

Application of the ICE-PIC method for the dimension reduction of chemical kinetics

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1 Introduction

There is a well-recognized need to develop methodologies that radically decrease the computational burden imposed by the direct use of detailed chemical kinetics in reactive flow calculations. Of the several different types of such methodologies, three approaches that are currently particularly fruitful (and which can be used in combination) are: the development of skeletal mechanisms from large detailed mechanisms by the elimination of inconsequential species and reactions [1, 2]; dimension-reduction techniques; and storage/retrieval methodologies such as ISAT [3].

In dimension reduction methods, compositions in reactive flows are assumed to lie on an n_r low-dimensional manifold in the full composition space; and the chemistry is described in terms of the n_r reduced composition variables r (e.g., in terms of some major species). Many dimension reduction methods have been proposed, such as the quasi-steady state assumption (QSSA) [4, 5], rate-controlled constrained equilibrium (RCCE) [6], intrinsic low-dimensional manifolds (ILDLM) [7], trajectory-generated low-dimensional manifolds (TGLDM) [8], and the pre-image curve method [9], etc.

All of these methods either explicitly or implicitly define a low-dimensional manifold in the full composition space. Mathematically, the desirable properties of the low-dimensional manifolds to describe chemical kinetic system are: existence and uniqueness; continuity and smoothness; and invariance. A manifold is invariant if it is composed of *reaction trajectories* of the full system.

In general, provided that a particular manifold exists and is unique, then the reduced variables can be used to parameterize the manifold. To each value of the reduced variables, there is a corresponding composition on the manifold in the full composition space. This process of determining the full composition from the reduced representation is termed “species reconstruction” [9]. An important distinction between dimension-reduction methodologies is whether or not they are *local*. In local methods, species reconstruction can be performed (for given values of the reduced variables) without constructing the whole (or a significant portion) of the manifold. Approaches such as QSSA, RCCE and ILDM are local. In contrast, methods such as TGLDM are *global*. The computational implementation of global methods soon becomes impracticable as the dimensionality of the manifold increases.

Recently, the ICE-PIC method has been developed by Ren et. al [10]. It is currently the only dimension-reduction methodology that is both based on an invariant manifold, and for which there is a local method of species reconstruction.

In this work, from the species reconstruction perspective, we demonstrate the application of the ICE-PIC method in hydrogen/air and methane/air systems. In the following, the ICE-PIC method is briefly described, and then its accuracy in application to laminar premixed flames is examined.

2 Homogeneous reacting system

To illustrate, we consider a closed, homogeneous, isobaric, isothermal reacting system with n_s chemical species composed on n_e elements. It is straightforward to apply the ICE-PIC method to an adiabatic system. We use the specific moles $\mathbf{z} = \{z_1, z_2, \dots, z_{n_s}\}$ to represent the composition of the system at any time. The *full composition space* \mathcal{C} is defined to be the real n_s -dimensional Euclidean space with canonical basis vectors \mathbf{e}_i , $i = 1, 2, \dots, n_s$.

During chemical reactions, the specific moles of atoms of element i is denoted by z_i^e , and the n_e -vector of element specific moles $\mathbf{z}^e \equiv \mathbf{E}^T \mathbf{z}$ is conserved, where \mathbf{E} is the $n_s \times n_e$ elemental matrix: the component E_{ij} indicates the number of atoms of element j in a molecule of species i . Thus for the system considered, conserved quantities (fixed for all time) are the mass, m , the pressure, p , the temperature, T , and the element specific moles \mathbf{z}^e .

Given that \mathbf{z}^e is conserved, the reactive system can be described in the $(n_s - n_e)$ -dimensional *reactive affine space*, defined by $\mathcal{C}(\mathbf{z}^e) \equiv \{\mathbf{z} \mid \mathbf{E}^T \mathbf{z} = \mathbf{z}^e, \mathbf{z} \in \mathcal{C}\}$. And the non-negativity of the species confines compositions to the *realizable region* of this reactive affine space, defined by

$$\mathcal{C}^+(\mathbf{z}^e) \equiv \{\mathbf{z} \mid z_i \geq 0, \mathbf{E}^T \mathbf{z} = \mathbf{z}^e, \mathbf{z} \in \mathcal{C}\}. \quad (1)$$

This is a bounded convex polytope.

