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The initiation of methane/air autoignition: the important chemical components for various initial conditions

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Abstract. A reactive system will be considered, the slow dynamics of which is characterized by time scales that are of explosive character; i.e., the components of the system that generate them tend to lead the system away from equilibrium. In particular, the initiation of a methane/air mixture autoignition will be considered for various initial temperatures and pressures. The species that relate to the explosive time scales and reactions that are responsible for the generation of these time scales will be identified. The analysis will be based on the Computational Singular Perturbation (CSP) algorithm, which is employed for the construction of the reduced system that governs the long range (slow) evolution of the system. It will be demonstrated that an excellent agreement with the existing literature is obtained.

1. Introduction
Reactive systems introduce a wide range of time scales, the fastest of which (i) are of dissipative character and (ii) tend to constrain the evolution of the system on a low-dimensional surface in phase space; i.e., on the slow invariant manifold (SIM). On this surface, the system is characterized by slower time scales, leading the system to equilibrium or away from it. The case where some of these slow time scales are of explosive character will be considered here. These are time scales that are generated by components of the system that tend to lead it away from equilibrium. Such a situation arises in autoignition processes or even in flames [1–4]. The influence of these time scales can be assessed only when it is possible to construct the reduced (non-stiff) system that governs the flow on the SIM.

In the past, this reduced system was constructed with the traditional singular perturbation techniques, so only simple reactive systems were analyzed and the characteristic explosive time scale was then identified [5, 6]. However, the traditional techniques cannot handle the large mechanisms that are of interest today. Nowadays, the reduced system is constructed by algorithmic methodologies [7–10] so that the complexity of the reactive system is not an obstacle anymore and reactions responsible for the development of explosive time scales can be identified with a simple numerical tool [11, 12].

In this study, the autoignition process of homogeneous CH4/air mixtures will be considered [13, 14]. The species and reactions that relate the most to the initiation of this process will be identified, by taking into account a wide range of initial temperatures and pressures and by employing the CSP algorithm. Recently, the reactions that favor or oppose the complete autoignition process and the related species were identified [8] for a single set of initial conditions. The analysis, here, is restricted to the start of the process, because the emphasis is placed on the influence of the initial values of temperature and pressure.
2. The Computational Singular Perturbation method

Consider a system consisting of \( N \) ordinary differential equations (ODE’s):

\[
\frac{dy}{dt} = g(y) = S_1 R^1(y) + \ldots + S_K R^K(y)
\]

where \( y \) is the \( N \)-dim. state vector and \( g(y) \) is the \( N \)-dim. vector field. The \( K \) additive terms in the RHS of Eq.(1) represent the various components (e.g. reactions) in the model. In chemical kinetics, \( y \) is the \( N \)-dim. vector of the species’ mass fractions, \( S_k \) is the \( N \)-dim. stoichiometric vector of the \( k \)-th reaction and \( R^k(y) \) is the corresponding reaction rate. Eq.(1) can be cast in CSP form as:

\[
\frac{dy}{dt} = \sum_{n=1}^{N} a_n f^n, \quad f^n = b^n \cdot g(z) = \sum_{k=1}^{K} (b^n \cdot S_k) R^k
\]

where \( a_n \) is the \( N \)-dim. CSP basis vector of the \( n \)-th mode, \( b^n \) is the \( N \)-dim. dual basis vector \((b^1 \cdot a_i = \delta^i_j)\) and \( f^n \) is the related amplitude [15, 16]. Assuming that the system in Eq. (2) exhibits \( M < N \) time scales that are of dissipative nature and much faster than the rest \((\tau_1 < \ldots < \tau_M << \tau_{M+1} < \ldots < \tau_N)\), yields:

\[
f^n \approx 0 \quad (m = 1, M)
\]

\[
\frac{dz}{dt} \approx \sum_{n=M+1}^{N} a_n f^n
\]

The first of these two relations is an algebraic one and defines the SIM, while the second governs the slow evolution of the process on the SIM. The evolution Eq. (2) is free of the fast time scales \((\tau_1 \text{ to } \tau_M)\), so that its dynamics are characterized by the fastest of the slow time scales. The identification and analysis of the slow characteristic time scales, among them the explosive ones, is allowed by the availability of this equation [17–19].

