Oral presentation | Incompressible/compressible/hypersonic flow Incompressible/compressible/hypersonic flow-IV Thu. Jul 18, 2024 2:00 PM - 4:00 PM Room D

# [11-D-04] Assessment of a Consistent Multi-temperature Kinetic Model for Hypersonic Neutral Air Flows using a High-orderaccurate Finite Volume Solver

\*Giuseppe Pascazio<sup>1</sup>, Davide Ninni<sup>1</sup>, Antonio Narracci<sup>1,3</sup>, Gianpiero Colonna<sup>2</sup>, Francesco Bonelli<sup>1</sup> (1. Politecnico di Bari, 2. Istituto per la Scienza e Tecnologia dei Plasmi, 3. Università del Salento) Keywords: Hypersonic flow, Thermochemical non-equilibrium, Reduced kinetic model

# Assessment of a Consistent Multi-temperature Kinetic Model for Hypersonic Neutral Air Flows using a High-order-accurate Finite Volume Solver

G. Pascazio<sup>\*</sup>, D. Ninni<sup>\*</sup>, A. Narracci<sup>\*,\*\*\*</sup>, G. Colonna<sup>\*\*</sup>, and F. Bonelli<sup>\*</sup> Corresponding author: giuseppe.pascazio@poliba.it
\* Politecnico di Bari, via Re David 200, 70125 Bari, Italy

 $^{\ast\ast}$ Istituto per la Scienza e Tecnologia dei Plasmi, Via Amendola, 122/D, 70126 Bari, Italy

\*\*\* Università del Salento, Centro Ecotekne - S.P. 6, Lecce - Monteroni, Lecce, Italy

#### Abstract:

A multi-temperature approach for hypersonic air kinetics has been consistently derived from the state-specific vibrational kinetics. Vibrational levels have been grouped in a limited number of subsets (one to three), each one characterized by its own concentration and temperature, approximating the entire distribution as a piecewise Boltzmann. The reduced model has been tested in 0D evolution comparing with the state-to-state approach. The model has been implemented in a finite volume solver of the Euler equations, employing a Flux Vector Splitting scheme with either MUSCL or hybrid WENO/central-difference reconstruction, used to solve an axial-symmetric flow past a sphere.

Keywords: Thermochemical non-equilibrium, State-to-State kinetics, Reduced-order model

# 1 Introduction

Nowadays, space exploration is encountering a renewed interest in the academic aerospace community in virtue of relevant investments by the industrial private sector as well as by space agencies. Costs and success of a space mission depend on several scientific and technological aspects that are the subjects of intense research and development activities. In this context, a critical issue is represented by the accurate characterization of the complex aerothermodynamic environment around a vehicle entering planetary atmospheres. In particular, the accurate evaluation of the extremely high heat load on the vehicle surface during its atmospheric entry is necessary in the view of an appropriate design of the vehicle thermal protection system. In fact, considering the continuum regime of the atmospheric entry, the flow past the vehicle is characterized by extremely high values of the velocity (of the order of 10 km/s, leading to the formation of a strong bow shock in front of the body [1, 2]. Across the bow shock enveloping the vehicle the huge kinetic energy of the flow is converted into internal energy with translational temperature reaching very high values (of the order of 10000 K), causing dissociation and ionization and progressively exciting vibrational and electronic states [3]. A plethora of phenomena arise: vibrational and electronic modes are excited, dissociation and ionization occur, as well, and free electrons absorb radio waves causing communication blackout. In this scenario, local thermodynamic and chemical equilibrium hypotheses are no longer valid [3]. Indeed, just downstream of the bow shock the fluid dynamic characteristic time is of the same order as internal energy transfer and chemical processes, thus the flow is in thermochemical non-equilibrium. Close to the vehicle surface, the translational temperature decreases to reach the wall value, forming a thermal boundary layer. Here, due to the large gradients, the flow meets non-equilibrium conditions again [4, 5, 6, 7], along with surface interaction phenomena, such as catalysis [4, 8], and ablation [9, 10].

