# Effects of thermochemical non-equilibrium in the boundary layer of an ablative thermal protection system: a state-to-state approach

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**Abstract:** The aim of this work is to investigate the effects of thermochemical non-equilibrium in the shock layer and boundary layer of hypersonic flows past blunt bodies entering planetary atmospheres. Ablative thermal protection systems change the mixture composition of the boundary layer with significant impact on the surface heat flux. In this context, a vibrationally resolved stateto-state approach is employed in order to understand the effect of non-equilibrium of the molecular energy level population on the surface heat flux.

Keywords: Ablation, Hypersonic Flows, Thermochemical Non-Equilibrium, State to State Kinetics.

### 1 Introduction

In recent years, the interest in space exploration has raised significantly due to a new impetus from the private sector. Among many complex problems related to space exploration, one of the greatest challenge is the tremendous heat load on the vehicle during its entry into a planetary atmosphere. Designing a suitable Thermal Protection System (TPS) can have a huge impact on the success and cost of space missions. Ablative TPSs dissipate energy through material evaporation and mass loss although this may cause some modification of the boundary layer gas composition. A positive effect consists in reducing the surface heat load by blocking the radiation coming from the shock layer. In this context, an intriguing phenomenon recently observed in the Plasmatron wind tunnel at the von Karman Institute for Fluid Dynamics (VKI) is the non-equilibrium population of the energy levels of the cyanogen molecule (CN) [1]. Spectroscopic measurements on both graphite and carbon bonded carbon fiber material suggest that the rotational and vibrational temperatures strongly depart from a Maxwell-Boltzmann equilibrium population close to the ablating surface. Nondissociated nitrogen in the boundary layer can play a significant role in the vibrational excitation of the CN molecule. A state-to-state (StS) approach will help us to identify the cause of this non-equilibrium effect and its impact on the surface heat flux, either through increased radiation or exothermic surface reactions. At present, an effective vibrationally resolved StS approach for N<sub>2</sub>, O<sub>2</sub> and CO molecules has been implemented in a multi-GPU solver of the Navier-Stokes equations [2]. In the present work, we will simulate a hypersonic air flow past a graphite sphere to examine if molecules are characterized by non-Boltzmann distributions and eventually assess such non-equilibrium effect on the surface heat flux. Previous results, obtained with a five species air mixture  $(N_2, O_2, NO, N, O)$ , including StS of  $N_2$  and  $O_2$ , have shown that, downstream of a strong bow shock, non-Boltzmann distributions affect reaction rates and, consequently, temperature profiles and stand-off distance [2]. Specifically,  $O_2$  high energy levels are underpopulated thus reducing the dissociation rate. In the present work, the StS model will be extended by including CO plasma chemistry and CO vibrational kinetics [3], whereas mass balance at wall will be computed by using the VKI Mutation++

library [4]. This approach will be employed to investigate the effects of non-equilibrium in the boundary layer. Results will provide information regarding temperature, pressure, species mass fractions, vibrational distribution of molecules, mass blowing rate and surface heat flux.

### 2 Fluid Dynamic Model

#### 2.1 Governing Equations

Hypersonic flows in the continuum regime were investigated by solving the Navier-Stokes equations for a reactive multicomponent mixture in axial symmetric configuration. Equations in integral form, for both the StS and the Park's multi-temperature (mT) model, read

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

where  $\mathbf{U}$  is the vector of conservative variables, whereas  $\mathbf{F}$  and  $\mathbf{W}$  are fluxes and source term vectors, respectively:

$$\mathbf{U} = [\rho_{1,1}, \dots, \rho_{1,V_1}, \dots, \rho_{S,1}, \dots, \rho_{S,V_S}, \rho u, \rho v, \rho E, \rho \varepsilon_{int}]^T,$$
(2)

$$\mathbf{F} = (\mathbf{F}_I - \mathbf{F}_V, \mathbf{G}_I - \mathbf{G}_V),\tag{3}$$

