Simplifying plasma chemistry via ILDM

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Abstract. A plasma fluid model containing a large number of chemical species and reactions yields a high computational load. One of the methods to overcome this difficulty is to apply Chemical Reduction Techniques as used in combustion engineering. The chemical reduction technique that we study here is ILDM (Intrinsic Lower Dimensional Manifold). The ILDM method is used to simplify an argon plasma model and then a comparison is made with a CRM (Collisional Radiative Model).

1. Introduction

Plasma sources are used extensively for the purpose of surface treatment of materials[1], semiconductor manufacturing[2], fluorescent lamps for lighting[3], growth of thin film solar cells[4], and biomedical applications like skin treatment[5]. These plasma sources contain a large number of chemical species and reactions. A numerical description of these plasma models is given by solving the coupled set of partial differential equation. These equations are spatio-temporal continuity equations, namely mass, momentum, and energy conservation. A complete simulation to study the behaviour of the system involves the solution of all the equations for each species present in the system simultaneously. The numerical solution becomes challenging if the model has a large number of species and reactions. An example of such a plasma fluid model is the conversion of methane into higher hydrocarbons containing 36 species and 367 gas phase reactions[6]. These types of plasma models containing a large number of species and reactions makes the computation expensive. In addition to the high computational cost and time the data generated from these simulations is massive and the interpretation of results becomes difficult. A branch of science that deals with the same problem of chemical complexity alongside plasma science is combustion research. One of the examples from combustion research is the modelling of a 1-D laminar flame[7]. To overcome the difficulty associated with chemical complexity, the combustion community employs various chemical reduction techniques. Some examples of chemical reduction techniques are ILDM (Intrinsic Lower Dimensional Manifold) [7], TGLDM (Trajectory Generated Lower Dimensional Manifold) [8], FGM (Flamelet Generated Manifold) [9], and PCA (Principle Component Analysis) [10].

In this study we apply the ILDM technique to simplify plasma chemistry. The ILDM technique uses the fact that a reaction system containing a large number of species has widely varying time scales for the evolution of different species in the system. A system of chemical reactions can be studied by taking a fewer number of slow reactions, from a

complete set of reactions occurring in a system. Other reactions are so fast that the change in the system due to the fast reactions occurs quickly.
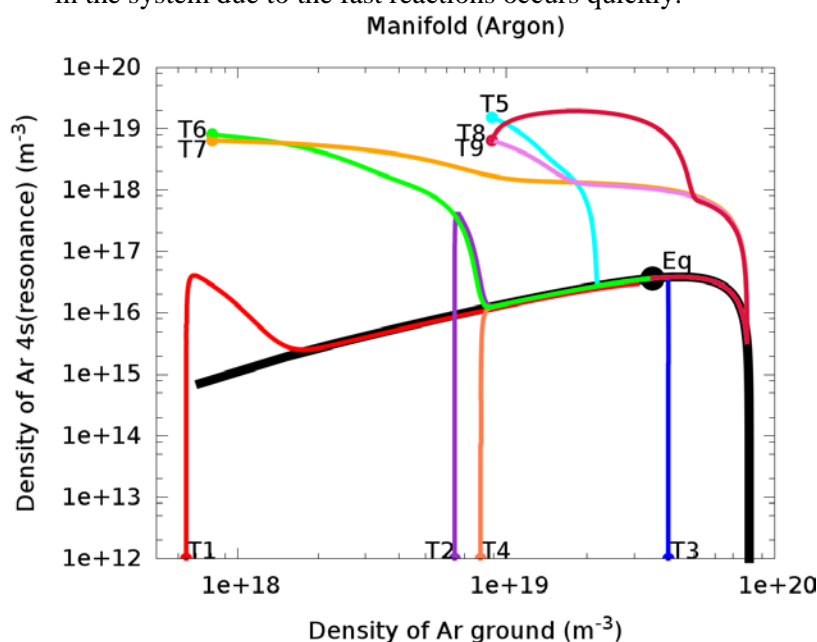
Figure 1. The time evolution of the state in the composition space for an argon plasma simulated with 5 distinct species. Each line (T1 to T9) represent a trajectory with distinct initial condition. The trajectories do not cross each other. It appears as though trajectories are crossing because it is a projection of a 6D composition space (5 species and electron) on a 2D plane. The trajectories first move to a 1D manifold (shown in black) and then along the manifold to the equilibrium point (labelled as Eq).