All thermodynamic variables—energy, enthalpy, entropy, etc.—are scalar functions defined in $\mathcal{C}^+(\mathbf{z}^e)$. Of particular interest is the Gibbs function $G(\mathbf{z})$. It is well known (see e.g., [11], [12]), that $G(\mathbf{z})$ is a convex function with a unique global minimum in the interior of $\mathcal{C}^+(\mathbf{z}^e)$. For the isothermal, isobaric systems under consideration, the location of this minimum corresponds to chemical equilibrium.

Due to chemical reactions, the composition $\mathbf{z}(t)$ evolves in time, t , according to the autonomous set of ordinary differential equations (ODEs)

$$\frac{d\mathbf{z}(t)}{dt} = \mathbf{S}(\mathbf{z}(t)), \quad (2)$$

where the rate-of-change vector $\mathbf{S}(\mathbf{z})$ is determined by the detailed chemical kinetics mechanism.

The solutions of Eq. 2 are conveniently denoted by the *reaction mapping* (or flow) $\mathbf{R}(\mathbf{z}, t)$, which is defined by

$$\mathbf{R}(\mathbf{z}, 0) = \mathbf{z}, \quad \frac{\partial \mathbf{R}(\mathbf{z}, t)}{\partial t} = \mathbf{S}(\mathbf{R}(\mathbf{z}, t)). \quad (3)$$

Thus, $\mathbf{R}(\mathbf{z}, t)$ is the solution to Eq. 2 after time t , starting from the initial condition, \mathbf{z} .

3 The ICE-PIC method

The state of the system is completely specified by p , T and \mathbf{z} . The ICE-PIC method approximate the dynamics of the system by fewer variables, which are taken to be p , T , \mathbf{z}^e and \mathbf{r} , where $\mathbf{r} = \{r_1, r_2, \dots, r_{n_r}\}$ is a specified set of n_r *reduced compositions*, for $1 \leq n_r < (n_s - n_e)$. Usually, the reduced compositions are specified as certain ‘‘major’’ species. But we allow for a more general linear combination of species by defining $\mathbf{r} = \mathbf{B}^T \mathbf{z}$, where \mathbf{B} is a specified $n_s \times n_r$ matrix. The reduced composition \mathbf{r} is an n_r -vector confined to the *reduced realizable region*

$$\mathcal{B}^+(\mathbf{z}^e) \equiv \{\mathbf{r} \mid \mathbf{r} = \mathbf{B}^T \mathbf{z}, \mathbf{z} \in \mathcal{C}^+(\mathbf{z}^e)\}. \quad (4)$$

From the manifold perspective, dimension reduction consists primarily of identifying an n_r -dimensional attracting manifold $\mathcal{M}(\mathbf{z}^e)$ in the realizable region $\mathcal{C}^+(\mathbf{z}^e)$. For each point \mathbf{r} in the reduced realizable region $\mathcal{B}^+(\mathbf{z}^e)$, there is a corresponding point on the manifold, denoted by $\mathbf{z}^{\mathcal{M}}(\mathbf{z}^e, \mathbf{r})$. By assumption, the compositions which occur lie close to $\mathcal{M}(\mathbf{z}^e)$, and the dynamics are well approximated by those on $\mathcal{M}(\mathbf{z}^e)$. A closely related perspective is that of *species reconstruction* [9] which, given \mathbf{z}^e and \mathbf{r} , seeks to determine $\mathbf{z}^{\mathcal{M}}(\mathbf{z}^e, \mathbf{r})$. The distinction between these two perspectives is that in species reconstruction the goal is to determine a single manifold point, without generating or representing the whole manifold.

