Dynamical System Analysis of Ignition Phenomena

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Abstract

We introduce a novel index to analyze numerical datasets simulating ignition in reactive systems. The new index is obtained by combining the concept of stretching rate in dynamical systems with the CSP method, and is validated with reference to a planar model of branched-chain reactions and a test case involving CH4/Air (GRI 1.2) kinetics.

1. Introduction

Ignition of hydrocarbon fuels is controlled by branched-chain reactions and its complexities increase with the length/size of the fuel molecule. The Computational Singular Perturbation (CSP) method has been used to analyze two-stage ignition of n-heptane by Kazakov, et al. [1], and Goussis, et al. [2]. They observed the occurrence in spatially homogeneous systems of two branches of positive eigenvalues during both chain-branching and thermal ignition. Lu, et al. [3] proposed an explosion index for Chemical Explosive Modes (CEM) to analyze DNS datasets of turbulent flames; they also found eigenvalues with a positive real part in other limit processes in combustion. Najm, et al., [4], found explosive modes in edge flame data sets. All these ignition studies stress the role of eigenvalues with a positive real part in ignition and other limit phenomena. Willing to explore ignition with the simplest possible model, we consider a planar (2D) model for spatially homogeneous systems: an isothermal branched-chain explosion model proposed by Williams [5]. We analyzed Williams’ model by means of the local (tangential and normal) stretching rates introduced in [6]. The stretching rate defined in [6] degenerates when the trajectory crosses a region of complex eigenvectors. Hence, we modified the Tangential Stretching Rate (TSR) definition by combining the eigen-decomposition of the Jacobian matrix with the original definition of the TSR. The modified TSR is a weighted average of the modulus of the eigenvalues of the problem, with weights that depend on (i) the mode amplitudes, and (ii) the degree of co-linearity in-between each eigenvector and the vector field. We also introduce a normalized index measuring the relative contribution of each mode to TSR, which can be further combined with the CSP Participation Index of a reaction to a mode to obtain a direct link between a reaction and TSR. In the following, we first present the theory for the modified TSR, and next we validate it with reference to Williams’ model and a test case involving CH4/Air (GRI 1.2) kinetics.

2. Theory

Consider the point dynamics of a chemical kinetic system described by a set of ODEs

\[
\frac{dz}{dt} = g(z), \quad z(0) = z_0 \quad z \in \mathbb{R}^N. \tag{1}
\]

The state vector $z$ can be identified with the species concentration vector, the vector field $g(z) = S r(z)$ with the species reaction rate vector, $S$ with the stoichiometric coefficients matrix, $r(z)$ with the net reaction rates vector, and $z_0$ with the initial concentrations vector.
Now, consider two initial conditions, \( z_{0,1} \) and \( z_{0,2} \), for the point dynamics of Eq. (1), such that:

\[
z_{0,2} = z_{0,1} + \varepsilon
\]

with \( \varepsilon \) a small (vector) perturbation. Eq. (1) will generate two trajectories \( z_1(t) \) and \( z_2(t) \). Let us now define the vector \( \mathbf{v}(t) := \lim_{\varepsilon \to 0} (z_2(t) - z_1(t))/|\varepsilon| \). The vector \( \mathbf{v}(t) \) is a scaled measure of how much in time the evolution of the two initial mixtures differs. The vector dynamics of \( \mathbf{v} \) is described by the set of ODEs [6]:

\[
\frac{d\mathbf{v}}{dt} = J_g(z) \mathbf{v}, \quad \mathbf{v}(0) = \mathbf{1},
\]

where \( J_g := \partial g(z)/\partial z \) is the Jacobian matrix of the vector field \( g \), and \( \mathbf{1} \) is a unit vector at \( z_0 \) taken along any direction. Clearly, Eq. (3) can be solved only after, or simultaneously with, the integration of Eq. (1) with initial condition at \( z_{0,1} \).