With the aim of developing strategies and models to accurately reproduce hypersonic flight conditions, several approaches have been devised to properly account for thermal and chemical non-equilibrium. One of the most popular approaches is the multitemperature model proposed by Park [11], considering each energy mode associated to different temperatures, namely translational (tr), rotational (rot), vibrational (vib), and electronic (el). Normally, the first two are assumed to be at equilibrium  $(T_{tr} = T_{rot} = T_{gas})$ , whereas vibrational and electronic modes are usually considered at equilibrium at a different vibrational temperature  $(T_{vib} = T_{el})$ . This approach, known as two-temperature model [11, 12], is then closed

by assuming a Boltzmann distribution to describe the internal state population for the energy levels, the exchange between energy modes being modelled using the cheap Landau-Teller approach with a relaxation time tuned on experiments. This results in a relatively cheap and easy to implement model and is being extensively employed to simulate hypersonic flows [13, 14, 15, 16, 4, 17, 18]. On the other hand, recent studies have shown that the use of a fundamental molecular kinetics has an important impact on the prediction of macroscopic properties of high-enthalpy flows [19]. In fact, the distribution for the vibrational mode often differs from the Boltzmann one, resulting in large deviations of the rate coefficients of chemical processes from the Arrhenius law [20] and thus providing non satisfactory predictions under certain conditions, such as boundary layer [21, 22, 23] and across shock waves [24, 25, 19, 26]. To overcome this problem, a more fundamental molecular kinetics model must be employed, such as the vibrationally resolved state-to-state (StS) approach. The StS approach, treating all the vibrational levels of molecules as a separate species, evolving according to internal relaxation and chemical processes [20, 27], is able to evaluate internal distributions without any assumption [28]. The increased accuracy of such an approach comes however with a relevant increase of the computational cost, due to the large number of species and processes involved with respect to the multi-temperature approach, thus preventing the applications of StS models in the cases of 2D and 3D configurations. As an example, a macroscopic model describes a neutral air mixture by considering five species (N<sub>2</sub>, O<sub>2</sub>, NO, N, O), 17 reactions and three vibrational temperatures, whereas a vibrationally resolved StS approach requires hundreds of species and thousands of processes. For this reason, the application of the StS model has been usually limited to simple 0D/1D configurations [5, 6, 29, 30], with few 2D/3D exceptions [31, 19, 8, 26, 32, 33]. However, with the availability of StS data, an effective way to reduce the computational cost while maintaining the accuracy of the detailed model is to employ consistent reduced order models. Following this idea, several authors have proposed reduced models built using StS data [34, 35, 36]. Indeed, a generic vibrational resolved StS distribution [19] seems to show a piecewise equilibrium behaviour. Thus, it is possible to reduce the number of vibrational levels by clustering them into N groups, each characterized by a Boltzmann distribution at its own vibrational temperature. Energy exchange and dissociation/recombination rates are computed self-consistently, from the rate coefficients of the full vibrationally resolved StS database. Such a multi-internal-temperature approach, recently developed in the literature (Guy et al. [37] and Munafò et al. [38]) is extended here to a five species neutral air mixture. The new consistent multitemperature model, referred to in the following as mT, is implemented in a finite volume flow solver of the Euler equations using a Flux Vector Splitting scheme with MUSCL reconstruction. In order to extend the code capabilities to solve flows involving both shock waves and turbulence, a hybrid WENO/centraldifference scheme is also implemented [39]. In particular, a fifth-order WENO scheme [40] is used in conjunction with a sixth-order central scheme with a shock sensor that limits the use of the shock capturing scheme to region of strong gradients. The resulting method, already verified by the authors in one-dimensional thermochemical non equilibrium test cases [41], is a unique tool in the present scene.

The manuscript is organized as follows: in section 2, the governing equations for a reacting mixture in thermochemical non-equilibrium are illustrated, together with the numerical and computational approaches employed; section 3 describes the thermochemical non-equilibrium models; lastly, numerical results are discussed in section 4, whereas conclusive remarks are drawn in section 5.

# 2 Fluid dynamic model

## 2.1 Governing Equations

The simulation of hypersonic flows in the continuum regime is carried out by solving the Euler equations for a reactive multicomponent mixture. In integral form, the governing equations read

$$\int_{V_0} \frac{\partial}{\partial t} \mathbf{U} dV + \oint_{S_0} \mathbf{F} \cdot \mathbf{n} dS = \int_{V_0} \mathbf{W} dV \tag{1}$$

where  $V_0$  and  $S_0$  indicate the generic control volume and surface, respectively. **U** is the vector of conservative variables, whereas **F** and **W** are fluxes and source terms. Such vectors assume different forms depending on the thermochemical model employed, either mT or StS. For 2D axis-symmetric flows  $\mathbf{F} = (\mathbf{F}^x, \mathbf{F}^y)$ , x and y indicating the axial and radial coordinates, respectively, and for the case of neutral air mixture discussed in this manuscript, the vectors read:



