

The role of explosive modes in homogeneous ignition and premixed flames

J. C. Lee, H. N. Najm*, S. Lefantzi, J. Ray,

Sandia National Laboratories, 7011 East Ave, MS9051, Livermore, CA 94550, USA.

M. Frenklach

University of California at Berkeley & Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA.

M. Valorani

University of Rome “La Sapienza”, 00184 Roma, Italy.

and D. A. Goussis

Agiou Georgiou 49, 26500 Rio, Greece.

January 6, 2005

1 Introduction

Gas phase combustion kinetic systems are driven by chain reactions (initiation, propagation, branching, and termination (see e.g. [1,2]) and reactive intermediate species – radicals. In the hydrogen-oxygen 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 steps. 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 factor. Having a fast rate of reaction relies on the overall branching ratio [1] of the system being > 1 . When this is so, there is an exponential growth (in time) in the number of molecules of the radical species, thus the dynamical system would exhibit at least one eigenvalue with a positive real part i.e. an *explosive mode*. 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. For instance, consider $dT/dt = Q \cdot e^{-T_a/T}$, $Q, T_a > 0$, which is a simple representation of an exothermic system with a high activation energy ($E_a = k \cdot T_a$); it can be easily verified that the eigenvalue of this system is real and positive. We expect, for a general chemical kinetic system (via either mechanism – branching factor > 1 or thermal-run-away) that some components of the system have at least one eigenvalue with positive real part i.e. an explosive regime. Those mechanisms that lead to exponentially fast reaction rates are then used to explain the propagation of a premixed flame. A phenomenological explanation for the premixed flame propagation 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. In this work, we will examine the “exponential” growth phenomenon in the homogeneous ignition of two fuel/air mixtures and in the propagation of their respective premixed flames.

We consider a general chemical kinetic system $d\vec{Y}/dt = \vec{g}(\vec{Y})$, $\vec{Y} \in \mathbb{R}^N$, $\vec{g}: \mathbb{R}^N \rightarrow \mathbb{R}^N$. An *explosive mode* exists when there is an eigenvalue of the Jacobian matrix $J \equiv \partial \vec{g}(\vec{Y})/\partial \vec{Y}$ with a non-trivial positive real part. In contrast, when an eigenvalue has a negative real part, 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

*Corresponding author: hnnajm@sandia.gov, (Tel:) 925 294 2054, (Fax:) 925 294 2595

associated time scale, can be achieved as follows. Let us consider an ordered set of time scales associated with the dynamical system: $|\tau_1| \leq |\tau_2| \leq \dots \leq |\tau_N|$, defined as $\tau_i \equiv -1/R(\lambda_i)$, where the λ_i , $i = 1, \dots, N$, are the eigenvalues of J , and $R(\lambda_i)$ denotes its real part. The next step is to decide if a mode, explosive or not, is of relevance. This is done using Computational Singular Perturbation (CSP) [3–5] analysis of the chemical system. Using CSP, we identify the attractive slow-manifold of the chemical system, and distinguish among the fast exhausted modes ($i = 1, \dots, M$) and the non-exhausted modes ($i = M + 1, \dots, N$). The fastest of the non-exhausted modes (mode $M + 1$) is the “driving” mode whose time scale τ_{M+1} controls the time evolution of the system at that instant. Whether or not a given non-exhausted mode is active depends on the amplitude of its projection on the slow-manifold. If this is sufficiently large, the mode is active, otherwise it is dormant and does not determine the time evolution of the system. With this analysis, the role of explosive modes in determining the time evolution of the chemical system is examined below.

2 Results: Homogeneous ignition of the hydrogen and methane systems

We considered both hydrogen and methane mixtures of various degrees of dilution and equivalence ratios (from rich to lean). All are ignited by setting the system to a sufficiently high initial temperature (1000 K) while pressure was kept constant at 1 atmosphere. All these ignition calculations exhibited a two-stage ignition process starting with an initial stage characterized by the existence of one or more explosive modes (positive eigenvalue(s)) followed by a regime having only the decaying modes (negative eigenvalue). Also, in the second regime, the magnitude of the controlling time scale is much smaller (faster) than those in the initial explosive stage. We will show here only the results obtained with the stoichiometric hydrogen/air mixture as all other calculations made with different equivalence ratios and those made with the methane/air mixtures showed similar trends. In particular the Yetter mechanism [6] was used in the ignition simulation (although the results are not shown in this abstract, the GRI3.0 mechanism [7] was used for all the methane/air mixture calculations).

The graphs shown in Fig. 1 depict plots of τ_{M+1} , temperature and the mass fractions of a few radical and intermediate species versus time, for the hydrogen/air ignition study. The homogeneous ignition process exhibits explosive modes in the induction 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 Fig. 1. We also observe that the real parts of all the eigenvalues become negative before the temperature starts to rise, which indicates that the explosive mode is not associated with the thermal-run-away phenomenon (as all explosive modes cease to exist before the temperature begins to rise). Similar results concerning to the role of the thermal-run-away phenomenon were also observed in the ignition studies with the methane/air mixtures tested.

3 Results: Premixed flames

We also computed freely propagating one-dimensional premixed hydrogen/air [6] and methane/air [7] flames using PREMIX [8]. We examined the hydrogen/air flame at equivalence ratios of 0.5, 1, and 2; and the methane/air flame at equivalence ratios of 0.7, 1, and 1.5. We present in Fig. 2 below the results for one case only, the stoichiometric hydrogen/air flame.

