

On chain branching and its role in homogeneous ignition and premixed flame propagation

J.C. Lee^{a,*}, H.N. Najm^a, S. Lefantzi^a, J. Ray^a, M. Frenklach^b, M. Valorani^c,
D.A. Goussis^d

^a Sandia National Laboratories, Livermore, CA 94550, USA

^b Department of Mechanical Engineering, University of California at Berkeley, and Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^c University of Rome 'La Sapienza', 00184 Roma, Italy

^d Agiou Georgiou 49, 26500 Rio, Greece

Abstract

The role of chain branching in a chemical kinetic system was investigated by analyzing the eigenvalues of the system. We found that in the homogeneous ignition of the hydrogen/air and methane/air mixtures, the branching mechanism gives rise to explosive modes (eigenvalues with positive real parts) in the induction period as expected; however, in their respective premixed flames, we found none. Thus, their existence is not a necessary condition for the propagation of a premixed flame.

Keywords: Chemical kinetic system; Homogeneous ignition; Premixed flame

1. Introduction

Gas phase combustion kinetic systems are driven by chain reactions and the existence of reactive intermediate species called radicals. A system consists of a number of thermodynamic variables and a set of chain reactions that are generally categorized into four groups: initiation, propagation, branching, and termination (see, e.g. [1,2]). In the hydrogen system, for instance, the radicals are H, O, OH, and to a lesser degree HO₂; the reaction steps $O + H_2 \rightarrow H + OH$ and $H + O_2 \rightarrow O + OH$ are two well-known chain branching mechanisms. The number of molecules of the radical species generated (as a product) for each consumed (as a reactant) by the kinetic system is defined as the branching ratio or branching factor. The condition to have a fast rate of reaction relies on the overall branching ratio [1] of the system being > 1 . When this is so, there is a geometric growth in the number of molecules of the radical species, thus at least one component of the dynamical system would exhibit an exponential growth in time or an explosive regime. Another physical phenomenon often

quoted to explain the fast reaction rate found in combustion systems is the 'thermal-run-away' mechanism – exothermic reactions increase the temperature of the system which in turn increases the reaction rates. In both cases – branching ratio > 1 or thermal-run-away – we expect some components of the dynamic system to exhibit exponential growth in time i.e. the existence of eigenvalues with positive real parts. A phenomenological explanation for the propagation of a premixed flame is that the heat or radical species generated in the reaction zone diffuse into the unburnt mixture and bring the system into an explosive regime. This 'exponential' growth phenomenon in the homogeneous ignition of the two fuel/air mixtures and in the propagation of their respective premixed flames will be examined in this work.

A chemical kinetic system can be represented in the following general form:

$$\frac{d\vec{Y}}{dt} = \vec{g}(\vec{Y}), \quad \vec{Y} \in \mathfrak{R}^N, \quad \vec{g}: \mathfrak{R}^N \rightarrow \mathfrak{R}^N \quad (1)$$

An *explosive mode* exists when there is an eigenvalue of $J \equiv \frac{\partial(\vec{g}(\vec{Y}))}{\partial \vec{Y}}$ with a non-trivial positive real part i.e. a mode that increases exponentially with time. Whereas, when

* Corresponding author. Tel.: +1 (860) 610 7553; Fax: +1 (925) 294 2595; E-mail: leejc@utrc.utrc.com

the real part of an eigenvalue is negative, the corresponding mode decays exponentially in time. The determination of whether an explosive mode is affecting the evolution of the system, and the identification of its associated time scale, can be achieved as follows.

We consider an ordered set of time scales $|\tau_1| \leq |\tau_2| \leq \dots \leq |\tau_N|$ associated with Eq. (1) defined as $\tau_i \equiv -\frac{1}{\mathbf{R}(\lambda_i)}$ where the $\lambda_i, i = 1, \dots, N$, are eigenvalues of J , and $\mathbf{R}(\lambda_i)$ denotes its real part. Thus, the i^{th} mode is an *explosive mode* if $\tau_i < 0$ and a *decaying mode* if $\tau_i > 0$. The next step is to decide if a mode, explosive or not, is of relevance.