3 ICCFD12



The number of species is  $N_s = 5$  for both the mT and the StS model (N<sub>2</sub>, O<sub>2</sub>, NO, N, O). Indeed, in the vibrationally resolved StS approach, each level is considered as a pseudo-species, thus the generic species s is characterized by a vibrational energy quantized by  $V_s$  vibrational states, likewise the partial densities of each level. Hence, subscripts s and l indicate the s-th species and the l-th vibrational state  $(V_{N_2} = 68, V_{O_2} = 47 \text{ and } V_{NO} = V_N = V_O = 1)$ . For the proposed mT model, the vibrational energy distributions of molecules  $N_2$  and  $O_2$  are described by a group of Boltzmann functions each one with its own vibrational temperature. The number of groups is indicated with  $v_m$  for the generic molecule m, with the exception of NO  $(v_{NO} = v_N = v_O = 1)$ , allowing one to maintain for the species the same nomenclature as the StS model substituting  $V_s$  with  $v_s$ . Therefore,  $\rho_s = \sum_l \rho_{s,l}$  and  $\rho = \sum_s \rho_s$ give the density of the s-th species and the fluid density, respectively. The number of groups in the mT model affects the accuracy of the reduced model; in the applications presented in this work groups equal to 3 provide accurate results. Flow velocity components in the axial, x, and radial, y, directions are given by u and v, respectively, whereas p is the thermodynamic pressure. E and  $\varepsilon$  represent the specific total and vibrational energies, being rotational state at equilibrium at T. Concerning the source terms,  $\dot{\omega}_{ax} = \frac{p - \sigma_{\theta,\theta}}{n}$  is considered to account for the axial symmetry of the body, being  $\theta$  the tangential coordinate in the cylindrical reference system. Of course, this term is null for planar geometries.

In order to close the system of governing equations, the perfect gas [42] assumption is employed to link p and E:

$$p = (\bar{\gamma} - 1) \left[ \rho E - \rho \left( \varepsilon_{vib} + \varepsilon_{form} \right) - \rho \frac{u^2 + v^2}{2} \right].$$
(3)

Expression of  $\varepsilon_{vib}$  depends on the employed thermochemical model, as illustrated in section 3, whereas  $\varepsilon_{form}$  is the formation energy, given by

$$\varepsilon_{form} = 1/\rho \sum_{s=1}^{N_s} \rho_s h_s^f,\tag{4}$$

where  $h_s^f$  is the specific formation enthalpy of the component s.  $\bar{\gamma}$  is the specific heats ratio of the gas mixture

$$\bar{\gamma} = \frac{\bar{c}_p}{\bar{c}_v} = \frac{\alpha}{\alpha - 1}.$$
(5)

where  $\bar{c}_p$  and  $\bar{c}_v$  are the constant pressure and constant volume specific heats. The overbar indicates that these quantities refer to the roto-translational mode of energy, hence it holds

$$\bar{c}_p = \alpha R$$
  $\bar{c}_v = \bar{c}_p - R = R(\alpha - 1)$  (6)

where R is the specific gas constant and  $\alpha$  is given by

$$\alpha = \sum_{s} \chi_s \alpha_s \tag{7}$$

where  $\chi_s$  is the molar fraction of the species s and  $\alpha_s$  is equal to 5/2 for monoatomic and 7/2 for diatomic components, respectively.

#### 2.2 Numerical method

The system of equations (1) is solved by employing a cell-centered finite volume approach on a structured mesh. In order to cope with the stiffness of source terms, an operating splitting approach separating fluid dynamics from chemical kinetics is employed. In such an approach the system of equations (1) without source terms is first solved (frozen-step); then, conservative variables obtained from the frozen-step are updated solving a system of chemical equations including source terms but without fluid dynamic fluxes (chemical-step). In such a way it is possible to apply the best algorithm for the two different problems.

Specifically, inviscid fluxes discretization is performed employing two different schemes. On one hand, the flux vector splitting scheme of Steger and Warming [43] is used, with a second order accurate MUSCL reconstruction of primitive variables and a flux limiter to obtain a TVD (total variation diminishing) scheme [44]. Recently, in order to extend the code to accurately solve supersonic/hypersonic turbulent flow problems, the authors implemented a hybrid WENO/central-difference scheme [41], in virtue of its capability to deal with problems involving shocks and turbulence interacting dynamically [45]. In the present implementation, the popular fifth-order accurate WENO reconstruction is used following a characteristic-wise finite volume method [40]. Then, to reduce numerical dissipation, the WENO scheme is hybridized with a numerical flux built from a sixth order central scheme (CD6). The hybrid approach switches from CD6 to WENO when a shock sensor ( $\chi$ ) [39] is larger than a threshold ( $\chi_L$ ).

The method of lines is employed to separate time integration from space discretization [46], thus using an explicit third order Runge-Kutta algorithm to advance the solution in time [47].