The rate of change of the vector norm \( \sqrt{\mathbf{v}^T \mathbf{v}} \) is related to the overall rate of production/consumption of intermediate and product species due to reactions. The equation for the time evolution of \( \mathbf{v} \) is readily found by taking the scalar product of the left- and right-hand side of Eq. (3) with \( \mathbf{v}^T \), and reads

\[
\frac{d\mathbf{v}}{dt} = (\mathbf{v}^T J_g \mathbf{v})/\mathbf{v}, \quad \mathbf{v}(0) = 1.
\]

The rate at which \( \mathbf{v} \) changes (grows/shrinks) with time is governed by the coefficient in the parentheses on the rhs of Eq. (4). It is thus proper naming this coefficient: the (local) rate of stretching of the dynamics, \( \omega_\parallel \), evaluated along the direction identified by the unit vector \( \tilde{\mathbf{u}} := \mathbf{v}/|\mathbf{v}| \) and defined as:

\[
\omega_\parallel := \tilde{\mathbf{u}}^T J_g \tilde{\mathbf{u}}.
\]

The (local) stretching rate \( \omega_\parallel \) takes positive/negative values when the dynamics acts so as to amplify/dampen the initial vector \( \mathbf{1} \).

In Adrover, et al. [6], we introduced the tangential stretching rate (TSR) by setting \( \tilde{\mathbf{r}} := \mathbf{g}/|\mathbf{g}| \), which spans the vector field direction, and \( N-1 \) normal stretching rates spanning the orthogonal complement of the vector field subspace. In a two-dimensional system (as is the Williams model), and defining the unit normal vector as \( \tilde{\mathbf{n}}(z) = \{\tilde{\mathbf{r}}_2(z), -\tilde{\mathbf{r}}_1(z)\} \), we obtain the following definitions of tangential/normal stretching rates:

\[
\omega_\parallel := \tilde{\mathbf{r}}^T J_g \tilde{\mathbf{r}}, \quad \omega_\parallel := \tilde{\mathbf{n}}^T J_g \tilde{\mathbf{n}}.
\]

For \( \omega_\parallel /\omega_\parallel > 0 \), the tangential/normal perturbations are amplified, while for \( \omega_\parallel /\omega_\parallel < 0 \) they are dampened.

The Jacobian matrix can be always decomposed as \( J_g = A \Lambda B \), where \( A = \{a_i\}_{i=1,N} \) and \( B = \{b'_j\}_{j=1,N} \) are the right and left normalized eigenvector matrices of \( J_g \), respectively, and \( \Lambda = \{\lambda_i\}_{i=1,N} \) is the eigenvalue matrix of \( J_g \).

The unit vector \( \tilde{\mathbf{r}} \) can be rewritten after projecting the vector field over the right eigenvector basis as \( \tilde{\mathbf{r}} = \frac{\mathbf{g}}{|\mathbf{g}|} = \frac{1}{|\mathbf{g}|} \sum_{i=1}^N a_i f'_i \), with \( f'_i := b'_i \cdot \mathbf{g} \), and \( \mathbf{g} = \sum_{i=1}^N a_i f'_i \). Given that \( J_g = A \Lambda B \), we now have

\[
\omega_\parallel = \tilde{\mathbf{r}}^T J_g \tilde{\mathbf{r}} = \frac{1}{|\mathbf{g}|^2} (\mathbf{g}^T A \Lambda B \mathbf{g}) = \frac{1}{|\mathbf{g}|^2} \sum_{i=1}^N a_i \lambda_i (b'_i \cdot \mathbf{g})
\]

\[
= \frac{1}{|\mathbf{g}|^2} \sum_{i=1}^N a_i \lambda_i f'_i = \frac{1}{|\mathbf{g}|^2} \sum_{i=1}^N (g^T \cdot a_i) \lambda_i f'_i.
\]
Using the expansion of \( g \) we can write
\[
g^T \cdot a_i = \left( \sum_{k=1}^{N} a_k f^k \right)^T \cdot a_i = \sum_{k=1}^{N} f^k (a_k^T \cdot a_i), \tag{8}
\]
where \( a_k^T \cdot a_i \) is the direction cosine (the phase) between \( a_i \) and \( a_k \) (with \( |a_k^T \cdot a_i| \leq 1 \)).