$$\mathbf{F}_{I} = [\rho_{1,1}u, \dots, \rho_{1,V_{1}}u, \dots, \rho_{S,1}u, \dots, \rho_{S,V_{S}}u, \rho u^{2} + p, \rho uv, (\rho E + p)u, \rho \varepsilon_{int}u]^{T},$$

$$\tag{4}$$

$$\mathbf{G}_{I} = [\rho_{1,1}v, \dots, \rho_{1,V_{1}}v, \dots, \rho_{S,1}v, \dots, \rho_{S,V_{S}}v, \rho uv, \rho v^{2} + p, (\rho E + p)v, \rho \varepsilon_{int}v]^{T},$$

$$(5)$$

$$(\mathbf{F}_{V},\mathbf{G}_{V}) = [-\rho_{1,1}\boldsymbol{\mathcal{V}}_{1,1},\ldots,-\rho_{1,V_{1}}\boldsymbol{\mathcal{V}}_{1,V_{1}},\ldots,-\rho_{S,1}\boldsymbol{\mathcal{V}}_{S,1},\ldots,-\rho_{S,V_{S}}\boldsymbol{\mathcal{V}}_{S,V_{S}},\boldsymbol{\sigma},\mathbf{u}\cdot\boldsymbol{\sigma}-\mathbf{q},-\mathbf{q}_{int}]^{T},$$
(6)

$$\mathbf{W} = [\dot{\omega}_{1,1}, \dots, \dot{\omega}_{1,V_1}, \dots, \dot{\omega}_{S,1}, \dots, \dot{\omega}_{S,V_S}, 0, \dot{\omega}_{ax}, 0, \dot{\omega}_{int}]^T.$$
(7)

In the vibrationally resolved StS approach each level is considered as a pseudo-species thus the generic species s has  $V_s$  internal states and partial densities are characterized by two subscripts, i.e. s and l indicating the s-th species and the l-th internal state respectively (obviously, no internal state is considered in the mT model, i.e.  $V_s = 1$ ). 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. 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  $\varepsilon_{int}$  represent the specific total and internal energies, the latter including the contributions of the degrees of freedom in non-equilibrium with respect to the translational temperature, i.e. vibrational ( $\varepsilon_{vib}$ ) and electronically excited states ( $\varepsilon_e$ ) for molecules and electronic states for atoms, being rotational state at equilibrium at T. The transport equation for the specific internal energy is considered only for the mT model, whereas in the StS this quantity is transported by the level population. Source terms for species mass and for internal energy are given by  $\{\dot{\omega}_{s,l}\}$  and  $\{\dot{\omega}_{int}\}$  (the latter defined only for the mT model), respectively. Moreover, being the configuration axial symmetric, in order to consider the effects of fluxes in the tangential direction  $\theta$ , a source term in the radial momentum equation has to be considered  $\dot{\omega}_{ax} = \frac{p - \sigma_{s,\theta}}{\sigma}$ .

Diffusive fluxes are computed by modeling diffusion velocities, viscous stress tensor, total heat flux and internal heat flux ( $\mathbf{q}_{int}$ , defined only for the mT model) as follows

$$\rho_{s,l} \boldsymbol{\mathcal{V}}_{s,l} = -\rho D_s \nabla Y_{s,l},\tag{8}$$

$$\boldsymbol{\sigma} = \boldsymbol{\mu} [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] - \frac{2}{3} \boldsymbol{\mu} \left( \nabla \cdot \mathbf{u} \right) \mathbf{I}, \tag{9}$$

$$\mathbf{q} = -\lambda_t \nabla T - \lambda_{int} \nabla T_v + \sum_{s=1}^{S} \sum_{l=1}^{V_S} h_{s,l} \rho_{s,l} \boldsymbol{\mathcal{V}}_{s,l}, \tag{10}$$

$$\mathbf{q}_{int} = -\lambda_{int} \nabla T_v + \sum_s \varepsilon_{int,s} \rho_s \boldsymbol{\mathcal{V}}_s, \tag{11}$$

where Y is the mass fraction, T is the roto-translational temperature,  $T_v$  is the temperature of internal levels, the same for all the species, and  $h_{s,l}$  is the single species specific enthalpy including formation contributions.  $D_s$ ,  $\mu$ ,  $\lambda_t$  and  $\lambda_{int}$  represent the mixture diffusion coefficient of species s, the mixture viscosity, the mixture roto-translational conductivity and the internal conductivity, respectively.