On the other hand, an implicit Gauss-Seidel scheme, with a fixed number of inner iterations, is used to solve the chemical-step. In general a sub-time step that is a fraction of the fluid dynamic time step can be considered. Such an approach is suitable for reactive flows [48] and the performances provide same results of a fully implicit scheme [26, 32]. More details are given in Refs. [49, 28, 50].

The solver is written using a MPI-CUDA protocol in order to run simulations on both CPU or GPU clusters [50].

## 3 Physical Models

#### 3.1 State-to-State model

Instead of assuming a Boltzmann distribution for the internal states as done in classical multi-temperature models, a more sophisticated physically based approach must be devised to better describe the distribution of all vibrational states of the mixture. The *State-to-State* approach for a neutral air mixture accounts for all the vibrational levels of  $N_2$  (68) and  $O_2$  (47), whereas only the ground state is considered for NO, N and O for a total of 118 pseudo-species and, consequently, the set of kinetics mechanisms is huge (more than 10000 processes).

The elementary processes contributing to the vibrational relaxation are classified as: vibrationvibration (VV) and vibration-translation by molecules (VTm) and by atoms (VTa) energy transfer, together with dissociation-recombination by molecules (DRm) and by atoms (DRa) and other chemical reactions. Indicating with A and B generic elements, the generic set of processes can be summarized as follows:

- Vibration-Vibration (VV):  $A_2(v) + B_2(w) \leftrightarrow A_2(v-1) + B_2(w+1)$
- Vibration-Translation by molecules (VTm):  $A_2(v) + B_2 \leftrightarrow A_2(v-1) + B_2$
- Vibration-Translation by atoms (VTa):  $A_2(v) + B \leftrightarrow A_2(w) + B$
- Dissociation-Recombination by molecules (DRm):  $A_2(v) + B_2 \leftrightarrow 2A + B_2$
- Dissociation-Recombination by atoms (DRa):  $A_2(v) + B \leftrightarrow 2A + B$

being v and w the vibrational quantum numbers. Differently from the mT model, transport equations for the vibrational energy are not needed, as each level is qualified by its own energy  $\varepsilon_{s,l}$  calculated by

means of the anharmonic oscillator expression [51, 52]. The total vibrational energy per unit mass is defined as follows:

$$\varepsilon_{vib} = \frac{1}{\rho} \sum_{s=1}^{N_s} \sum_{l=1}^{V_s} \rho_{s,l} \varepsilon_{s,l} \tag{8}$$

Moreover, for non–equilibrium distributions, the vibrational temperature loses its meaning. Nevertheless, low energy levels approximately follow a Boltzmann distribution, thus providing the vibrational temperature (from the first two levels) as:

$$T_{v,m} = \frac{\varepsilon_{m,2} - \varepsilon_{m,1}}{R_m \ln\left(\frac{\rho_{m,1}}{\rho_{m,2}}\right)} \tag{9}$$

#### 3.2 Consistent multi-internal-temperature model

The consistent multi-internal-temperature model stems from the observation that the shape of the vibrational energy distribution can be approximated by  $v_m$  Boltzmann groups. Starting from this assumption, a transport equation is written for the mass and vibrational energy of each group, with the corresponding source terms being calculated self-consistently from the rate coefficients of the detailed StS model, namely, the source terms in the right column of Eq. (2e).

In particular, following the approach of Guy at al. [37], the internal partition function of group i for the generic molecule  $A_2$  is defined as

$$f_i(v, T_V^i) = \frac{e^{-\frac{\epsilon_v}{k_B T_V^i}}}{\sum_{w \in i} e^{-\frac{\epsilon_w}{k_B T_V^i}}}$$
(10)

 $\epsilon_v$  indicating the energy of vibrational level v,  $k_B$  the Boltzmann constant, and  $T_V^i$  the internal temperature of the i - th group. This allows one to evaluate global VT reaction rates

$$K_{i \to j}^{VT,M} = \sum_{v \in i} \sum_{w \in j} k_{v \to w}^{VT,M}(T) f_i(v, T_V^i)$$

$$\tag{11}$$

the reaction rates  $k_{v \to w}^{VT,M}(T)$  given by the detailed StS model [51]. Then, the VT source term reads

$$\dot{\omega}_{VT}^{A_2,i} = m_{A_2} \sum_M \sum_j^{v_{A_2}} \left[ K_{j \to i}^{VT,M} A_2^j - K_{i \to j}^{VT,M} A_2^i \right] M \tag{12}$$

In the same manner, the DR source term reads

$$\dot{\omega}_{DR}^{A_2,i} = m_{A_2} \sum_{M} \left[ K_i^{r,M} A^2 M - K_i^{d,M} A_2^i M \right]$$
(13)

 $K_i^{r,M}$  and  $K_i^{d,M}$  being the recombination and dissociation global rates of group *i* for component *A*. Finally,  $\dot{\omega}_{s,l} = \dot{\omega}_{VT}^{s,l} + \dot{\omega}_{DR}^{s,l}$ .