With this result, Eq. (7) becomes
\[
\omega_{\tau} = \sum_{i=1}^{N} \left( \frac{1}{g} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \right) \lambda_i f^i
= \sum_{i=1}^{N} \left( \frac{f^i}{g} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \right) \lambda_i = \sum_{i=1}^{N} W_i \lambda_i \tag{9}
\]
where
\[
W_i := \frac{f^i}{g} a_i^T \cdot a_i = \frac{f^i}{g} \sum_{k=1}^{N} f^k (a_k^T \cdot a_i). \tag{10}
\]

The vector field is an invariant direction for the dynamics as well as the (local) eigendirections. The perturbation (unit) vector tangent to the vector field \( \tilde{\tau} \) changes according with the rate \( \omega_{\tau} = \sum_{i=1}^{N} W_i \lambda_i \) because of the action of the (linearized) dynamics as represented by \( J_g \). By construction, this term takes the maximum value when all \( a_i \) are co-linear with \( g \), that is:
\[
\frac{g^T \cdot a_i}{g} = \sum_{k=1}^{N} f^k (a_k^T \cdot a_i) \leq \frac{f^i}{g}.
\]

and substituting this result in Eqs. (8-10), provides an upper bound for \( \omega_{\tau} \):
\[
\omega_{\tau} \leq \sum_{i=1}^{N} \left( \frac{f^i}{g} \right)^2 \lambda_i. \tag{11}
\]

This shows that, because of the quadratic term, the sign of \( \omega_{\tau} \) depends on those of the prevailing eigenvalues.

### 3. Williams’ model

We first show to what extent we can take Williams’ model as a valid surrogate of a true kinetic mechanism. In this regard, let us consider first Williams’ model for isothermal branched-chain reactions [5], which can be described by three irreversible reactions: \( R \rightarrow C \) (initiation), \( R + C \rightarrow \alpha C + P \) (propagation), \( C \rightarrow P \) (termination), where \( R= \)reactants, \( C= \) intermediates, \( P= \)products, the three reaction rates \( k_{i,p,t} \) are taken constant because of the assumed isothermicity. The branching factor \( \alpha \) can take the values \( \alpha = 1 \) for linear propagation, and \( \alpha > 1 \) for branching propagation. The three non-dimensional ODEs that describe the kinetics of the model are:
\[
\begin{align*}
    x_1' &= -x_1 - x_1 x_2, \\
    x_2' &= x_1 + (\alpha - 1)x_1 x_2 - \gamma x_2, \\
    x_3' &= \gamma x_2 + x_1 x_2,
\end{align*}
\]
with initial conditions \( (x_1(0), x_2(0), x_3(0)) = (1.0, 0, 0) \), where the symbol \( (\cdot)' \) denotes differentiation with respect to the non-dimensional time \( \tau = t k_i \), with \( t \) the dimensional time; the non-dimensional state variables
are \( x_1 := r/r_0, x_2 := ck_p/k_i, \) and \( x_3 := pk_p/k_t, \) with \( r, c, \) and \( p \) the molar concentrations of R, C, and P, respectively, and \( r_0 \) the initial molar concentration of R. Because the third equation is decoupled from the other two, Williams’ model is effectively two-dimensional with state vector defined by the pair \((x_1, x_2)\). The dimensionless rate constants are defined as \( \epsilon = k_i/(k_p r_0) \) and \( \gamma = k_t/(k_p r_0) \). A super-critical trajectory for \( \alpha = 2, \epsilon = 0.01, \gamma = 0.5\ gamma_c, \) with \( \gamma_c = \alpha - 1 \), is plotted in the phase space \((x_1, x_2)\) in Fig. 1 (blue, solid). The trajectory (i) is nearly tangent to the fast eigenvector (red) \( a_1 \) at \((1, 0)\), and to the slow eigenvector (blue) \( a_2 \) at \((0, 0)\), and, (ii) at time \( t \approx 0.3 \) (\( x \approx 0.15 \) in Fig. 1 (left)), it lands on the QSSA of the Slow Invariant Manifold (red, dashed) when both mode amplitudes have the same magnitude, and eventually reaches the fixed point \((0,0)\). The region of complex eigenvalues lies above the black dashed line in Fig. 1 (left). The green dashed line is the locus of zero real part of the complex conjugate eigenvalues. The eigenvalue analysis carried out along the supercritical trajectory exhibits the evolution shown in Fig. 1 (right). There exists a first stage during which a pair of eigenvalues with positive real parts form; this stage ends when the pair of positive eigenvalues merge to form a complex conjugate pair with positive real parts. Eventually, the complex conjugate pair crosses the imaginary axis so that the real parts becomes negative. Finally, the imaginary parts reduce to zero, and a pair of real negative eigenvalues emerge and remain until the system reaches the equilibrium state. For easy reference, we will refer to the time period when the eigenvalues are real and positive/negative as Period 1 (P1) and Period 3 (P3), respectively, while when the eigenvalues are complex as Period 2 (P2). Note that when the real parts of the eigenvalues cross zero (Fig. 1 (right)), the eigenvalues’ modulus is defined by the imaginary part and is non-zero. Therefore, introducing a time scale as the reciprocal of only the real part leads to an infinite scale at the zero crossing, while the reciprocal of the modulus will always remain bounded.