The fast time scale reactions can be considered in the steady state and the full description of the system can be given by the slow time scales without any significant loss in chemical kinetics description. Taking into account the difference in time scales, the ILDM method finds a lower dimensional space inside the complete composition space. After a short interval of time the fast time scale processes will quickly move towards this lower dimensional manifold and the slow time scale processes will move tangential or along the manifold to finally reach the equilibrium point as shown in figure 1. All the trajectories quickly move towards a line (shown in black) and then along that line to the equilibrium point (labeled as Eq in the figure 1). The line on which the trajectories bundle together is the one-dimensional manifold. Identification of the low dimensional manifold allows the decoupling of fast and slow time scales. Once the fast time scales have attained partial equilibrium, the full system description is given accurately by the lower dimensional manifold.

The advantage of ILDM over other conventional techniques like QSSA (Quasi steady state assumption) is that the ILDM technique automatically extracts the required information from the full system description. The only input required for ILDM is the set of user defined parameters and the dimension of the manifold. It is not dependent on the so called *experience* or *intuition* of the modeler to distinguish the slow and fast time scales. By constructing a lower dimensional manifold the reaction space is defined in terms of a few parameters. It becomes possible to tabulate the results in terms of those few parameters. Once the data is tabulated in the form of a look up table, the continuity equations are solved for only a few parameters and the remaining values are given explicitly. In addition the ILDM method also reduces the stiffness present in the system. Once the stiffness is reduced, there is a speed up in the computation and longer times can be reached. In this paper the ILDM method is applied to generate a manifold for an argon model containing five levels. The effect of transport is not taken into account.

2. Mathematical description of ILDM

The mathematical model[7] for a system consists of a set of $N = n_s + 2$ equations, that is n_s species balances and 2 equations that define temperature and pressure. The species balances are given as

$$\frac{\partial \mathbf{n}}{\partial t} = \mathbf{S}(\boldsymbol{\psi}), \tag{1}$$

where $\boldsymbol{\psi} = (T, P, \mathbf{n})$ with T the temperature, P the pressure, $\mathbf{n}$ the set of densities for n_s species, and $\mathbf{S}$ the source term. For each point in the state space the eigenvalues of the Jacobian of the source term give the time scale of the movement in the space. The eigenvectors define the characteristic direction associated with the time scale. The Jacobian of the source term is

$$J_{ij} = \frac{\partial \mathbf{S}_i}{\partial \boldsymbol{\psi}_j}. \tag{2}$$

The eigenvalues and eigenvectors are obtained from diagonalization of the Jacobian matrix J.

$$J = V \Lambda V^{-1}, \tag{3}$$

where V is the eigenvector matrix and Λ is the diagonal matrix with eigenvalues as the diagonal element. Eigenvalues are related to the time scale of the process given as

$$t_i = \frac{1}{\lambda_i}. \tag{4}$$

If any chemical reaction system is given a small perturbation there are four possibilities of how that system will react depending on the nature of eigenvalue of the Jacobian matrix obtained from equation (2). For a real and positive eigenvalue, the perturbation increases and for a real and negative eigenvalue, the perturbation decreases. If the eigenvalue is 0 the perturbation does not change with time. Perturbation due to imaginary eigenvalue has an oscillating nature. The amplitude of oscillation increases, decreases or remains constant, depending on whether the real portion of the eigenvalue is positive, negative or 0 respectively.

Diagonalization is not always possible for a given Jacobian matrix. In many cases the Jacobian matrix will contain repeated eigenvalues. The presence of repeated eigenvalues can lead to linearly dependent eigenvectors, and inversion of the eigenvector matrix is not possible. The problem of diagonalization can be solved by using another basis namely, a basis of Schur vectors denoted as Q. The Schur decomposition of the Jacobian is given as

$$Q^T J Q = M, \tag{5}$$

where M is an upper triangular matrix with eigenvalues on the diagonal arranged in descending order of magnitude, and Q^T is the transpose of the Schur vector matrix. The Schur vectors give the characteristic direction associated with the particular time scale. The fast Schur vectors are perpendicular to the manifold. All the Schur vectors are orthogonal to each other in the N dimensional space, hence the slow Schur vectors are parallel to the manifold. The equation of the manifold is defined as the dot product of source vector with the fast Schur vectors.

$$Q_f^T \cdot \mathbf{S}(\boldsymbol{\psi}) = \mathbf{0}, \tag{6}$$

where Q_f^T is the matrix consisting of fast Schur vectors. The fast Schur vector matrix is formed by neglecting the $n_C + n_P$ rows of the Schur vector matrix from the top. n_C is the number of conserved quantities like elements, total number of particles, and charge. n_P is the number of user defined parameters. The numbers of user defined parameters, defines the number of dimensions of the manifold. So we need additional $2 + n_C + n_P$ equations to complete the set of N equations.