In order to close the system of governing equations the perfect gas [5] assumption is employed to link p and E.

$$p = (\bar{\gamma} - 1) \left[ \rho E - \rho \left( \varepsilon_{int} + \varepsilon_{form} \right) - \rho \frac{u^2 + v^2}{2} \right], \tag{12}$$

where  $\bar{\gamma}$  is the specific heats ratio of the gas mixture and  $\varepsilon_{form}$  the total contribution of formation enthalpies.

#### 2.2 Numerical Method and Computational Approach

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 was employed. In such an approach the system of equations (1) without source terms (frozen-step) is first solved, then conservative variables obtained from the frozen-step are updated solving a system of chemical equations including source terms (chemical-step) but without fluid dynamic fluxes. In such a way it is possible to apply the best algorithm for the two different problems.

Specifically, inviscid fluxes are solved by using the flux vector splitting scheme of Steger and Warming [6], with a second order MUSCL reconstruction of primitive variables, whereas a second order scheme is employed to solve viscous fluxes applying the Gauss' theorem for gradients computations. The method of lines is employed to separate time integration from space discretization, thus using an explicit third order Runge-Kutta algorithm to advance the solution in time.

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. More details are given in Refs. [7, 8].

The solver is written using a CUDA-MPI protocol in order to run simulations on both CPU and GPU clusters. An ad hoc treatment is needed when using Mutation++ libraries that at present can run only on CPUs. Indeed, if the main solver is running on GPUs when it calls a Mutation++ routine it needs to copy input variables on CPU memory, perform the Mutation++ routine and finally copy output variables on GPU memory. At the moment such approach seems to be effective only when the StS model is employed since most of the computational time is spent solving StS kinetics.

# 3 Physical Models

In order to simulate hypersonic air flows past graphite spheres considering also gas-surface interaction (GSI) phenomena of both ablation and catalysis, a neutral air mixture with the addition of carbon and carbon compounds was considered. Thus, the mixture includes 11 species, i.e, N<sub>2</sub>, O<sub>2</sub>, NO, N, O, CO<sub>2</sub>, CO, CN, C<sub>3</sub>, C<sub>2</sub>, C. Chemical non-equilibrium is modeled through the law of mass action. Such an equation requires the evaluation of rate coefficients which can be affected by thermal non-equilibrium. The full list of processes considered in this work are given in appendix A and B. Two different thermochemical non-equilibrium models were employed, i.e., the mT Park's model and a hybrid vibrationally resolved StS approach. Both models consider the translational and rotational mode in equilibrium at a roto-translational temperature T, whereas a different approach is used to cope with vibrational non-equilibrium.

#### 3.1 mT Park's model

The main assumption of mT models is that internal populations follow an equilibrium Boltzmann distribution at a vibrational temperature  $T_v$ , independent from T. In this work a single thermal bath for the vibrational mode was considered. Regarding the vibrational energy source term, two energy exchange contributions are considered, i.e, the vibrational-translational and the chemical-vibrational. The first is modelled by writing for each molecule a Landau-Teller equation. In such an equation the relaxation time is evaluated by the Millikan-White expression with a correction for high temperature values. Then, the total vibrational-translational