4. CSP and TSR Analyses

Figure 2 compares the evolution of the tangential (brown)/normal (green) stretching rates, computed using the definitions in Eq. (6), with respect to variations of the eigenvalues. We observe that \( \omega_\tau \) follows the fast positive eigenvalue (blue) in P1 and the negative one (red) up to time \( t = 0.2 \) (P3a). In the interval \( t = 0.2 \rightarrow 0.45 \), the two stretching rates switch between the eigenvalues, so that after \( t = 0.45 \) (P3b), \( \omega_\tau \) follows the slow eigenvalue (blue). The opposite trend is followed by the normal rate.
In the CSP method, the contribution of the $M$ fastest modes ($r = 1, M$) to the system dynamics is considered negligible until the following inequality is satisfied

$$\tau_{M+1} \sum_{r=1,M} a_i^r f^r < \varepsilon^j = r\text{tol}^j|z^j| + a\text{tol}^j, \quad j = 1, N,$$

(12)

where $\tau_{M+1} = 1/|\lambda_{M+1}|$, and $\varepsilon^j$ is a user-defined error vector. The first integer $M$ for which the inequality is not satisfied for all the $N$ components of the state $z$, identifies the decomposition of the tangent space, $T_z$, in fast, $F$, and slow, $S$, subspaces, that is $T_z = F \oplus S$, with $F = \{a_i\}_{r=1,M}$ and $S = \{a_i\}_{s=M+1,N}$. Thus, to identify the controlling scale, CSP performs two actions: (i) evaluate the eigensystem, and (ii) apply the criterion, Eq. (12), which also involves a user-defined error threshold. Instead, $\hat{\omega}_\tau$ provides similar information by closely following the largest positive eigenvalue (blue) in P1, the largest negative eigenvalue (red) in P3a, and the smallest negative eigenvalue (blue) in P3b. This demonstrates that $\hat{\omega}_\tau$ is able to track the controlling time scale at all times, independently of any user-defined error threshold.