Accordingly, one can compute the source terms  $\dot{\Omega}_{VT}^{A_2,i}$  and  $\dot{\Omega}_{CV}^{A_2,i}$  in the energy equation of group i for the molecule of element A accounting for VT and chemistry-vibration (CV) processes, VV processes being considered negligible. Such terms are obtained by multiplying the continuity equation for each vibrational level v by its energy and then by summing these equations over the levels in group i and are used to evaluate  $\dot{\Omega}_{m,i} = \dot{\Omega}_{VT}^{m,i} + \dot{\Omega}_{CV}^{m,i}$ .

## 4 Results

The hybrid WENO/central-difference scheme has been verified in Ref. [41], however a further proof is presented here by considering Lax's shock tube problem:

$$(\rho_L, u_L, p_L) = (0.445, 0.698, 3.528)$$
  
 $(\rho_R, u_R, P_R) = (0.5, 0, 0.571)$ 

6 ICCFD12

The shock tube extends between x = 0 and x = 1 m and it includes 100 cells. The pure fifth order WENO scheme and the hybrid one with two different thresholds of the shock sensor ( $\chi_L=100$  and 200) have been employed. The results are in very good agreement with the exact solution, although some oscillation in the velocity profiles are provided by the hybrid scheme (Fig. 1).



Figure 1: Lax's shock tube problem: (a) density profile; (b) velocity profile.



Figure 2: 0D oxygen reactor, reduced models and StS comparison: (a) temperature profiles; (b)  $O_2$  mass fraction profiles.

In order to verify the reduced model, 0D reactor simulations have been performed by considering mixtures of pure oxygen, pure nitrogen and five species neutral air with the following initial conditions:

$$\begin{split} Y_{O_2} &= 1; \ T = 9000 \ K; \ p = 10^5 Pa \\ Y_{N_2} &= 1; \ T = 9000 \ K; \ p = 10^5 Pa \\ Y_{N_2} &= 0.767; \ Y_{O_2} = 0.233; \ T = 9000 \ K; \ p = 10^5 Pa \end{split}$$

Figure 2 shows the temperature and the  $O_2$  mass fraction profiles obtained by the full StS and the reduced models with one, two and three groups for the pure oxygen mixture. The agreement with the full StS model increases by increasing the number of internal groups, thus the model with three groups provides profiles that almost overlap the reference ones.



Figure 3: 0D oxygen reactor, T and Tv profiles: (a) one group model; (b) two groups model; (c) three groups model.

In order to understand the differences between the three reduced models the vibrational temperature profiles are provided along with the translational temperature in Fig. 3. The different dissociation rates among the three models is related to the underpopulation of high energy vibrational levels that cannot be seen with only one internal group (Tv1 $\approx$  T) while it is partially detected by the two groups configuration (Tv2<Tv1 $\approx$ T) and it is more evident with three groups (Tv3<Tv2<Tv1 $\approx$ T). This thermal non-equilibrium reduces the dissociation rate as shown in Fig. 2 (b).

The reduced model with three internal groups has been verified also in the case of a pure nitrogen mixture and a five species neutral air mixture as shown in Figs. 4 and 5.

Finally, a 2D Euler axial-symmetric simulation has been performed by considering a hypersonic flow past a sphere reproducing an experiment by Nonaka et al. [53]. The test case regards a sphere with a radius of 7 mm with the following free-stream conditions:  $Y_{N2}=0.767$ ,  $Y_{O2}=0.233$ ,  $T_{\infty} = 293$  K  $u_{\infty} = 3490$  m/s.

Figure 6 (a) shows the pressure contour obtained on a uniform computational grid that includes  $57 \times 98$  computational cells. Figure 6 (b) compares the full StS results, in terms of molecule mass fractions, with those obtained by the reduced model with three groups: a good agreement is observed.



Figure 4: 0D nitrogen reactor, reduced models and StS comparison: (a) temperature profiles; (b)  $N_2$  mass fraction profiles



Figure 5: 0D air reactor, reduced models and StS comparison: (a) temperature profiles; (b) mass fraction profiles.

# 5 Conclusion and future work

The in-house developed finite volume flow solver has been equipped with a consistent reduced order kinetic model for simulating hypersonic flows.