Let $\{ \langle \vec{\mathbf{a}}_i, \vec{\mathbf{b}}_i^* \rangle \mid i = 1, \dots, N \}$ be the set of vectors and convectors or the dual of $\vec{\mathbf{a}}_i$ that corresponds to $\{ \tau_i \mid i = 1, \dots, N \}$ such that $\vec{\mathbf{b}}_i^* (\vec{\mathbf{a}}_j) = \delta_{ij}$. This construction is part of a general theory called Computational Singular Perturbation (CSP), details on this topic can be found elsewhere [3,4,5] and we include here only a small part that is needed. The source term $\vec{g}(\vec{Y})$ can be decomposed using

$$\frac{d\vec{Y}}{dt} = \sum_{i=1,N} f^i \vec{\mathbf{a}}_i, \quad f^i = \vec{\mathbf{b}}_i^* \vec{g}, \quad i = 1, N. \quad (2)$$

Modes are separated into different categories. First, the fast and exhausted modes are identified. They correspond to the ones in the quasi-equilibrium state and restrict the dynamical system to evolve in a slow-manifold (an attractor); in this sense, they play no active role in the dynamics of the system. For the identification of these exhausted modes, we search for the maximum value of M ($N - M$ is the dimension of the slow-manifold) such that

$$\vec{g} = \overbrace{\sum_{k=1,2,\dots,M} f^k \vec{\mathbf{a}}_k}^{\text{'small'}} + \sum_{k=M+1,M+2,\dots,N} f^k \vec{\mathbf{a}}_k \quad (3)$$

where being 'small' in Eq. (3) is determined by

$$\left\| \tau_{M+1} \left[\sum_{k=1,2,\dots,M} a_k^i f^k \right] \right\| < \epsilon^i \equiv \epsilon_r \|y^i\| + \epsilon_a, \quad (\forall i = 1, 2, \dots, N) \quad (4)$$

where ϵ_a and ϵ_r are tolerance parameters. The $M+1^{\text{th}}$ mode, the fastest of the non-exhausted modes, is the 'driving' mode, and the time scale τ_{M+1} controls the time evolution of the system at that instant. Whether or not the i^{th} non-exhausted mode ($M < i < N$) is active depends on the value of f^i . If it is not a small value, this mode is active; otherwise, it is dormant and irrelevant. Furthermore, in the extreme case when $f^i \rightarrow 0$ and $|\tau_i| > \tau_{M+1} \rightarrow \infty$, the i^{th} mode corresponds to a conservation law. With these mathematical devices, the role of explosive modes in the hydrogen [6] and methane (GRI-Mech 3.0) [7] oxidation mechanisms, in the context of homogeneous ignition and premixed flames will be examined.

2. Results: homogeneous ignition of the hydrogen and methane systems

Both the hydrogen and methane mixtures are ignited by setting the system to a sufficiently high initial temperature. For the hydrogen case, the mixture was composed, by mass, of 2.85% H_2 and 22.6% O_2 (N_2 balance) and the initial temperature was set at 1000 K. For the methane case, the mixture was composed of 5.48% CH_4 , and 21.9% O_2 (N_2 balance) with an initial

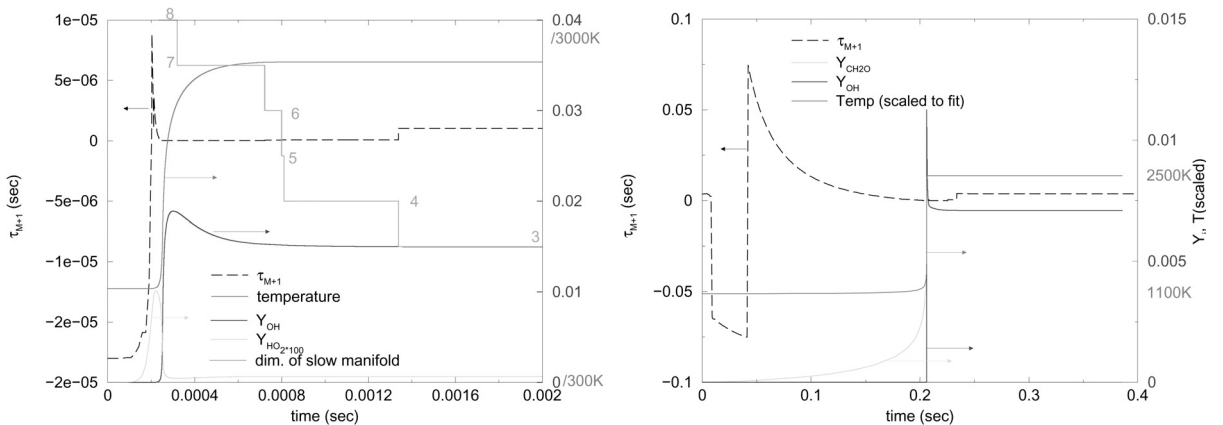


Fig. 1. (a) Homogeneous ignition of a hydrogen-air mixture: plots of τ_{M+1} , T , Y_{OH} , Y_{HO_2} versus time. (b) Homogeneous ignition of a methane-air mixture: plots of τ_{M+1} , T , Y_{OH} , and $Y_{\text{CH}_2\text{O}}$ versus time.