source term comes from the sum of all molecule contributions. On the other hand, the chemical-vibrational energy exchange takes into account the energy removed or added during dissociation or recombination, respectively. This term is modelled with a non-preferential approach considering that dissociation and recombination occur at Boltzmann equilibrium at  $T_v$ . Finally, a rigid-rotor-harmonic oscillator (RRHO) assumption provides the equation to link vibrational energy to  $T_v$ 

$$\varepsilon_{vib} = \sum_{m=1}^{N_m} \frac{R_m \theta_m}{exp(\theta_m/T_v) - 1},\tag{13}$$

where  $N_m$  is the number of molecules, whereas  $R_m$  and  $\theta_m$  are the specific gas constant and the characteristic vibrational temperature of molecule m, respectively, while  $\varepsilon_e$  is calculated summing over the Boltzmann distribution of electronic levels.

Then, in order to take into account the effects of thermal non-equilibrium on the chemical one a geometrical average of T and  $T_v$  is used as an effective temperature in the semiempirical Arrhenius law.

In this work the mT model is fully handled by Mutation++ and more modeling details can be found in Refs [4, 9, 10].

#### 3.2 StS model

In contrast with mT models, the hybrid vibrationally resolved StS approach implemented here allows to predict internal state distributions even when they deviate from the Boltzmann one. This is accomplished by considering the evolution of each internal state through vibrational-vibrational (VV) and vibrational-translational, with molecules (VTm) and atoms (VTa), and dissociation/recombination (DR) reactions. In general such processes are governed by non-Arrenhius relations [11].

In the present work, the StS model for a five species neutral air mixture [2] was extended by including CO plasma chemistry (i.e., direct dissociation) and CO vibrational kinetics (i.e., vibration-vibration and vibration-translation energy exchanges) [3]:

$$CO(v) + X \leftrightarrow C + O + X$$
 (DR), (14)

$$CO(v) + CO(w) \leftrightarrow CO(v-1) + CO(w+1)$$
 (VV), (15)

$$CO(v) + CO \leftrightarrow CO(v-1) + CO \quad (VTm),$$
 (16)

$$CO(v) + O \leftrightarrow CO(v-1) + O$$
 (VTa), (17)

where X is the generic collision partner and v and w are generic vibrational levels. 68, 47 and 81 vibrational levels were considered for  $N_2$ ,  $O_2$  and CO, whereas only the ground state was considered for all other species. StS kinetics data are not available for all reactions, therefore, a hybrid approach was devised, i.e., a single-temperature model with Arrenhius law is employed for reactions that cannot be handled by StS. Details of the full mechanism is given in appendix B.

The total vibrational energy per unit mass is computed on the basis of internal states' distributions as follows

$$\varepsilon_{int} = \varepsilon_{vib} = \frac{1}{\rho} \sum_{s=1}^{S} \sum_{v=1}^{V_s} \rho_{s,l} \varepsilon_{s,l}, \qquad (18)$$

here neglecting the electronic mode  $\varepsilon_{int} = \varepsilon_{vib}$ . For non-Boltzmann distributions, vibrational temperature has no precise meaning and its definition cannot be uniquely defined. However, since low energy levels approximatively follow a Boltzmann shape, the first two levels can be used to define  $T_{v,m}$ 

$$T_{v,m} = \frac{M_m \left(\varepsilon_{m,2} - \varepsilon_{m,1}\right)}{\Re \ln \left(\frac{\rho_{m,1}}{\rho_{m,2}}\right)},\tag{19}$$

where  $\Re$  and  $M_m$  are the universal gas constant and the molar weight of molecule m, respectively.

#### 3.3 Transport models

Mutation++ was employed to compute transport coefficients. Using the mT model, a multicomponent Chapman-Enskog formulation is employed. Thus, transport properties are provided runtime by Mutation++. On the other hand, when the StS kinetics is employed, in order to limit the time spent on CPU, a different approach is followed. A preprocessing step builds tables of single-component transport properties vs temperature, using Mutation++. Then, once copied on GPU's memory, a runtime GPU routine computes mixture properties by employing classical mixing rules [12, 13, 14]. In both cases the mixture-averaged diffusion coefficients are computed with a weighted harmonic mean of the binary diffusion coefficients. Hence, in order to ensure mass conservation, a velocity correction is added to the Fick's law given in Eq. 8.

