologies for the multi-scale analysis of dynamical systems, such as CSP or ILDM [13], facilitated considerably the investigation of the explosive components. However, up until now only items (ii) and (iii) listed previously were addressed [1–11]. Here an algorithmic tool for the identifications listed in item (i) will be employed in the case of auto-ignition of a methane/air mixture. This tool is a by-product of the CSP algorithm [12,17] and will be employed here for the first time in the analysis of explosive time scales.

Naturally, a full-scale analysis of an explosive component of a reacting system requires the availability of all information listed in items (i)–(iii). However, since this is the first time item (i) is addressed, the emphasis will be placed on this item. In the following, the CSP methodology will be briefly stated and the tool for the identification of the reactions that are responsible for the generation of the explosive time scales will be presented. This tool will be validated next in the case of a methane/air mixture auto-ignition.

2. The algorithmic tools

Consider the auto-ignition at constant volume of a homogeneous mixture that is modeled by a chemical kinetics mechanism involving K elementary reactions, N species and E elements. The governing equations are:

$$\frac{d\mathbf{y}}{dt} = \frac{1}{\rho}\mathbf{W}\cdot\dot{\boldsymbol{\omega}} \tag{1}$$

$$\frac{dT}{dt} = \frac{1}{\rho c_v}\left(-\mathbf{h}_c\cdot\mathbf{W}\cdot\dot{\boldsymbol{\omega}} + RT\sum_{i=0}^{N}\dot{\omega}_i\right) \tag{2}$$

where $\mathbf{y}$ is the N-dim. state vector of the species mass fraction, ρ is the mixture density, $\mathbf{W}$ is a $N\times N$ diagonal matrix with the species molecular weights, T is the temperature, $\mathbf{h}_c$ is the N-dim. row vector of the species' absolute enthalpies, c_v is the heat capacity and R is the universal gas constant. Accounting for the forward and backward directions of the elementary reactions separately, the N-dim. vector of molar production rate of all species $\dot{\boldsymbol{\omega}}$ is defined as:

$$\dot{\boldsymbol{\omega}} = [\dot{\omega}_1,\ \ldots,\ \dot{\omega}_N]^T = \sum_{k=1}^{2K}\mathbf{S}_k R^k \tag{3}$$

where $\dot{\omega}_n$ is the molar production rate of the n-th species, and $\mathbf{S}_k$ and R^k are the N-dim. stoichiometric column vector and the rate of the k-th reaction. Here the GRI-3.0 methane/air mechanism will be employed, which involves $K = 325$ reactions, $N = 53$ species and $E = 5$ elements [18].

The two evolution equations in Eqs. (1) and (2) can be cast in a vector form and then in the CSP form [12,17]:

$$\frac{d\mathbf{z}}{dt} = \mathbf{g}(\mathbf{z}) = \sum_{k=1}^{2K}\hat{\mathbf{S}}_k R^k = \sum_{n=1}^{N-E+1}\mathbf{a}_n f^n \tag{4}$$

where $\mathbf{z}$ is the $(N+1)$-dim. state column vector $\mathbf{z} = [\mathbf{y}, T]^T$, $\mathbf{a}_i$ is the $(N+1)$-dim. CSP column basis vector of the i-th mode, $f^i = \mathbf{b}^i\cdot\mathbf{g}(\mathbf{z})$ is the related CSP amplitude:

$$f^i = \sum_{k=1}^{2K}\left(\mathbf{b}^i\cdot\hat{\mathbf{S}}_k\right)R^k \tag{5}$$