In species reconstruction, an important concept is that of the *feasible region*. Given the reduced representation \mathbf{z}^e and \mathbf{r} , the feasible region $\mathcal{F}(\mathbf{z}^e, \mathbf{r})$ is defined as the union of compositions \mathbf{z} in $\mathcal{C}^+(\mathbf{z}^e)$ which have the reduced composition \mathbf{r} , i.e.,

$$\mathcal{F}(\mathbf{z}^e, \mathbf{r}) \equiv \{\mathbf{z} \mid \mathbf{B}^T \mathbf{z} = \mathbf{r}, \mathbf{z} \in \mathcal{C}^+(\mathbf{z}^e)\}. \quad (5)$$

Given \mathbf{z}^e and \mathbf{r} , without further knowledge or assumptions, it is not generally possible to determine \mathbf{z} uniquely. But it is known that \mathbf{z} is in the feasible region $\mathcal{F}(\mathbf{z}^e, \mathbf{r})$.

The ICE-PIC method draws ideas from the RCCE and TGLDM methods. In RCCE, the n_r -dimensional attracting manifold is taken to be the *constrained equilibrium manifold* (CEM), which we denote by $\mathcal{M}^{CE}(\mathbf{z}^e)$. Here we use the CEM for different purposes. In the isobaric, isothermal systems being considered, for given \mathbf{z}^e and \mathbf{r} , the corresponding point on the CEM, denoted by $\mathbf{z}^{CE}(\mathbf{z}^e, \mathbf{r})$, is the point in the feasible region at which the Gibbs function $G(\mathbf{z})$ is minimum. And the CEM is defined as the union of all such points

$$\mathcal{M}^{CE}(\mathbf{z}^e) \equiv \{\mathbf{z} = \mathbf{z}^{CE}(\mathbf{z}^e, \mathbf{r}) \mid \mathbf{r} \in \mathcal{B}^+(\mathbf{z}^e)\}. \quad (6)$$

The *constrained equilibrium edge* $\partial \mathcal{M}^{CE}(\mathbf{z}^e)$ is defined (in general) as the intersection between $\mathcal{M}^{CE}(\mathbf{z}^e)$ and the boundary of the realizable region

$$\partial \mathcal{M}^{CE}(\mathbf{z}^e) \equiv \mathcal{M}^{CE}(\mathbf{z}^e) \cap \partial \mathcal{C}^+(\mathbf{z}^e). \quad (7)$$

To each point in the boundary $\partial \mathcal{B}^+(\mathbf{z}^e)$ of the reduced realizable region there is a unique corresponding point in the constrained equilibrium edge.

As proposed in the TGLDM method, a conceptually simple way to obtain an n_r -dimensional invariant manifold is to define it as the union of the reaction trajectories originating from points in a specified $(n_r - 1)$ -dimensional manifold. In the ICE-PIC method, we use this approach, taking the $(n_r - 1)$ -dimensional constrained equilibrium edge to define the origin of the trajectories. Hence in the ICE-PIC method, the Invariant Constrained-equilibrium Edge manifold (or the *ICE manifold* for short), $\mathcal{M}^{ICE}(\mathbf{z}^e)$, introduced is

$$\mathcal{M}^{ICE}(\mathbf{z}^e) \equiv \{\mathbf{z} \mid \mathbf{z} = \mathbf{R}(\mathbf{z}^g, t), t \geq 0, \mathbf{z}^g \in \partial \mathcal{M}^{CE}(\mathbf{z}^e)\}, \quad (8)$$

which is the union all reaction trajectories $\mathbf{R}(\mathbf{z}^g, t)$ (forward in time) emanating from *generating boundary points* \mathbf{z}^g in the edge of the constrained equilibrium manifold $\partial \mathcal{M}^{CE}(\mathbf{z}^e)$.

