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Nonequilibrium ionization phenomena behind shock waves

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Abstract. An accurate investigation of the behavior of electronically excited states of atoms and molecules in the post shock relaxation zone of a trajectory point of the FIRE II flight experiment is carried out by means of a one-dimensional flow solver coupled to a collisional-radiative model. In the rapidly ionizing regime behind a strong shock wave, the high lying bound electronic states of atoms are depleted. This leads the electronic energy level populations of atoms to depart from Boltzmann distributions which strongly affects the non-equilibrium ionization process as well as the radiative signature. The importance of correct modeling of the interaction of radiation and matter is discussed showing a strong influence on the physico-chemical properties of the gas. The paper clearly puts forward the shortcomings of the simplified approach often used in literature which strongly relies on the escape factors to characterize the optical thickness of the gas.

Keywords: Ionization of plasmas; shock waves and discontinuities; collisional-radiative models
PACS: 52.25.Jm; 52.35.Tc

INTRODUCTION

A deep understanding of ionization processes is crucial for the correct modeling of the weakly ionized plasma flows characterizing the shock layer around re-entry bodies. The radiative and convective heat loads generated by the vehicle during Earth entry are strongly dependent on the degree of ionization in the gas. In ionizing air, the formation of the first electrons is due to the association of nitrogen and oxygen atoms into ionized nitric-oxide. This process is very fast and it is favored by the relatively low activation energy. In a second step, when the number of electrons is sufficiently large, the fast electrons easily ionize the neutral atoms, rapidly increasing the electron density. The accurate modeling of this two step process requires the correct modeling of the thermo-chemical relaxation leading to the formation of the atomic species, as well as a detailed modeling of the excitation and ionization of the molecular and atomic chemical components. A truthful representation of the chemical-physical processes occurring in shock heated air can be achieved through the explicit calculation of the population of the internal atomic and molecular states, adopting a kinetic description (or state to state description) of the gas, (i.e., by treating the quantum states of atoms and molecules as separate pseudo-species). In this work we limit ourselves to the explicit calculation of the population of atomic and molecular densities of the electronic states, adopting a multi-temperature approach for the estimation of the population of rotational and vibrational levels. Examples can be found in literature [1, 2, 3]. When dealing with high temperature gas mixtures, the modeling of the radiative processes is of crucial importance since it is well-known to strongly affect the ionization processes. In the application of interest of the present work, when entry speed exceeds 9-10 km/s, the main contributor to the radiative processes are atomic species (nitrogen atoms), which account for about 90% of the overall radiation output. Often in literature the calculation of the radiation field is decoupled by the solution of the flow-field quantities (species densities, temperatures etc.), and *escape factors* are used to model the effects of the radiative processes on the population of the excited states. Needless to say the results are very much dependent on the assumption made when selecting the value of these and they strongly depend on the case under investigation (as suggested in [4]). In this work we propose a fully consistent treatment of the radiation processes where the influence of the radiation processes on the population of the excited states is correctly modeled as well as the cooling effects.

The paper is organized in the following manner: the physical model is first discussed a brief description of the kinetic processes is given. Then, the radiative processes and the radiative transfer model adopted is presented, as well as the coupling between flowfield and radiation field. The physical model developed is then used to study the non-equilibrium ionization process behind a strong normal shock. The flight conditions are taken from a trajectory point of FIRE II flight experiment flown in the 60's [5].