The remaining equations are given as

1. Temperature

$$T - T_{ref} = 0. \tag{7}$$

2. Pressure

$$P - \sum n_i k_B T = 0. \qquad (8)$$

3. Conservation equations (n_C) for elements

$$f(\chi_i) - \tau_i = 0, \qquad (9)$$

where $f(\chi_i)$ is the function for calculating the total number of element χ in the system from all the species present in the system. If the electrons and the charged species are present an additional equation for quasineutrality is added to the elemental conservation equations.

4. Parameter equation (n_P)

$$\varphi_i - p_i = 0, \qquad (10)$$

where φ refers to the parameter and p is the value of the parameter. The parameter is the density of the species. The choice of the parameter and the number of parameters are user defined.

3. Application of ILDM to an argon plasma

The ILDM method is applied to generate the manifold for an argon system[11]. The argon plasma that we study contains 5 levels: the ground level (Ar), 4s metastable ($Ar(4s)^m$), 4s resonance ($Ar(4s)^r$), 4p ($Ar(4p)$) and ion level(Ar^+). The temperature of the electrons is 3 eV and the temperature of the heavy particles is 600 K. The pressure of the background gas is 5 mTorr. The density of electrons is calculated from quasineutrality. The reactions are mainly excitation, de-excitation and ionization as given in table 1.

Table 1. Table showing the rate coefficient for argon system as taken from [11]

Reactions	Rate Coefficient
$Ar + e \rightarrow Ar(4s)^r + e$	$5.00 \cdot 10^{-15}\ Te^{0.74} \exp(-11.56/Te)$
$Ar + e \rightarrow Ar(4s)^m + e$	$5.00 \cdot 10^{-15}\ Te^{0.74}\ \exp(-11.56/Te)$
$Ar(4s)^r + e \rightarrow Ar + e$	$4.30 \cdot 10^{-16}\ Te^{0.74}$
$Ar(4s)^m + e \rightarrow Ar + e$	$4.30 \cdot 10^{-16}\ Te^{0.74}$
$Ar + e \rightarrow Ar(4p) + e$	$1.40 \cdot 10^{-14}\ Te^{0.71} \exp(-13.20/Te)$
$Ar(4p) + e \rightarrow Ar + e$	$3.90 \cdot 10^{-16}\ Te^{0.71}$
$Ar(4s)^r + e \rightarrow Ar(4p) + e$	$8.90 \cdot 10^{-13}\ Te^{0.51} \exp(-1.59/Te)$
$Ar(4s)^m + e \rightarrow Ar(4p) + e$	$8.90 \cdot 10^{-13}\ Te^{0.51}\ \exp(-1.59/Te)$
$Ar(4p) + e \rightarrow Ar(4s)^r + e$	$3.00 \cdot 10^{-13}\ Te^{0.51}$
$Ar(4p) + e \rightarrow Ar(4s)^m + e$	$3.00 \cdot 10^{-13}\ Te^{0.51}$
$Ar + e \rightarrow Ar^+ + e$	$2.30 \cdot 10^{-14}\ Te^{0.68} \exp(-15.76/Te)$
$Ar(4s)^r + e \rightarrow Ar^+ + 2e$	$6.80 \cdot 10^{-15}\ Te^{0.67} \exp(-4.20/Te)$
$Ar(4s)^m + e \rightarrow Ar^+ + 2e$	$6.80 \cdot 10^{-15}\ Te^{0.67} \exp(-4.20/Te)$
$Ar(4p) + e \rightarrow Ar^+ + 2e$	$1.80 \cdot 10^{-13}\ Te^{0.61} \exp(-2.61/Te)$
$Ar(4s)^m + e \rightarrow Ar(4s)^r + e$	$2.00 \cdot 10^{-13}$
$Ar(4s)^r \rightarrow Ar + h\upsilon$	$3.00 \cdot 10^{7}$
$Ar(4p) \rightarrow Ar + h\upsilon$	$3.20 \cdot 10^{7}$

Te is the electron temperature in eV and $h\upsilon$ is the energy released.

The equations used for generating a 1D manifold for the argon system are

1. Since the temperature and pressure are constant for the system, the total number of particles is constant. The total amount of argon in the system will remain constant.

2. The plasma is electrically neutral hence the charge conservation equation can be written as

$$\sum e\mu_i n_i - en_e = 0, \qquad (11)$$

where e is the electron charge, n_i is the density of the ion species i and μ_i is the charge number of the ion species i. (for electrons $\mu = -1$)

3. Since we are generating a 1D manifold, there is one user defined parameter. The parameter can be any of the species densities as given in equation (10).
4. The remaining equations are given by the manifold equation (6) as described in section 2.

A 1D manifold can be constructed for an argon plasma as shown in figure 1.

