On air-chemistry reduction for hypersonic external flow applications

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ABSTRACT

In external hypersonic flows, viscous and compressibility effects generate very high temperatures leading to significant chemical reactions among air constituents. Therefore, hypersonic flow computations require coupled calculations of flow and chemistry. Accurate and efficient computations of air-chemistry kinetics are of much importance for many practical applications but calculations accounting for detailed chemical kinetics can be prohibitively expensive. In this paper, we investigate the possibility of applying chemical kinetics reduction schemes for hypersonic air-chemistry. We consider two chemical kinetics sets appropriate for three different temperature ranges: 2500 K to 4500 K; 4500 K to 9000 K; and above 9000 K. By demonstrating the existence of the so-called the slow manifold in each of the chemistry sets, we show that judicious chemical kinetics reduction leading to significant computational savings is possible without much loss in accuracy.

1. Introduction

Hypersonic boundary layers encounter high temperature conditions triggering vibrational excitation, chemical reactions and ionization of air constituents. These thermochemical processes can substantially modify the transition and subsequent breakdown to turbulence in hypersonic flows. Therefore, it is critical that hypersonic external flow calculations accurately account for flow-thermochemical interactions. In many problems of interest, accurate calculations of flow-thermochemistry interactions are rendered difficult by a wide range of thermochemical and flow timescales. Fig. 1 shows the range of fluid and chemistry timescales in a typical combustion environment. In general, chemistry timescales span a wider range than those of the flow. If all of the chemistry scales are slow than that of the flow then it is reasonable to invoke the frozen-chemistry approximation. At the other extreme, if all of the chemistry scales are faster than the flow scales, then equilibrium-chemistry is the appropriate simplification. In many practical flows, the fluid and thermochemical timescales can potentially overlap ruling out the simple assumptions of *frozen* or *equilibrium* thermochemistry. Such situations call for detailed nonequilibrium calculations, which would add substantial computational burden to the parent computational fluid dynamic (CFD) simulations. In hypersonic flows, these computations could prove to be even more challenging as this overlap can substantially change in time and space owing to a wider range of flow velocity and temperatures

prevalent across the flow field. The highly disparate thermochemical timescales introduce severe computational stiffness into the flow solver. It is highly desirable to develop appropriate chemistry reduction methods which can reduce the computational burden without significantly compromising the accuracy of the flow solution (Peeters and Rogg, 1993; Smooke, 1992; Maas and Pope, 1992). Much progress toward chemistry reduction has been made in the field of combustion. Quasi-steady state assumption (QSSA, (Maas and Pope, 1992)), intrinsic low-manifold method (ILDM, (Maas and Pope, 1992)) and the locally linear assumption (LLA, (Girimaji and Ibrahim, 2014)) are some of the reduction techniques that have been developed and applied to air–fuel mixtures (Maas and Pope, 1992; Skrebkov and Karkach, 2007) and atmospheric pollutant chemistry (Tomlin et al., 2001). However, application of these reduction methods has the pre-condition that a *slow lower-dimensional manifold* must inherently exist in the chemical kinetic system under consideration.

Presence of vibrational non-equilibrium and endothermic reactions make a hypersonic external flow air chemistry fundamentally different from an internal combustion flow chemistry, wherein vibrational nonequilibrium is less important and reactions are mainly exothermic. Thus the existence of slow manifolds in nonequilibrium reacting air mixture cannot be taken for granted, and their existence must be clearly demonstrated before any reduction method can be applied. With this motivation, the objective of this work is to examine if the same combustion chemical kinetics strategies can be utilized for reducing the computational burden – stemming from thermochemical non-equilibrium – of large scale

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n_s	total number of species	T	temperature, K
v'_{ji}	stoichiometric coefficient of the ith species in the jth forward reaction	K_{eq_j}	equilibrium constant for the jth reaction
v''_{ji}	stoichiometric coefficient of the ith species in the jth reverse reaction	c_{p_i}	specific heat of the ith species at constant pressure, J kg^{-1} K^{-1}
ς_i	chemical symbol of the ith species	h	enthalpy, J
n_r	total number of reactions	P	pressure, atmosphere
t	time, s	h_i	specific enthalpy of the ith species, J kg^{-1} K^{-1}
w_i	mass production-rate of the ith species, kg m^{-3} s^{-1}	R_i	gas constant, J kg^{-1} K^{-1}
M_i	molecular weight of the ith species	h_i^o	zero-point specific enthalpy of the ith species, J kg^{-1} K^{-1}
K_{fj}	forward reaction rate coefficient for the jth reaction	R	universal gas constant, J mol^{-1} K^{-1}
ρ	density, kg m^{-3}	e_{vib}^{eq}	equilibrium vibration energy
Y_i	mass fraction of the ith species	$\hbar$	Planck's constant
K_{bj}	backward reaction rate coefficient for the jth reaction	v	fundamental vibration frequency
		τ	vibration relaxation time