In order to reduce the computational load of the StS kinetics, the multi-internal temperature model has been implemented for neutral air and verified by comparing the results with those of the full StS approach. Such model, representing the distributions as piecewise Boltzmann, reduces the air chemical kinetics by an order of magnitude. The results, compared with the StS approach, have shown an improved agreement as the number of groups increases.

However, the runtime direct calculation of the multi-temperature rates from the state-to-state ones does not give an effective gain in term of computational time. Therefore, to overcome this problem, our future plans are to pre-calculate and fit the multi-temperature rate coefficients. Moreover, extension to the Navier–Stokes equations and thorough verification and validation are also planned.



Figure 6: Nonaka sphere test case: (a) pressure contour; (b) mass fraction profiles.

## Acknowledgments

G. Pascazio, F. Bonelli and D. Ninni were partially supported by the Italian Ministry of University and Research under the Programme "Department of Excellence" Legge 232/2016 (Grant No. CUP - D93C23000100001).

This work is part of the project NODES which has received funding from the MUR – M4C2 1.5 of PNRR funded by the European Union - NextGenerationEU (Grant agreement no. ECS00000036)

F. Bonelli was funded by the European Union – Next Generation EU - "Piano Nazionale Resistenza e Resilienza (PNRR), Missione 4 Componente C2 Investimento 1.1 - Decreto Direttoriale n. 104 del 2 febbraio 2022, Avviso pubblico per la presentazione di Progetti di ricerca di Rilevante Interesse Nazionale (PRIN) da finanziare nell'ambito del PNRR, Bando PRIN 2022," CUP - D53D23004350001, Hypersonic vehicles Enhancement via Robust Multi-fidelity optimization for the Exploitation of Space - HERMES.

## References

- Peter A Gnoffo. Planetary-entry gas dynamics. Annual Review of Fluid Mechanics, 31(1):459–494, 1999.
- [2] John J Bertin and Russell M Cummings. Critical hypersonic aerothermodynamic phenomena. Annual Review of Fluid Mechanics, 38:129, 2006.
- [3] John D Anderson Jr. *Hypersonic and high-temperature gas dynamics*. American Institute of Aeronautics and Astronautics, 2006.
- [4] Graham V Candler. Rate effects in hypersonic flows. Annual Review of Fluid Mechanics, 51:379–402, 2019.
- [5] I Armenise, M Capitelli, G Colonna, N Koudriavtsev, and V Smetanin. Nonequilibrium vibrational kinetics during hypersonic flow of a solid body in nitrogen and its influence on the surface heat-flux. *Plasma Chemistry and Plasma Processing*, 15(3):501–528, 1995.
- [6] G Colonna and M Capitelli. Electron and vibrational kinetics in the boundary layer of hypersonic flow. Journal of thermophysics and heat transfer, 10(3):406–412, 1996.
- [7] I Armenise. Excitation of the lowest CO<sub>2</sub> vibrational states by electrons in hypersonic boundary layers. *Chemical Physics*, 491:11–24, 2017.
- [8] F. Bonelli, G. Pascazio, and G. Colonna. Effect of finite-rate catalysis on wall heat flux prediction in hypersonic flow. *Phys. Rev. Fluids*, 6:033201, Mar 2021.
- [9] Pierre Schrooyen. Numerical simulation of aerothermal flows through ablative thermal protection systems. PhD thesis, PhD thesis, UCL, 2015.
- [10] Francesco Bonelli, Davide Ninni, Lucia Daniela Pietanza, Gianpiero Colonna, Bernd Helber, Thierry E. Magin, and Giuseppe Pascazio. Effects of thermochemical non-equilibrium in the bound-

ary layer of an ablative thermal protection system: A state-to-state approach. *Computers Fluids*, 270:106161, 2024.