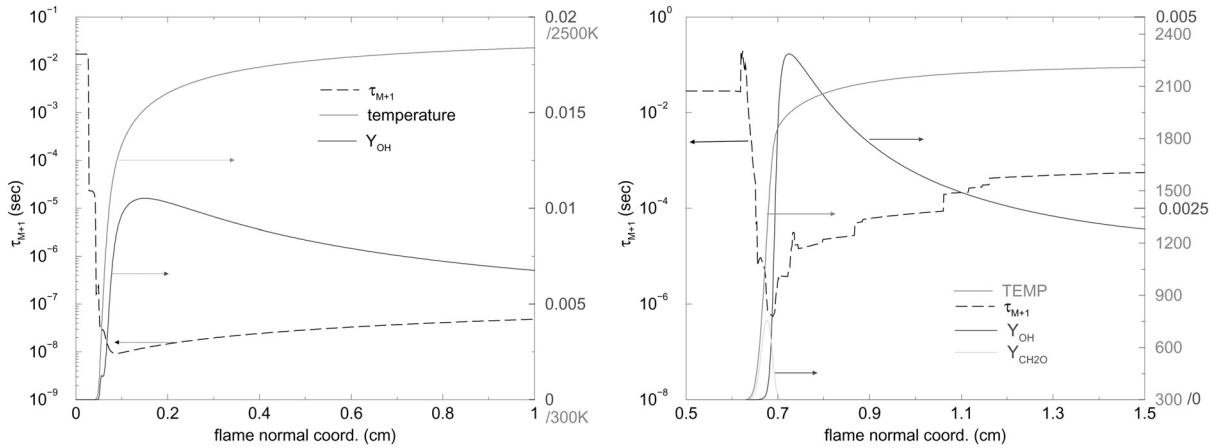


Fig. 2. (a) Hydrogen-air premixed flame: plots of τ_{M+1} , T , and Y_{OH} versus the flame normal coordinate (cm). (b) Methane-air premixed flame: plots of τ_{M+1} , T , Y_{OH} , and Y_{CH_2O} versus the flame normal coordinate (cm).

temperature set at 1100 K. In both cases, pressure was kept at a constant value of 1 atmosphere.

The graphs shown in Fig. 1(a) and (b) depict plots of τ_{M+1} , temperature and the mass fractions of a few radical and intermediate species versus time for the two ignition studies. Unsurprisingly, the homogeneous ignition of both mixtures exhibits explosive modes in the initial stage. By initial or *induction* stage, we refer to the duration in time *before* any significant rise in temperature occurs. Since these explosive modes occur when temperature remains constant, their occurrence must correspond to some active branching processes in the kinetic system (overall branching ratio > 1) building up a pool of radicals or important intermediate species. By considering the time plots of different species in this period, one can easily discern the ones being produced by the branching processes. We show, for example, the time variation of Y_{HO_2} in the hydrogen case and Y_{CH_2O} in the methane case, respectively, in Fig. 1. We also observe that the real parts of all the eigenvalues become negative before the temperature starts to rise, and after this point the system relaxes with successive exponentially decaying modes which ‘attracts’ the trajectory in the phase space toward the equilibrium point via several intermediate slow-manifolds. We illustrate this by plotting the dimension $(N - M)$ of these slow-manifolds as a function of time for the hydrogen mixture ignition case in the left side graph in Fig. 1. The phenomenon of thermal-run-away is not seen in direct association with the explosive modes in these homogeneous ignition studies, as all explosive modes cease to exist before the temperature begins to rise.

3. Results: premixed flames

The code PREMIX [8] was used to calculate the freely propagating one-dimensional premixed flame whereas for the case involving a strained flame, the code described in [9] was utilized. Shown in Fig. 2(a) are plots of temperature, Y_{OH} , Y_{HO_2} , and τ_{M+1} versus the flame normal coordinate of the hydrogen flame. Notice that τ_{M+1} is always positive, i.e. the first active mode is always a decaying mode in the entire spatial domain. In fact, there is no explosive mode at any spatial grid point. The results for the methane flame shown in Fig. 2(b) tell the same story – no explosive modes. The same premixed flame when subjected to a large strain rate also exhibits no explosive modes. Thus, the existence of an explosive mode is *not* a necessary condition for the existence of a premixed flame. One cannot however rule out the possibility of having explosive modes in the kinetic system since the diffusion process has a stabilizing effect. We observed that for a leaner premixed flame ($Y_{H_2} = 1.8\%$), in the low temperature region (below 460 K), explosive modes are present although their associated time scales are much longer than those of the active modes and their associated modal amplitude f^i in Eq. (3) are small.