#### 3.4 Gas-surface interaction approach

Catalytic and ablative boundary conditions are imposed by solving a mass balance directly calling Mutation++ [4, 15]. For each species the balance equation reads

$$(\rho_s \nu_{blowing})_{wall} + (\rho_s \boldsymbol{\mathcal{V}}_s)_{wall} = \dot{\omega}_{s,wall}, \tag{20}$$

where the sum of the convective flux due to blowing and the diffusive flux at wall is balanced by the species source term due to surface reactions. For ablative boundaries  $\nu_{blowing}$  is a nonzero surface normal blowing velocity, that conversely is zero for catalytic conditions. Surface source terms are computed by using a probability approach

$$\dot{\omega}_{s,wall} = \gamma m_s \mathcal{F}_{s,impin} \tag{21}$$

where  $\gamma$  represents the process efficiency, being the ratio of reacting to impinging particle fluxes  $\gamma = \mathcal{F}_{s,react}/\mathcal{F}_{s,impin}$ , and  $m_s$  is the mass of species s [15]. Then, summing over all species, the blowing speed is obtained as

$$\nu_{blowing} = \frac{\dot{m}}{\sum_{s} \rho_s} \tag{22}$$

where  $\dot{m} = \sum_{s} \dot{\omega}_{s,wall}$  is the mass blowing rate.

Such a balance equation is solved directly by Mutation++, then species densities and blowing speed are applied at wall boundaries.

### 4 Test cases details

Two test cases were considered. The first (Test-1) was studied in order to verify the correct coupling of Mutation++ in the in-house body fitted finite volume solver (CHESSbf: CHESS [16] body fitted). Simulations were set up on the basis of an experiment carried out at the von Karman Institute by Helber et al. [17]. In such an experiment, a graphite sample with a hemispherical nose of radius 25 mm was exposed to a subsonic nitrogen plasma. Nitridation reactions

$$C_{\text{solid}} + N \to CN$$
 (23)

occur at wall causing ablation. Nitridation efficiency tuned on this experiment [17] was given by

$$\gamma_{nitridation} = 7.91 \cdot 10^{-2} \exp\left(-\frac{5653}{T_{wall}}\right),\tag{24}$$

Verification was carried out by comparing the present mT results with those provided by the US3D solver [18, 16], which was already validated against such experiment in Ref [18, 16]. Being confident in the US3D implementation and in order to limit the computational cost, a 2-D planar geometry without ionized species was simulated [16]. The aforementioned 11 species mixture for air and carbon compounds reduced to a 6 species mixture, i.e., N<sub>2</sub>, N, CN, C<sub>3</sub>, C<sub>2</sub>, C. Freestream conditions are given in Tab. 1. Concerning grid resolution, both solvers employed a stretched mesh with a total of  $100 \times 59$  fluid cells and a height at wall of  $1 \times 10^{-5}$  m.

The second test case (Test-2) was taken from the work of Chen and Milos [19]. A graphite sphere cone

Table 1: Freestream conditions for the planar subsonic nitrogen plasma flow [16].

$u_{\infty}  \mathrm{[m/s]}$	$T_{\infty}$ [K]	$T_{wall}$ [K]	$p_{\infty}$ [Pa]	$Y_{N_2}$	Y <sub>N</sub>
1570	10280	2407	1500	$9.77659 \cdot 10^{-5}$	0.9999022341

with nose radius of 1.905 cm is exposed to a hypersonic flow of dissociated air, whose freestream conditions are given in Tab 2. A temperature profile along the sphere cone was also measured and is provided in Ref. [19]. However in this work, following Ref. [20], only the nose was investigated with a uniform  $T_{wall}$ equal to 3250 K (i.e., the one mesured at around 45°). As regards the resolution of the structured stretched mesh, a total of  $152 \times 196$  fluid cells were employed with a height at wall of  $5 \times 10^{-6}$  m.