4. Collisional Radiative Model for an argon plasma

A Collisional Radiative Model[12] takes into account the processes of electron collision and radiative transition for the change of state of an atom. All the species in the CRM are classified into two types: Transport Sensitive (TS) and Local Chemistry (LC) [13]. The levels in which the time scales of the chemical processes are comparable to the time scales of transport are termed as the transport sensitive levels. The levels in which the chemical processes are much faster than the transport are termed as the local chemistry levels. Since the chemical processes are very fast, the local chemistry levels can be assumed to be in quasi-steady state. Transport sensitive species are typically the ground and the ion species. The intermediate species are termed as local chemistry species. If the system is linear the source term can be written as

$$\mathbf{S} = \mathbf{F} \cdot \mathbf{n}, \qquad (12)$$

where $\mathbf{S}$ is the source term, F is the Jacobian matrix and $\mathbf{n}$ is the density vector. The source term is split into TS and LC levels.

$$\begin{pmatrix} \mathbf{S_t} \\ \mathbf{S_l} \end{pmatrix} = \begin{pmatrix} \mathbf{F_{tt}} & \mathbf{F_{lt}} \\ \mathbf{F_{tl}} & \mathbf{F_{ll}} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{n_t} \\ \mathbf{n_l} \end{pmatrix} \qquad (13)$$

The local chemistry species are assumed to be in a quasi-steady state. Hence, the source term for LC species is 0 and the density of LC species can be expressed in terms of TS species as

$$\mathbf{n_l} = -\left(\mathbf{F_{ll}^{-1}} \cdot \mathbf{F_{tl}}\right) \cdot \mathbf{n_t} \qquad (14)$$

Substituting the density of LC species from equation (14), the source term for TS species can be given as

$$\mathbf{S_t} = (\mathbf{F_{tt}} \cdot \mathbf{n_t}) - \left(\mathbf{F_{lt}} \cdot \mathbf{F_{ll}^{-1}} \cdot \mathbf{F_{tl}} \cdot \mathbf{n_t}\right) \qquad (15)$$

The source for TS species in equation (15) has two terms. The first term in the equation denotes the direct transition between the ion and the ground level. The second term represents the step wise processes of excitation/de-excitation and ionization/de-ionization through the local chemistry levels.

5. Comparison of CRM and ILDM for an argon plasma

CRM is a commonly used reduction technique for plasma chemistry. In case of CRM there is no mass conservation. For comparison of the manifold of ILDM with CRM the mass conservation is not taken into account (unlike as in section 3). The only equations are charge conservation and parameter equations. The ground density is kept fixed to a constant value as it is high compared to the density of intermediate species and the ion density. The ion density is taken as the parameter. The ILDM manifold is found from equation (6). The manifold of CRM is given by equation(14). The result of the comparison of manifold between ILDM and CRM shows a good agreement for the argon system considered here. The ILDM method can be used to simplify the plasma chemistry.
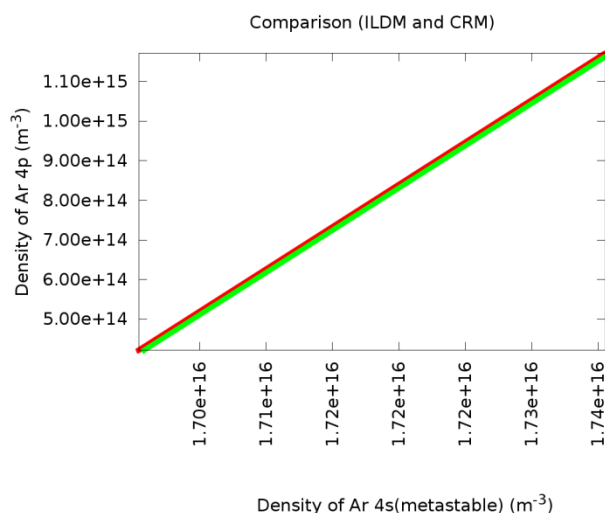
Figure 2. Comparison of the manifold for five species argon model as found from CRM (red) and the ILDM (green). The plot is a projection of 6D composition space on a 2D plane represented by the density of 4s metastable state and 4p state of argon. Similar projections can also be drawn on a different plane represented by different states of argon.

6. Conclusion

A manifold is generated using ILDM for an argon plasma containing two temperatures. The manifold was also compared with another reduction technique used in plasma modelling that is CRM which relies on quasi steady state assumption. The ILDM method has the advantage of being a mathematical technique that separates the slow from the fast reaction. The manifold is described by a look up table as discreet points. Once the look up table is generated the continuity equations are solved for fewer species and the values of the rest of the species are read directly from the table. Thus the computational costs are reduced by using the reduction techniques like ILDM.

7. References

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