The decomposition in fast/slow processes of the vector field \( g(y) \) allows the acquisition of significant physical understanding of complex chemical systems and it is possible by the use of CSP-related algorithmic tools. In particular, the contribution of each of the \( K \) reactions to the time scale \( \tau_n \) and to the amplitude of each CSP mode \( f^n \) can be assessed by employing the Time Scale Participation Index (TPI) \( J^n_k \) and the Amplitude Participation Index (API) \( P^n_k \), respectively, while the relation of the \( n \)-th mode to the \( i \)-th component of \( y \) can be assessed by employing the CSP Pointer (Po) \( D_i^n \):

\[
J^n_k = \frac{c^n_k}{|c^n_1| + \ldots + |c^n_K|} \quad P^n_k = \frac{b^n \cdot S_k R^k}{|b^n \cdot S_1 R^1| + \ldots + |b^n \cdot S_K R^K|} \quad D_i^n = a^n_i b^n_i
\]

where, by definition \( \sum_{K=1}^{K} |J^n_k| = \sum_{K=1}^{K} |P^n_k| = \sum_{i=1}^{N} a^n_i b^n_i = 1 \) [10–12]. \( J^n_k \) measures the relative contribution of the \( k \)-th reaction to the \( n \)-th eigenvalue \( \lambda_n \) (therefore, to the time scale \( \tau_n \)), while \( P^n_k \) measures the relative contribution of the \( k \)-th reaction to the amplitude of the \( n \)-th CSP mode \( f^n \). Finally, \( D_i^n \) measures the relation of the \( n \)-th mode to the \( i \)-th component of \( y \).

CSP algorithmic tools will be employed next, in order to investigate the explosive modes that develop at the initiation of the autoignition process of various \( CH_4/air \) mixtures.

3. The Physical Problem

The homogeneous adiabatic autoignition at constant volume of a homogeneous stoichiometric \( CH_4/air \) mixture is considered. The reduced chemical kinetics mechanism employed here was derived from the GRI 3.0 mechanism[20] after ignoring the nitrogen chemistry reactions.

The \( t=0 \) case will be considered only. The purpose of this investigation is to examine the initiation of the process, by considering various initial pressures and temperatures. Here, four different values of the initial pressure \( p_0 \) will be examined, while three different values for the initial temperature \( T_0 \) will be accounted for each \( p_0 \). The slow dynamics of the system considered here exhibits two explosive time scales. Only the fastest one, say \( \tau_e \), will be considered, since this is the one that characterizes the autoignition process.
Figure 1: Explosion limit of methane/air [13, 14]. The twelve bullets denote the initial conditions for the temperature $T_o$ and pressure $p_o$ considered here, located below and above the explosion limit; subscripts A, B and T denote temperature right below (B), right above (A) and far above (T) the explosion limit.

4. Analysis of the fast explosive mode

In all cases considered, the reaction contributing the most towards the temperature evolution is reaction $H_2O + CH_3 \leftrightarrow O_3 + CH_4$ (118b), followed in a distance by reaction $H + CH_3(+M) \leftrightarrow CH(3)+M$ (52b). API data show that at $t = 0$ the amplitude $f^o$ of the fast exhausted mode is entirely due to reaction (118b), in all cases considered.