The figure includes plots of temperature, Y_{OH} , Y_{HO_2} , and τ_{M+1} versus the flame normal coordinate. Note 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. We also note that the same premixed flame, when subjected

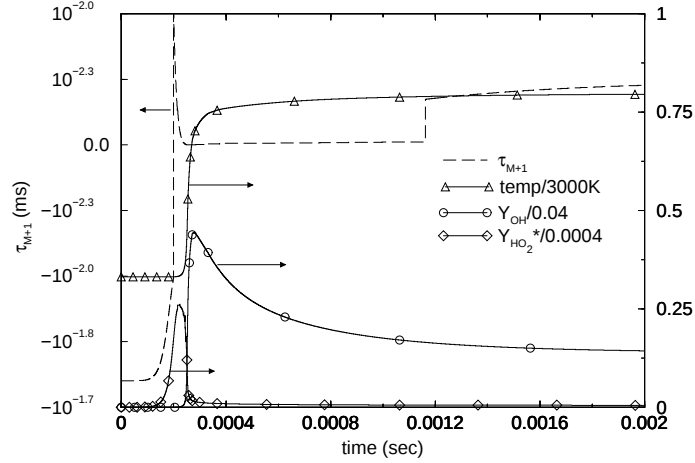


Figure 1: Left: Homogeneous ignition of a hydrogen–air mixture: plots of τ_{M+1} , T , Y_{OH} , Y_{HO_2} versus time. Right: Homogeneous ignition of a methane–air mixture: plots of τ_{M+1} , T , Y_{OH} , and Y_{CH_2O} versus time.

to a large strain rate in a two-dimensional flow context, also exhibits no explosive modes. We conclude that the existence of an explosive mode is clearly *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. The results were similar in all the other hydrogen/air and methane/air premixed flame cases indicated above, in the sense that no explosive modes were observed in any of them.

In a premixed flame, 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. The absence of explosive modes in the above premixed flames is clearly related to the transport processes. It is possible that the introduction of radical species (via diffusion) into the mixture upstream of the reaction zone caused the disappearance of the explosive modes in a premixed flame. We performed other hydrogen-mixture homogeneous ignition calculations by adding radical species to the initial mixture, while setting the initial temperature to 298K. We found that the ensuing homogeneous ignition process does not exhibit any explosive modes, in contrast with the high-temperature homogeneous ignition discussed above. We also repeated, for the hydrogen mixture, the high-temperature homogeneous ignition calculation but with some HO_2 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 may 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.

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.

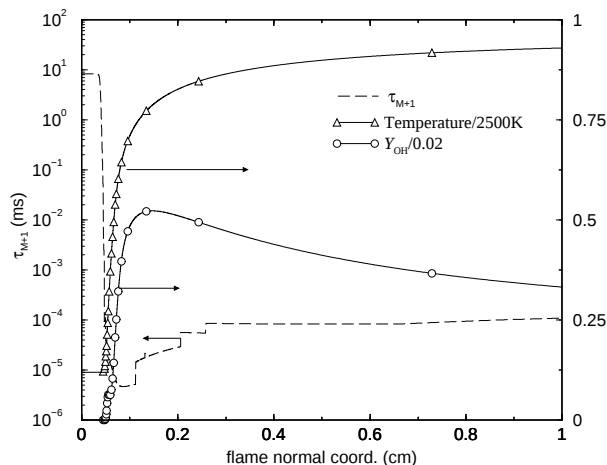


Figure 2: Stoichiometric hydrogen–air premixed flame: plots of τ_{M+1} , T , and Y_{OH} versus the flame normal coordinate (cm).

Homogeneous ignition calculations for mixtures with an initial concentration of radical species suggest 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. Frenklach acknowledges the financial support of DOE, BES under contract no. DE-AC03-76SF00098. M.Valorani acknowledges the support of the Italian Space Agency (ASI) and the Italian Ministry of Education, University and Research (MIUR).

References

- [1] I. Glassman. *Combustion*. Academic Press, Harcourt Brace Jovanovich, Publishers, New York, 1987.
- [2] F.A. Williams. *Combustion Theory*. Addison-Wesley, New York, 2nd edition, 1985.
- [3] S.H. Lam. Singular perturbation for stiff equations using numerical methods. In C. Casci, editor, *Recent Advances in the Aerospace Sciences*, page 3. Plenum Press, New York, 1985.
- [4] S.H. Lam and D.A. Goussis. Understanding complex chemical kinetics with computational singular perturbation. In *22nd Symposium (Intl.) on Combustion*, page 931, 1988.
- [5] D.A. Goussis and S.H. Lam. On the homogeneous methane-air reaction system. Report 1892-MAE, Princeton Univ., 1990.
- [6] R.A. Yetter, F.L. Dryer, and H. Rabitz. A comprehensive reaction mechanism for carbon monoxide/hydrogen/oxygen kinetics. *Combust. Sci. Technol.*, 79:97, 1991.
- [7] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Jr. Gardiner, V. V. Lissianski, and Qin A. Gri3.0. www.me.berkeley.edu/gri_mech, Version:3.0 7/30/99.
- [8] R.J. Kee, F.M. Rupley, and J.A. Miller. 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.