Table 2: Freestream conditions for the Chen and Milos test case [19].

$u_{\infty}  \mathrm{[m/s]}$	$T_{\infty}$ [K]	$T_{wall}$ [K]	$ ho_\infty~{\rm [kg/m^3]}$	$Y_{N_2}$	$Y_{O_2}$	$Y_{\rm NO}$	$\mathbf{Y}_{\mathbf{N}}$	Yo
5354	1428	3250	0.003	0.6169	0.0	0.0046	0.1212	0.2573

Concerning GSI, the following oxidation, sublimation and catalytic recombination reactions were taken into account (not exactly the same used by Chen and Milos [19])

$$C_{\text{solid}} + O \to CO,$$
 (25)

$$3C_{\text{solid}} \to C_3,$$
 (26)

$$2O \rightarrow O_2.$$
 (27)

Oxidation efficiency is equal to (see Ref. [19])

$$\gamma_{oxidation} = 0.63 \exp\left(-\frac{1160}{T_{wall}}\right),\tag{28}$$

whereas the rate of production for the sublimation reaction is given by (see Refs. [19, 20])

$$\dot{\omega}_{C_3} = \gamma_{sub} \left( \rho_{C_3, equil} - \rho_{C_3} \right) \sqrt{\frac{k_B T_{wall}}{2\pi m_{C_3}}}.$$
(29)

Here,  $\gamma_{sub}$  is the vaporization coefficient assumed equal to 1 [19] and  $\rho_{C_3,equil}$  is the equilibrium surface density of  $C_3$  which is computed from the saturated vapor pressure [21, 19]

$$p_{C_3,equil} = 5.19 \times 10^{14} \exp\left(-\frac{90845}{T_{wall}}\right).$$
 (30)

Finally, the catalytic recombination efficiency was taken equal to 0.5. For this test case both the StS and the mT Park's model were employed. Using StS kinetics, one needs to choose how to distribute internal states of species produced by surface reactions. Two different approaches, named StS-1 and StS-2, were considered. In the first approach (StS-1) only the ground state is filled, whereas, when the StS-2 is employed, molecules coming from surface have the same distribution of gas molecules. These approaches were also followed for the recombination reaction of Eq. 14, because only the rate coefficient for the global recombination reaction is available [3].

### 5 Results and Discussion

Figure 1 shows the mass blowing rate provided by CHESSbf and US3D [16, Fig. 10 (b)] for Test-1. Results obtained by the two solvers are in very good agreement, thus confirming the correct implementation of



Figure 1: Test-1 – mass blowing rate provided by CHESSbf and US3D [16].



Figure 2: Test-2 – Roto-translational temperature contour plots: StS-1 (a), Park (b).

Mutation++ in CHESSbf.

Figures 2 (a) and (b) show the contour of the roto-translational temperature obtained by using both the StS-1 approach and the mT Park's model. Both models provide a peak temperature that exceeds 12000 K, however the Park's model shows larger temperature values in the whole flowfield.

A better comparison, among the StS-1, the StS-2 and the Park's model, in terms of temperature profiles along the stagnation line is given in Fig. 3. The mT model provides a larger peak temperature which decreases slower downstream of the bow shock. As a consequence the shock layer is larger when the mT model is employed. StS-1 and StS-2 approaches provide the same temperature profiles in the shock layer, whereas a



Figure 3: Test-2 – Temperature profiles along the stagnation line : full view (a), close up at wall (b)



Figure 4: Test-2 – Mass fractions profiles along the stagnation line (a) and wall pressure profiles (b).

different behaviour of vibrational temperatures can be observed in the boundary layer (see Fig 3 (b)). Here, one has to notice that, differently from the mT model, in the StS approaches  $T_{v,m}$  are not fixed at wall. Fig 3 (b) shows that the StS-1 provides a larger thermal non-equilibrium.