However, computationally, the process of generating and representing the ICE manifold rapidly becomes infeasible as the dimensionality n_r of the manifold increases. Rather than the global method of generating the whole ICE manifold (with $n_r > 10$, say), in practice for the dimension reduction of combustion chemistry a local species reconstruction procedure is developed: this is the ICE-PIC method which determines the ICE manifold point $\mathbf{z}^{ICE}(\mathbf{z}^e, \mathbf{r})$, for given values of \mathbf{z}^e and \mathbf{r} . This procedure is based on the Constrained-Equilibrium Pre-Image Curve.

An important concept employed in the procedure is the *pre-image manifold* $\mathcal{M}^{PI}(\mathbf{z}^e, \mathbf{r})$. Given the reduced representation of the composition, $\{\mathbf{z}^e, \mathbf{r}\}$, from each point $\hat{\mathbf{z}}$ in $\mathcal{F}(\mathbf{z}^e, \mathbf{r})$ the reaction trajectory can be followed backwards in time until (at time $-\tau^b(\hat{\mathbf{z}})$) it intersects the boundary, $\partial \mathcal{C}^+(\mathbf{z}^e)$, at $\mathbf{z}^b(\hat{\mathbf{z}})$. The pre-image manifold is defined to be the union of all of these trajectories:

$$\mathcal{M}^{PI}(\mathbf{z}^e, \mathbf{r}) \equiv \{\mathbf{z} \mid \mathbf{z} = \mathbf{R}(\hat{\mathbf{z}}, t), \hat{\mathbf{z}} \in \mathcal{F}(\mathbf{z}^e, \mathbf{r}), -\tau^b(\hat{\mathbf{z}}) \leq t \leq 0\}. \quad (9)$$

It follows from the well-known properties of ODEs that the dimension of the pre-image manifold $\mathcal{M}^{PI}(\mathbf{z}^e, \mathbf{r})$ is one more than the dimensionality of the feasible region $\mathcal{F}(\mathbf{z}^e, \mathbf{r})$ from which it is generated. That is, $\mathcal{M}^{PI}(\mathbf{z}^e, \mathbf{r})$ is of dimension $(n_s - n_e - n_r + 1)$.

In ICE-PIC method, the *constrained-equilibrium pre-image curve* (CE-PIC) denoted by $C^{CE}(\mathbf{z}^e, \mathbf{r})$, is the intersection between the pre-image manifold and the constrained equilibrium manifold:

$$C^{CE}(\mathbf{z}^e, \mathbf{r}) \equiv \mathcal{M}^{PI}(\mathbf{z}^e, \mathbf{r}) \cap \mathcal{M}^{CE}(\mathbf{z}^e). \quad (10)$$

Note that these two manifolds are of dimension $(n_s - n_e - n_r + 1)$ and n_r , respectively, and so (provided that they are transverse), their intersection C^{CE} is one-dimensional (i.e., a curve) in the $(n_s - n_e)$ -dimensional realizable region $\mathcal{C}^+(\mathbf{z}^e)$. It is important to appreciate that the CE-PIC is not a reaction trajectory.

Based on the constrained-equilibrium pre-image curve, the species reconstruction provided by the ICE-PIC method locally determine the full composition on the ICE manifold. Given values of the reduced variables, the ICE-PIC method performs species reconstruction through three steps: the determination of the constrained equilibrium composition; in the full composition space, following the *constrained-equilibrium pre-image* (CE-PIC) curve to a particular point on the edge of the manifold; following the reaction trajectory from this point along the ICE manifold to the required point — the reconstructed composition.

4 Application of ICE-PIC method

In this section, from the species reconstruction perspective, the ability of ICE-PIC method is investigated for the test cases of premixed laminar flames of both hydrogen/air and methane/air mixtures with an unburnt temperature of 300K and pressure of 1atm. And quantitative comparisons are made with other methodologies, namely RCCE, ILDM and QSSA.

With detailed mechanisms, the steady, isobaric, adiabatic, one-dimensional laminar flame equations are solved using PREMIX to yield profiles of the full composition, denoted by \mathbf{z}^P , through the flame. For H_2/air , the Li mechanism [13] with 3 elements and 9 species is used. For CH_4/air , GRI1.2 [14] with 4 elements and 31 species is used. (We use this older mechanism to facilitate comparison with previous QSSA methods.)