hypersonic boundary layer transition and turbulence calculations. Toward this objective we (i) first demonstrate the existence of attracting slow manifolds in the hypersonic reacting air mixture, and subsequently (ii) evaluate the performance of the QSSA method in approximating these reduced slow manifolds at different temperature ranges.

This paper is organized into five sections. In Section 2, we discuss the detailed chemical kinetic sets and describe the flow-thermodynamic system of high temperature air mixture examined in this study. In addition, we introduce the perfectly-stirred reactor simplification and the governing equations of chemical species evolution. In Section 3, the reduction of general dynamical systems is described and applied to homogeneous perfectly-stirred reactor system. In Section 4, we establish the existence of slow manifold of the air-chemistry kinetics and demonstrate that QSSA performs adequately in capturing this manifold. The final section provides a brief summary.

Preliminary results of the reduction of simple air-chemistry reaction set valid at low-to-moderate temperatures have been presented in an AIAA conference paper – Suman et. al. (Suman et al., 2011). In the present paper we present a more detailed theoretical development and investigate the reduction of realistic detailed reaction sets at three different temperature regimes encountered in hypersonic flight.

2. Chemical kinetics

Atmospheric air undergoes different thermochemical events depending on the resident temperature (Fig. 2). Below 800 K rotational and translational modes are the only major modes of internal energy of air. Above 800 K diatomic molecules start to vibrate which, depending on the flow conditions, may or may not be in equilibrium with local thermodynamic conditions. Above 2500 K oxygen molecules start to dissociate and this phenomena is complete by 4000 K. Around the same temperature N_2 begins to dissociate and by 9000 K all Nitrogen molecules are fully dissociated into the constituent atoms. Around 9000 K, ionization commences. In this work, we consider thermochemical (chemical and vibrational) non-equilibrium air mixture over a temperature range of 2500–10,000 K. We categorize our study into various sub-ranges of temperature (see Table 5). In the low and mid temperature ranges (2500–4500 K and 4500–9000 K), we use an air mixture model comprising of 5 species and 17 reactions. On the other hand, in the high temperature range (above 9000 K) we use an air mixture model comprising of 7 species and 24 reactions to appropriately include the ionization physics. Further, to include the vibrational non-equilibrium effects, we employ the Landau-Teller relaxation model (Anderson, 1989).

2.1. Flow and thermodynamic equations

For a chemically reactive flow, the species mass conservation equation is:

$$\frac{\partial Y_i}{\partial t} + u_j \frac{\partial Y_i}{\partial x_j} = \frac{w_i}{\rho} + D_i, \tag{1}$$

where Y_i is the mass fraction of species i, u_j is the j component of the velocity field, w_i is the mass production-rate of species i and D_i is diffusion. The velocity field u_j is governed by compressible Navier–Stokes equations.

The total enthalpy of the mixture h and pressure P are related to species mass fractions (Y_i) through the following relationships:

$$h = \sum_i^{n_s} h_i Y_i \tag{2}$$

and the ideal gas law

$$P = \rho R T \sum_i^{n_s} \frac{Y_i}{M_i}. \tag{3}$$

The calculations of the species mass production-rate w_i involve computing reaction rates which, in turn, are highly dependent on temperature. Therefore, the chemistry timescales are influenced by temperature and they cover a wider range relative to the flow timescales. When the flow timescales and the chemistry timescales are of the same order of magnitude, then there is a need for detailed
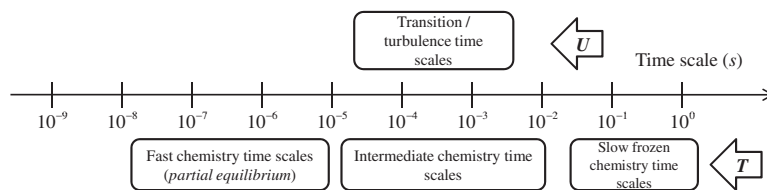

Fig. 1. Typical fluid and chemistry timescales in a combustion environment (adapted from Maas and Pope (1992)). U and T represent velocity and temperature.