In the two flame solutions shown, the heat and reactive species transported from the reaction zone toward the unburnt gas ‘push’ the system into a regime in which all modes are decaying exponentially in time at very fast rates. These decaying modes bring the system toward the equilibrium point through successive slow-manifolds (all being attractors) of decreasing dimension. We performed another hydrogen-mixture homogeneous ignition calculation by adding a sufficient concentration of radical species to the initial mixture while setting the

initial temperature to 298 K. We found that the ensuing homogeneous ignition process does not exhibit any explosive modes, in contrast with the high-temperature homogeneous ignition discussed before. We also repeated, for the hydrogen mixture, the high-temperature homogeneous ignition calculation but with some HO₂ added to the initial composition. In this case also, all the explosive modes disappeared. These two numerical experiments suggest an explanation for why explosive modes are not always observed in a premixed flame. The transport of radical species put the chemical system in a region where all the modes decay toward the equilibrium point at a very fast rate without having to go through a regime with explosive modes. The high mass diffusivity of some radical species in the hydrogen system would favor this mechanism and the trend of having no explosive mode in the premixed flame of a richer hydrogen mixture and some explosive modes in a leaner mixture support this conjecture.

4. Conclusions

We performed calculations to investigate the classical theories of chain branching and thermal-run-away that lead to the rapid oxidation of fuels. Mathematically, both theories infer the existence of eigenvalues with positive real parts, i.e. explosive modes. We found in studies of homogeneous hydrogen-air and the methane-air mixtures that when ignition is initiated by a sufficiently high initial temperature, the transient response of the system exhibits two stages. The first stage is characterized by the existence of explosive modes. The ensuing second stage consists of fast exponential decay modes that bring the system to its equilibrium point. We demonstrated with two examples that the existence of explosive modes is not a necessary condition for the existence of a premixed flame. Homogeneous ignition calculations for mixtures with an initial concentration of radical species indicate that the diffusive transport of radical species is probably responsible for the lack of explosive modes in premixed flames.

Acknowledgments

This work was supported by the US Department of Energy (DOE), Office of Basic Energy Sciences (BES),

SCIDAC Computational Chemistry Program. Support was also provided by the DOE BES Division of Chemical Sciences, Geosciences, and Biosciences. Further support was provided by the DOE Office of Advanced Scientific Computing Research, Division of Mathematical, Information and Computational Sciences. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94-AL85000. M. Valorani acknowledges the support of the Italian Space Agency (ASI) and the Italian Ministry of Education, University and Research (MIUR). M. Franklach acknowledges the financial support of DOE, BES under contract no. DE-AC03-76SF00098 and DE-AC03-76SF00098.

References

- [1] Glassman I. Combustion. New York: Academic Press, 1987.
- [2] Williams FA. Combustion Theory, 2nd edn. New York: Addison-Wesley, 1985.
- [3] Lam SH. Singular perturbation for stiff equations using numerical methods. In: C Casci, editor, Recent Advances in the Aerospace Sciences. New York: Plenum Press, 1985, p. 3.
- [4] Lam SH, Goussis DA. Understanding complex chemical kinetics with computational singular perturbation. In: Proc of 22nd International Symposium on Combustion, 1988, p. 931.
- [5] Goussis DA, Lam SH. On the homogeneous methane-air reaction system. Report 1892-MAE, Princeton University, 1990.
- [6] Yetter RA, Dryer FL, Rabitz H. A comprehensive reaction mechanism for carbon monoxide/hydrogen/oxygen kinetics. Combust Sci Technol 1991;79:97.
- [7] Smith GP, Golden DM, Frenklach M, Moriarty NW, Eiteneer B, Goldenberg M, Bowman CT, Hanson RK, Song S, Gardiner WC Jr, Lissianski VV, Qin A. Gri3.0. Version:3.0 7/30/99 http://www.me.berkeley.edu/gri_mech.
- [8] Kee RJ, Rupley FM, Miller JA. Chemkin-II: a Fortran chemical kinetics package for the analysis of gas phase chemical kinetics. Sandia Report SAND89-8009B, Sandia National Labs., Livermore, CA, August 1993.
- [9] Najm HN, Knio OM, Paul PH. A numerical scheme for modelling reacting flow with detailed chemistry and transport. Sandia Report SAND2003-8412, Sandia National Laboratories, 2003.