Table 1: Species, the mass fractions of which are identified by the CSP Pointer. When $T_o \geq 900$K, $CH_3$ relates the most to the fast time scale. When $900K > T_o > 700K$, the major pointed variable changes to $CH_2O$ radical. In the cases $T_o \leq 700K$, the pointed variable is $T$. The presence of the O-H chemistry has a negligible influence here.

|       | 5 atm     | 10 atm    | 15 atm    | 20 atm    |
|-------|-----------|-----------|-----------|-----------|
| $T_T$ | $CH_3$: +0.74 | $CH_3$: +0.65 | $CH_3$: +0.61 | $CH_3$: +0.56 |
|       | $HO_2$: +0.14 | $HO_2$: +0.17 | $HO_2$: +0.17 | $HO_2$: +0.17 |
| $T_A$ | $CH_3$: +0.35 | $CH_3O$: +0.90 | $CH_3O$: +0.92 | $CH_3O$: +0.93 |
|       | $CH_2O$: +0.31 | $H_2O_2$: +0.08 | $H_2O_2$: +0.07 | $H_2O_2$: +0.06 |
| $T_B$ | $CH_2O$: +0.92 | $CH_2O$: +0.96 | $T$: +0.95 | $T$: +0.98 |
|       | $H_2O_2$: +0.07 | $H_2O_2$: +0.03 |              |              |

According to Table 1, when $T_o > 900$K (top row) the variable that relates the most to the fast explosive time scale is the $CH_3$ radical, followed by the $HO_2$ radical. This finding is full agreement with the TPI data which identify reaction $CH_3 + O_2 \rightarrow O + CH_3O$ (158f) as the one contributing the most to $\tau_e$, followed by reactions $2CH_3(+M) \rightarrow C_2H_6(+M)$ (158f) and $CH_3 + H_2O_2 \leftrightarrow HO_2 + CH_4$ (157b). Clearly, the identified variables are reactants of the reactions that generate $\tau_e$. At $T = 900K$ (second row, left entry) TPI data show that reaction $CH_3O + O_2 \rightarrow HO_2 + HCO$ (32f) contributes significantly to $\tau_e$ along with reactions (155f, 158f, 157b). The contribution of (32f) is greater to that of (157b), so that $CH_3O$ joins $CH_3$ as the variables identified by the CSP Pointer.

When $900K > T_o > 700K$ (three entries on the right in second row and two entries on the left in third row), Table 1 shows that the CSP Pointer identifies $CH_3O$ as the one related the most to $\tau_e$. TPI data show that reactions (158f), (32f) and $CH_3 + O_2 \rightarrow OH + CH_2O$ (156f) are the ones contributing the most to $\tau_e$. Of these reactions, (32f) involves the species $CH_3O$, the mass fraction of which was identified by the CSP Pointer as the one related the most to $\tau_e$.

In the two cases where $T_o < 700K$ (two entries on the right in the third row), Table 1 indicates that the variable associated the most with $\tau_e$ is the temperature $T$. TPI data show that the reactions contributing the most to $\tau_e$ are (158f), (156f) and (118b). As said previously, reaction (118b) is the one that drives the evolution of the temperature.

From the results displayed in Table 1 we can conclude that the fast exhausted time scale $\tau_e$ at $t = 0$ is mainly determined by the rate of oxidation of $CH_3$ when $T_o$ is high and of (ii) $CH_2O$ when $T_o$ is low. At very low temperatures the variable that relates to the explosive mode is the temperature. The effect of pressure does not seem to be that much important in determining the nature of the initiation of the autoignition process.

5. Conclusions

Algorithmic asymptotic analysis was employed in order to identify the species and the reactions in which they participate as reactants that relate the most to the explosive time scale that
characterizes an autoignition process. A homogeneous $CH_4/air$ mixture was considered at various initial temperatures and pressures. Only the starting ($t = 0$) point was considered, since the aim of the present analysis was the assessment of the initial operating conditions (temperature and pressure) on the initiation of the process.

Although in all cases considered reaction $HO_2 + CH_3 \leftarrow O_2 + CH_4$ (118b) was shown responsible for initiating the process, its reactants ($CH_4$ and $O_2$) were not shown to relate to $\tau_e$ at $t = 0$. Instead, the reactants (e.g., $CH_3$, $CH_2O$, $HO_2$) of reactions that become active later on in the process were shown to relate at this starting point.