Figure 4 (a) shows mass fractions profiles along the stagnation lines. StS-1 and StS-2 provide the same results with very small differences at wall. Both StS and mT model show a sudden oxygen recombination through the bow shock, with a larger  $O_2$  amount predicted by the mT model. At wall  $C_3$  comes from sublimation, whereas an important quantity of CO comes from ablation, with a mass fraction on the surface of about 0.37 for all 3 simulations. Then, further species form in the boundary layer, i.e.  $CO_2$ , CN,  $C_2$  and C.

A comparison between the wall pressure computed with the present models and those provided by Chen and Milos [19] and by Mortensen and Zhong [22] is given in Fig. 4 (b). Chen and Milos [19] predict a



Figure 5: Test-2 – Mass blowing rate (a) and wall heat flux (b).



Figure 6: Test-2 – Vibrational distributions evaluated around the stagnation point: StS-1 (a), StS-2 (b).

larger pressure along the wall, whereas an excellent agreement between the present and the Mortensen and Zhong [22] findings is shown.

Outcomes in terms of mass blowing and wall heat flux are given in Figs. 5 (a) and (b). StS-1 and StS-2 provide the same mass blowing rate that is slightly larger than the one predicted by the mT model. Present results are in satisfactory agreement with the experimental one and with those provided by other authors. Concerning the wall heat flux, values provided by the Park model are higher then those provided by StS. A relevant difference between the heat flux given by the two StS approaches can be notice, with the StS-2 providing the smallest heat flux.

Finally, it is very interesting to observe vibrational distributions of  $N_2$ ,  $O_2$  and CO near the stagnation point. In Fig. 6 continuos and dashed lines provide the predicted and the Boltzmann (extrapolated from

the first two levels) distributions, respectively. StS-1 and StS-2 show a different behaviour with a larger non-equilibrium, with respect to Boltzmann distributions, observed when the StS-1 approach is employed. However, it is worth noting that differences are only in low lying energy levels providing different  $T_{v,m}$ , but intermediate and high energy levels show the same distribution. Further analysis are ongoing in order to better understand the effects of such behaviour on wall heat flux.

# 6 Conclusion and Future Work

In this work a vibrationally resolved StS model for a neutral air mixture was extended including also CO StS kinetics. This allows us to investigate thermochemical non-equilibrium phenomena that occur in the shock and in the boundary layer of ablative TPSs. A well known hypersonic test case ablating a graphite sphere [19] was investigated by using both a classical mT model and the hybrid StS approach devised in this work. For the StS model two different approaches of populating internal states at wall were considered: StS-1 populating only the ground state, and StS-2 providing the same gas distribution. Some differences emerge between results obtained with the StS and the mT model in terms of stand-off distance, temperature and  $O_2$  and NO mass fractions profiles. On the other hand, mass blowing rate provided by the two approaches is comparable. StS-1 and StS-2 show differences in terms of low lying energy levels, with a smaller vibrational temperature predicted by the StS-1 in the boundary layer, whereas intermediate and high energy levels show the same distribution. Such different distributions at wall seem to affect the wall heat flux, however further analysis need to be carried out to better understand the influence of the molecular energy level population on macroscopic quantities.

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# A Arrhenius reactions

The full mechanism employed with the mT model is the following

$$N_2 + X \leftrightarrow 2N + X, \tag{31}$$

$$O_2 + X \leftrightarrow 2O + X,$$
 (32)

$$NO + X \leftrightarrow N + O + X,$$
 (33)

$$C_2 + X \leftrightarrow 2C + X, \tag{34}$$

$$CN + X \leftrightarrow C + N + X,$$
 (35)

$$CO_2 + X \leftrightarrow CO + O + X,$$
 (36)

$$CO + X \leftrightarrow C + O + X,$$
 (37)

$$C_3 + X \leftrightarrow C_2 + C + X, \tag{38}$$

$$NO + O \leftrightarrow N + O_2,$$
 (39)

$$N_2 + O \leftrightarrow NO + N,$$
 (40)

$$CO + C \leftrightarrow C_2 + O,$$
 (41)