- [11] Chul Park. Nonequilibrium hypersonic aerothermodynamics. John Wiley & Sons, 1989.
- [12] Chul Park. Review of chemical-kinetic problems of future NASA missions. I-Earth entries. Journal of Thermophysics and Heat transfer, 7(3):385–398, 1993.
- [13] D. Olynick, Y.-K. Chen, and M. E. Tauber. Aerothermodynamics of the stardust sample return capsule. Journal of Spacecraft and Rockets, 36(3):442–462, 1999.
- [14] C. Park. Stagnation-point ablation of carbonaceous flat disks. i theory. AIAA Journal, 21(11):1588– 1594, 1983.
- [15] C. H. Mortensen and X. Zhong. Simulation of second-mode instability in a real-gas hypersonic flow with graphite ablation. AIAA Journal, 52(8):1632–1652, 2014.
- [16] Y.-K. Chen and F. S. Milos. Navier-stokes solutions with finite rate ablation for planetary mission earth reentries. *Journal of Spacecraft and Rockets*, 42(6):961–970, 2005.
- [17] G.V. Candler. The Computation of Weakly Ionized Hypersonic Flows in Thermochemical Nonequilibrium. PhD Thesis, June 1988.
- [18] Ioannis Nompelis, Graham Candler, Matthew MacLean, Timothy Wadhams, and Michael Holden. Numerical Investigation of High Enthalpy Chemestry on Hypersonic Double-Cone Experiments. In 43rd AIAA Aerospace Sciences Meeting and Exhibit, page 584, 2005.
- [19] G Colonna, F Bonelli, and G Pascazio. Impact of fundamental molecular kinetics on macroscopic properties of high-enthalpy flows: The case of hypersonic atmospheric entry. *Physical Review Fluids*, 4(3):033404, 2019.
- [20] G Colonna, M Tuttafesta, M Capitelli, and D Giordano. Non-Arrhenius NO formation rate in one-dimensional nozzle airflow. Journal of thermophysics and heat transfer, 13(3):372–375, 1999.
- [21] I Armenise, M Capitelli, G Colonna, and G Gorse. Nonequilibrium vibrational kinetics in the boundary layer of re-entering bodies. *Journal of thermophysics and heat transfer*, 10(3):397–405, 1996.
- [22] I Armenise and M Capitelli. State to state vibrational kinetics in the boundary layer of an entering body in earth atmosphere: particle distributions and chemical kinetics. *Plasma Sources Science and Technology*, 14(2):S9, 2005.
- [23] I Armenise and F Esposito. N2, O2, NO state-to-state vibrational kinetics in hypersonic boundary layers: The problem of rescaling rate coefficients to uniform vibrational ladders. *Chemical Physics*, 446:30–46, 2015.
- [24] O Kunova, E Kustova, M Mekhonoshina, and E Nagnibeda. Non-equilibrium kinetics, diffusion and heat transfer in shock heated flows of N2/N and O2/O mixtures. *Chemical Physics*, 463:70–81, 2015.
- [25] L Campoli, O Kunova, E Kustova, and M Melnik. Models validation and code profiling in state-tostate simulations of shock heated air flows. Acta Astronautica, 175:493–509, 2020.
- [26] Davide Ninni, Francesco Bonelli, Gianpiero Colonna, and Giuseppe Pascazio. Unsteady behavior and thermochemical non equilibrium effects in hypersonic double-wedge flows. Acta Astronautica, 191:178–192, 2022.
- [27] G Colonna and M Capitelli. Self-consistent model of chemical, vibrational, electron kinetics in nozzle expansion. Journal of thermophysics and heat transfer, 15(3):308–316, 2001.
- [28] Francesco Bonelli, Michele Tuttafesta, Gianpiero Colonna, Luigi Cutrone, and Giuseppe Pascazio. An MPI-CUDA approach for hypersonic flows with detailed state-to-state air kinetics using a GPU cluster. Computer Physics Communications, 219:178–195, 2017.
- [29] G Colonna and M Capitelli. The influence of atomic and molecular metastable states in highenthalpy nozzle expansion nitrogen flows. *Journal of Physics D: Applied Physics*, 34(12):1812, 2001.
- [30] Gianpiero Colonna, Lucia Daniela Pietanza, and Annarita Laricchiuta. Ionization kinetic model for Hydrogen-Helium atmospheres in hypersonic shock tubes. *International Journal of Heat and Mass Transfer*, 156:119916, 2020.
- [31] D Giordano, V Bellucci, G Colonna, M Capitelli, I Armenise, and C Bruno. Vibrationally relaxing flow of N past an infinite cylinder. *Journal of thermophysics and heat transfer*, 11(1):27–35, 1997.
- [32] Davide Ninni, Francesco Bonelli, Gianpiero Colonna, and Giuseppe Pascazio. On the influence of non equilibrium in the free stream conditions of high enthalpy oxygen flows around a double-cone. *Acta Astronautica*, 201:247–258, 2022.
- [33] L Cutrone, M Tuttafesta, M Capitelli, A Schettino, G Pascazio, and G Colonna. 3D nozzle flow simulations including state-to-state kinetics calculation. In *AIP Conference Proceedings*, volume 1628, pages 1154–1161. American Institute of Physics, 2014.