5. N-dimensional extension

Extending to the $N$-dimensional case the definition of $\hat{\omega}_\tau$ given above for the 2D case, simply involves replacing the eigenvalue with its modulus in Eq. (9). If one needs to know the sign of TSR, it is sufficient to account for the sign of the real part of the eigenvalue. Therefore, we suggest computing

$$\bar{\omega}_\tau := \sum_{i=1}^{N} W_i \text{Sign}[\text{Re}[\lambda_i]] |\lambda_i|, \quad W_i = W_i^f / \sum_{j=1}^{N} |W_i|, \quad W_i^f := f^i g^T \frac{a_i g}{g}$$

(13)

We then introduce a Participation Index of the $i$-th mode to the TSR as $P_{i}^{\omega_\tau} = W_i |\lambda_i|/ \sum_{j=1}^{N} |W_j| |\lambda_j|$. Modes with a large $P_{i}^{\omega_\tau}$ are the ones that contribute the most to the development of the most energy containing time scale. Inspection of the CSP participation index for the $k$-th reaction to these modes, $P_{k}^{\omega_\tau}$, will identify what are the reactions that contribute the most to the development of the $\omega_\tau$ scale.

6. Validation and Conclusions

We apply now the new definition Eq. (13) to the branched-chain/thermal, auto-ignition process of CH4/Air (GRI 1.2), including 32 species. The initial conditions are $p=1$ atm, $T=950K$, for a stoichiometric mixture. In Fig. 3 (left), we plot the real parts of the negative/positive eigenvalues in light-gray/red
symbols, respectively. The negative eigenvalues are plotted using the absolute value of the real parts, so to plot them in the log-scale. The red markers clearly show that there exists a first stage during which one eigenvalue with positive real part is present; later, a second eigenvalue with positive real part emerges, and the two merge to form a complex conjugate pair with positive real parts similar to what is seen in Williams’ model. Later, the complex conjugate pair crosses the imaginary axis so that the real parts become negative. Finally, the imaginary parts reduce to zero, and several real negative eigenvalues emerge and remain until the system reaches its equilibrium state. Differently from Williams’ model, in this test case it is not obvious to identify the pair of negative eigenvalues emerging from the coalescence of the two positive ones. The outcome of the TSR analysis can be summarized in Fig. 3 (right). After a short transient, \( \overline{\omega}_I \) becomes coincident with \( \lambda_{\text{max}} \); a bit sooner than the merging of the two positive eigenvalue, \( \overline{\omega}_I \) departs from \( \lambda_{\text{max}} \) to track the "most energetic" dissipative scale until equilibrium; this behaviour is qualitatively similar to what is observed in Williams’ model. Therefore \( \overline{\omega}_I \) properly identifies which positive eigenvalue is the controlling one if more than one is simultaneously present. The modes mostly contributing to \( \overline{\omega}_I \) are those with large \( P_{ji}^{max} \); in Fig. 3 (right), the eigenvalues of the modes with \( P_{ji}^{max} > 10^{-05} \) are marked with light-grey filled circles. Note that, besides the region about the eigenvalue merging, very few modes contribute to \( \overline{\omega}_I \), that is, the active scale range is dominated by very few modes, and, consequently, the most significant reactions to the active dynamics are those contributing to these few modes (all reactions with a large CSP PI to the important modes for \( \overline{\omega}_I \)).

![Figure 3: CH4/Air (GRI 1.2) mechanism. Left: light-gray symbols: negative eigenvalues; red symbols: positive eigenvalues; samples are taken in the time interval t=0-30s. Right: Black filled circles: \( \omega_I \); black empty upper triangles: max[|\( \lambda_i \)| with \( P_{ji}^{max} > 10^{-05} \); black empty lower triangles: min[|\( \lambda_i \)| with \( P_{ji}^{max} > 10^{-05} \); light-grey empty circles: modes with \( P_{ji}^{max} > 10^{-05} \); red empty circles: \( \lambda_i \)'s with positive real part; small orange empty circles: \( \lambda_{M_{\text{max}}} \); samples are taken in the time interval t=0-30s.](image)

**References**