At different locations across the the flame, the ICE-PIC method is employed to perform species reconstruction, i.e., to determine the full composition \mathbf{z}^{ICE} on the corresponding ICE manifold as an estimate of \mathbf{z}^P . At each location, the thermochemical state is completely specified by pressure p , temperature T and species specific moles \mathbf{z} ; and given the reduced representation $\{\mathbf{z}^e, T, \mathbf{r}\}$, the ICE-PIC method is applied to the corresponding isothermal, isobaric closed system.

For H_2/air , we take $n_r = 4$, and specify the reduced compositions \mathbf{r} to be the specific moles of the species H_2 , O_2 , H_2O and H . Thus with given \mathbf{z}^e and T , the dimensionality of the low-dimensional manifolds is 4. For CH_4/air , we take $n_r = 12$ and specify the reduced compositions \mathbf{r} to be the specific moles of the species H_2 , H , O , O_2 , OH , H_2O , CH_3 , CH_4 , CO , CO_2 , CH_2O and C_2H_4 . Thus with given \mathbf{z}^e and T , the dimensionality of the low-dimensional manifolds is 12.

At each location, the species specific moles of the represented species \mathbf{r} , the element specific moles \mathbf{z}^e , and temperature are extracted from the accurate full composition $\{T^P, \mathbf{z}^P\}$. The reconstructed composition on the ICE manifold $\mathbf{z}^{ICE}(\mathbf{z}^e, T, \mathbf{r})$ is then obtained using the ICE-PIC method.

Also, we can apply ILDM, QSSA, or RCCE to perform species reconstructions. With the same reduced representation as in the ICE-PIC method, the RCCE method takes CEM as the low-dimensional attracting manifold. By definition, the ILDM is the set of compositions \mathbf{z} satisfying

$$\mathbf{U}_f^T \mathbf{S}(\mathbf{z}) = 0, \quad (11)$$

where \mathbf{U}_f is the fast subspace of the Jacobian matrix $\mathbf{J}(\mathbf{z})$ (see [7] for further details). Given the same reduced represen-

tation $\{\mathbf{z}^e, T, \mathbf{r}\}$ as in the ICE-PIC method, the ILDM method identifies ILDM compositions \mathbf{z}^{ILDM} satisfying Eq. 11 in the feasible region $\mathcal{F}(\mathbf{z}^e, T, \mathbf{r})$.

In ICE-PIC, CEM and ILDM, the same reduced representation $\{\mathbf{z}^e, T, \mathbf{r}\}$ is used, and hence these three methods can be compared directly. In QSSA, on the other hand, the reduced representation is $\{T, \mathbf{r}\}$, with no information about the elemental composition of the unrepresented species. As a consequence, the comparison with QSSA is somewhat less direct. For H_2/air , we consider a standard QSSA method [15] with 7 major (i.e., non-steady-state) species: H_2 , O_2 , H_2O , H , OH , O and N_2 . The steady-state-assumption is applied to the two minor species HO_2 and H_2O_2 . Given that there are 3 elements in the system, the dimensionality of the low-dimensional manifolds of the QSSA method is also $7-3=4$. With the values of the major species specific moles being taken from \mathbf{z}^P , the minor species are reconstructed from the quasi-steady state approximation. (This specification for the major species favors QSSA in later comparisons because of the omission of errors in two additional species, OH and O .) For CH_4/air , we consider ARM1 [16] which has 16 major species. Given that there are 4 elements, the dimensionality of the low-dimensional manifolds of ARM1 is also 12.