 $CO + O \leftrightarrow O_2 + C,$  (42)

$$\rm CO + N \leftrightarrow \rm CN + O,$$
 (43)

$$N_2 + C \leftrightarrow CN + N,$$
 (44)

$$CN + O \leftrightarrow NO + C,$$
 (45)

$$CN + C \leftrightarrow C_2 + N,$$
 (46)

$$CO_2 + O \leftrightarrow O_2 + CO,$$
 (47)

whose Arrhenius constants were take from [23].

# **B** StS processes

Source terms are computed according to vibrational-traslational (VT), vibrational-vibrational (VV) energies exchanges, dissociation/recombination (DR) or ladder climbing (LC) processes due to collisions with atoms (a, A) and molecules (m, M) [24]. The full list of processes is

$$N_2(v) + N_2(w) \leftrightarrow N_2(v-1) + N_2(w+1)$$
 (VV) (48)

$$N_2(v) + N_2 \leftrightarrow N_2(v-1) + N_2 \quad (VTm) \tag{49}$$

$$N_2(v) + N \leftrightarrow N_2(v - \Delta v) + N$$
 (VTa) (50)

$$O_2(v) + O_2(w) \leftrightarrow O_2(v-1) + O_2(w+1)$$
 (VV) (51)

$$O_2(v) + O_2 \leftrightarrow O_2(v-1) + O_2 \quad (VTm)$$

$$(52)$$

$$O_2(v) + O \leftrightarrow O_2(v - \Delta v) + O$$
 (VTa) (53)

$$N_2(v) + O_2 \leftrightarrow N_2(v-1) + O_2 \quad (VTm)$$

$$(54)$$

$$N_2(v) + O \leftrightarrow N_2(v-1) + O$$
 (VTa) (55)

$$O_2(v) + N_2 \leftrightarrow O_2(v-1) + N_2 \quad (VTm)$$

$$(56)$$

$$O_2(v) + N \leftrightarrow O_2(v-1) + N$$
 (VTa) (57)

$$O_2(v) + N_2(w-1) \leftrightarrow O_2(v-2) + N_2(w)$$
 (VV) (58)

$$N_2(v) + M \leftrightarrow 2N + M$$
 (DRm) (59)

$$N_2(v) + A \leftrightarrow 2N + A$$
 (DRa) (60)

$$O_2(v) + M \leftrightarrow 2O + M \quad (DRm)$$
 (61)

$$O_2(v) + A \leftrightarrow 2O + A \quad (DRa)$$
 (62)

$$N_2(v_{max}) + O_2 \leftrightarrow N_2(v_{max} + 1) + O_2 \equiv 2N + O_2 \quad (LCm)$$

$$(63)$$

$$N_2(v_{max}) + O \leftrightarrow N_2(v_{max} + 1) + O \equiv 2N + O \quad (LCa)$$
(64)

$$O_2(v_{max}) + N_2 \leftrightarrow O_2(v_{max} + 1) + N_2 \equiv 2O + N_2 \quad (LCm)$$

$$(65)$$

$$O_2(v_{max}) + N \leftrightarrow O_2(v_{max} + 1) + N \equiv 2O + N \quad (LCa).$$
(66)

Also NO dissociation processes were considered

$$NO + X \leftrightarrow N + O + X,$$
 (67)

where X is a generic component, and Zeldovich [25, 26] reactions

$$O_2(v) + N \leftrightarrow NO + O,$$
 (68)

$$N_2(v) + O \leftrightarrow NO + N,$$
 (69)

for a total of about 10000 elementary processes. More details can be found in [8, 2, 7]. All other reactions involving carbon and its compounds are handled by the Arrhenius reactions listed before.

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