The predominant role of mainly $CH_3$ and $CH_2O$ and secondary of $HO_2$ at high and low, respectively, initial temperatures is well documented in the existing literature regarding the action of the various reactions after the initiation of the process [13, 14, 21]. Here it was shown that the consumption of these intermediate species relate the most to $\tau_e$ at $t = 0$, although the rates of the consuming reactions there are practically zero, since the mass fraction of at least one of the reactants are zero at $t = 0$. In addition, it was shown that at very low temperatures, $\tau_e$ is mostly related to $T$.

The fact that the $CH_3$, $CH_2O$ and $HO_2$ consuming reactions (155f), (156f), (158f), (32f) and (157b) determine $\tau_e$ at $t = 0$ does not contradict the fact that their rates is zero there because the mass fraction of these species is zero [8]. Keeping in mind that $\tau_e$ measures the time frame in which the autoignition takes place, these findings suggest that, $\tau_e$ is mainly dependent to the mass fraction in the initial mixture of the other reactants ($O_2$ for (155f), (156f) and (32f), $M$ for (158f) and $CH_4$ for (157b)). In other words, the magnitude of $\tau_e$ is determined by the initial concentrations of $O_2$, $M$ and $CH_4$ to the extend the reactions (155f), (156f), (158f), (32f) and (157b) consume $CH_3$, $CH_2O$ and $HO_2$.

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References
[1] Lee J C, Najm H N, Lefantzi S, Ray J, Frenklach M, Valorani M and Goussis D 2005 Computational Fluid and Solid Mechanics ed Bathe K J (Elsevier, Amsterdam) pp 717–720
[2] Kazakov A, Chaos M, Zhao Z and Dryer F L 2006 The Journal of Physical Chemistry A 110 7003–7009
[3] Lu T, Yoo C, Chen J and Law C 2010 Journal of Fluid Mechanics 652 45–64
[4] Najm H N, Valorani M, Goussis D A and Prager J 2010 Combustion Theory and Modelling 14 257–294
[5] Williams F 1986 Physica D: Nonlinear Phenomena 20 21 – 34
[6] Buckmaster J, Clavin P, Lin A, Matalon M, Peters N, Sivashinsky G and Williams F 2005 Proceedings of the Combustion Institute 30 1 – 19
[7] Goussis D and Maas U 2011 Fluid Mechanics and its Applications 95 193–220
[8] Diamantis D J, Kyritsis D C and Goussis D A 2014 Proceedings Combustion Institute in press
[9] Kourdis P D, Palasantza A G and Goussis D A 2013 Computers and Mathematics with Applications 65 1516–1534
[10] Shan R and Lu T 2014 Combustion and Flame 161 1716–1723
[11] Goussis D and Skevis G 2005 Computational Fluid and Solid Mechanics ed Bathe K J (Elsevier, Amsterdam) pp 650–653
[12] Goussis D A and Najm H N 2006 SIAM Multiscale Modeling and Simulation 5 1297–1332
[13] Law C K 2006 Combustion Physics (New York: Cambridge University Press)
[14] Glassman I and Yetter R 2008 Combustion (Elsevier Science)
[15] Lam S H and Goussis D A 1988 Proceedings Combustion Institute, 22 931–941
[16] Lam S H and Goussis D A 1994 International Journal of Chemical Kinetics 26 461–486
17] Trevino C 1989 Prog. Aeronaut. Astronaut. 131 19–43
18] Sanchez A L, Linan A and Williams F A 1997 J. Eng. Math. 31 19–130
19] Peters N, Paczko G, Seiser R and Seshadri K 2002 Combust. Flame 128 38–59
20] 2000 GRI-Mech; release 3.0 http://www.me.berkeley.edu/gri_mech
21] Westbrook C and Dryer F 1984 Progress in Energy and Combustion Science 10 1 – 57