Let \mathbf{z}^M denote the reconstructed species specific moles using one of the four methods (i.e., \mathbf{z}^M is one of \mathbf{z}^{ICE} , \mathbf{z}^{CEM} , \mathbf{z}^{ILDM} or \mathbf{z}^{QSSA}). Then we define the normalized species-reconstruction error as

$$\varepsilon_z = 2 \times |\mathbf{z}^M - \mathbf{z}^P| / (|\mathbf{z}^M| + |\mathbf{z}^P|), \quad (12)$$

where $|\mathbf{z}|$ denotes the 2-norm.

Figure 1 shows the reconstruction errors for different methodologies for H_2/air system. Considering first temperatures above 705K, it is readily observed that CEM incurs much larger errors than all other methods with a peak of $\varepsilon_z^{CEM} = 0.016$ at $T = 1480K$. In this range ($T > 705K$), all other methods yield small errors (less than 2.8×10^{-4}), with ε_z^{ICE} being very similar to ε_z^{ILDM} . Below 705K, the ILDM does not exist, while QSSA yields large errors ε_z^{QSSA} as the low-temperature boundary is approached ($T = 300K$). On the other hand, for ICE-PIC and CEM the error are here well controlled. This is because the specific moles of elements in the unrepresented species are very small, and hence the specific moles of the unrepresented species are small, thus limiting the maximum possible error. In contrast, in QSSA, spuriously large values of minor species can occur. Of the species reconstruction methodologies that succeed over the entire temperature range, ICE-PIC yields the smallest maximum error: over the whole range ε_z^{ICE} is less than 3×10^{-4} .

Figure 2 shows the reconstruction errors for different methodologies for the CH_4/air flame. (Remember that this comparison favors QSSA because of the omission of errors in some major species.) It is readily observed that ICE-PIC incurs smaller errors than CEM over the entire temperature range, especially when $T > 600K$. For the same reasons, below 900K, QSSA yields large errors ε_z^{QSSA} as the low-temperature boundary is approached ($T = 300K$). On the other hand, for ICE-PIC and CEM the error are here well controlled. Over the entire temperature range, ICE-PIC yields the smallest maximum error: over the whole range ε_z^{ICE} is less than 2.4×10^{-4} .

5 Discussion and Conclusion

The recently developed ICE-PIC method is tested for premixed laminar flames of both hydrogen/air and methane/air mixtures. For the H_2/air flame, with four represented species, H_2 , O_2 , H_2O and H , the ICE-PIC method reconstructs the full composition accurately compared with the results obtained by PREMIX with the detailed mechanism [13]. The normalized error ε_z in the reconstructed composition by the ICE-PIC method is less than 3×10^{-4} . For the CH_4/air flame, with 12 represented species, the ICE-PIC method reconstructs the full composition accurately with normalized error ε_z less than 2.4×10^{-4} over the entire temperature range.

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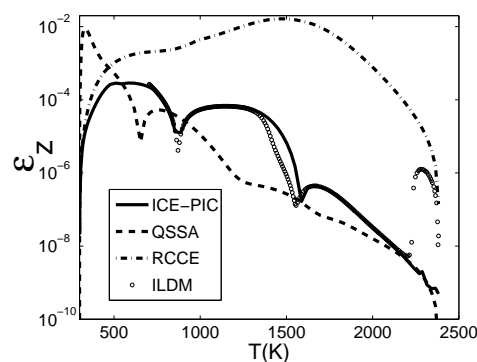


Figure 1: Normalized errors (Eq. 12) in reconstructed compositions for H_2/air premixed flame.

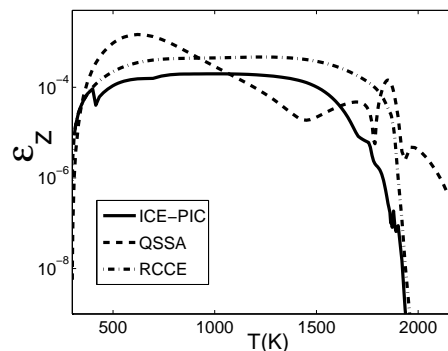


Figure 2: Normalized errors (Eq. 12) in reconstructed compositions for CH_4/air premixed flame.