- [34] Gianpiero Colonna, Lucia Daniela Pietanza, and Mario Capitelli. Recombination-assisted nitrogen dissociation rates under nonequilibrium conditions. *Journal of Thermophysics and Heat Transfer*, 22(3):399 – 406, 2008.
- [35] E.V. Kustova, E.A. Nagnibeda, T.Yu. Alexandrova, and A. Chikhaoui. Non-equilibrium dissociation rates in expanding flows. *Chemical Physics Letters*, 377(5):663–671, 2003.
- [36] Thierry E. Magin, Marco Panesi, Anne Bourdon, Richard L. Jaffe, and David W. Schwenke. Coarsegrain model for internal energy excitation and dissociation of molecular nitrogen. *Chemical Physics*, 398:90–95, 2012.
- [37] Aurélien Guy, Anne Bourdon, and Marie-Yvonne Perrin. Consistent multi-internal-temperatures models for nonequilibrium nozzle flows. *Chemical Physics*, 420:15 – 24, 2013.
- [38] Alessandro Munafò, Simone Venturi, Maitreyee P. Sharma, and Marco Panesi. Reduced-order modeling for non-equilibrium air flows. AIAA Scitech 2020 Forum, 1 PartF, 2020.
- [39] D.J Hill and D.I Pullin. Hybrid tuned center-difference-weno method for large eddy simulations in the presence of strong shocks. *Journal of Computational Physics*, 194(2):435–450, 2004.
- [40] Chi-Wang Shu. Essentially non-oscillatory and weighted essentially non-oscillatory schemes for hyperbolic conservation laws, pages 325–432. Springer Berlin Heidelberg, Berlin, Heidelberg, 1998.
- [41] Francesco Bonelli, Davide Ninni, Gianpiero Colonna, and Giuseppe Pascazio. A finite-volume hybrid weno/central-difference shock capturing approach with detailed state-to-state kinetics for highenthalpy flows. *Materials Research Proceedings*, 37:170–173, 2023.
- [42] M. Capitelli, G. Colonna, and A. D'Angola. Fundamental Aspects of Plasma Chemical Physics: Thermodynamics, volume 66 of Atomic, Optical, and Plasma Physics. Springer, New York, 1st edition, 2011.
- [43] Joseph L Steger and RF Warming. Flux vector splitting of the inviscid gasdynamic equations with application to finite-difference methods. *Journal of computational physics*, 40(2):263–293, 1981.
- [44] Bram Van Leer. Towards the ultimate conservative difference scheme. V. A second-order sequel to Godunov's method. Journal of computational Physics, 32(1):101–136, 1979.
- [45] Eric Johnsen, Johan Larsson, Ankit V. Bhagatwala, William H. Cabot, Parviz Moin, Britton J. Olson, Pradeep S. Rawat, Santhosh K. Shankar, Björn Sjögreen, H.C. Yee, Xiaolin Zhong, and Sanjiva K. Lele. Assessment of high-resolution methods for numerical simulations of compressible turbulence with shock waves. *Journal of Computational Physics*, 229(4):1213–1237, 2010.
- [46] Charles Hirsch. Numerical Computation of Internal and External Flows, Volume 1: The Fundamentals of Computational Fluid Dynamics. Elsevier, 2007.
- [47] Guang-Shan Jiang and Chi-Wang Shu. Efficient implementation of weighted ENO schemes. Journal of computational physics, 126(1):202–228, 1996.
- [48] Jan G Verwer. Gauss-seidel iteration for stiff odes from chemical kinetics. SIAM Journal on Scientific Computing, 15(5):1243–1250, 1994.
- [49] Michele Tuttafesta, Giuseppe Pascazio, and Gianpiero Colonna. Multi-GPU unsteady 2D flow simulation coupled with a state-to-state chemical kinetics. *Computer Physics Communications*, 207:243–257, 2016.
- [50] Giuseppe Pascazio, Davide Ninni, Francesco Bonelli, and Gianpiero Colonna. Hypersonic flows with detailed state-to-state kinetics using a GPU cluster. In *Plasma Modeling (Second Edition): Methods and applications.* IOP Publishing, 2022.
- [51] M. Capitelli, R. Celiberto, G. Colonna, F. Esposito, C. Gorse, K. Hassouni, A. Laricchiuta, and S. Longo. Fundamentals Aspects of Plasma Chemical Physics: Kinetics. Springer, New York, 2016.
- [52] Gianpiero Colonna, Lucia Daniela Pietanza, and Mario Capitelli. Recombination-assisted nitrogen dissociation rates under nonequilibrium conditions. *Journal of Thermophysics and Heat Transfer*, 22(3):399–406, 2008.
- [53] Satoshi Nonaka, Hiroyasu Mizuno, Kazuyoshi Takayama, and Chul Park. Measurement of shock standoff distance for sphere in ballistic range. *Journal of thermophysics and heat transfer*, 14(2):225– 229, 2000.