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PHYSICAL MODEL

A one-dimensional Eulerian solver, named SHOCKING, is used to describe the flow field behind a normal shock wave. Although very simple, SHOCKING yields a reasonable representation of the inviscid part of the shock layer region at a very low computational cost, thus allowing for a very accurate modeling of the thermo-physical processes taking place during the thermo-chemical relaxation. The shock is fitted by means of the Rankine-Hugoniot equations, considering the internal degrees of freedom and chemical composition frozen across the discontinuity. The temporal evolution of the electronic state densities of the different chemical components is obtained by solving a set of continuity equations for each state complemented by solving the Euler system of equations, namely mass, momentum and energy, allowing one to retrieve the remaining characteristic flow quantities, such as pressure, temperature and flow speed. Also, the relaxation of the vibrational and free-electron energy is modeled using a separate conservation equations accounting for the energy exchanges with the other modes (i.e. translation) and chemistry. Finally, the characterization of the radiative field is modeled solving the radiative transfer equation. The physico-mathematical structure of the model is summarized as follows:

- **Euler eqs.**: conservation of mass for species i, momentum and total energy

$$\frac{\partial}{\partial t}\begin{pmatrix}\rho_i\\ \rho u\\ \rho E\end{pmatrix}+\frac{\partial}{\partial x}\begin{pmatrix}\rho_i u\\ \rho u^2+p\\ \rho u H\end{pmatrix}=\begin{pmatrix}M_i\omega_i\\ 0\\ -\frac{\partial}{\partial x}q_{rad}\end{pmatrix}\qquad [i\in\mathscr{S}] \tag{1}$$

- **MultiT models**: additional energy conservation eqs., *e.g.* vibrational energy eq.

$$\frac{\partial}{\partial t}(\rho e_m)+\frac{\partial}{\partial x}(\rho u e_m)=\Omega^m-\frac{\partial}{\partial x}q^m_{rad}+\cdots \tag{2}$$

- **Radiation transport models**

$$\frac{dI_\lambda}{ds}=\varepsilon_\lambda-\kappa_\lambda I_\lambda \tag{3}$$

where $\mathscr{S}$ stands for the set of indices of the mixture species. The mixture considered in this work accounts for 11 chemical components, including their excited states which are considered as pseudo-species. The overall number of species/pseudo-species reads 116. All the details concerning the physical model are given in Ref. [2].

Kinetic processes

The collisions between the mixture species may lead to chemical changes or changes in internal energy of the interacting species. Several models exist for the related cross sections and rate coefficients. We have used the rate coefficients reported by Bultel *et al*. [3]. In the following sections a list of the processes accounted for is given. Also, some of the cross sections given in Ref. [3] have been substituted with more updated estimation from ab-initio calculations or experimental measurements. The details are given in the following sections.
The kinetic mechanism comprises different types of forward and backward reactions:

- Excitation / de-excitation by heavy-particle and electron impact,
- Ionization / recombination by heavy-particle and electron impact.

The N and O atoms are efficiently excited and ionized by electron impact reactions; due to their small mass, free electrons very easily change occupation of the attached electrons of atoms. We have updated the electron impact inelastic cross sections adopted in Ref. [3] with the kinetic data provided in Ref. [6, 7]. When the same rate constants is given in both references, we have decided to use the ab-initio results of Ref. [6]. The inelastic processes involving interaction of atoms with molecular species or other atoms are much less significant and their importance is relatively reduced by the fact that the formation of the first electrons is due to associative ionization reactions. The list of rate constants used in this work for these processes is given in Ref. [3].

The kinetic mechanism comprises different types of forward and backward reactions:

- Excitation / de-excitation by heavy-particle and electron impact,

- Ionization / recombination by heavy-particle and electron impact,
- Dissociation / recombination of N_2, O_2, and NO by atomic or molecular impact,
- Dissociation / recombination of N_2 by electron impact,
- Associative ionization / dissociative recombination,
- Radical reactions (including Zel'dovich reactions),
- Charge exchange reactions.

In the present work, we propose to use the rate coefficients for excitation, ionization and dissociation of molecular species by electron impact recently calculated by Teulet *et al* [8] by estimating the inelastic rate constants using the method of weighted total cross section (WTCS) developed by Bacri and Medani [9]. The modifications suggested by Sarrette *et al* [10] are introduced to account for pre-dissociation of some electronic states of O_2 and NO in the calculation of the dissociation rate coefficients.The cross section for excitation of molecules involved in molecular or atomic impact behaves approximately as explained by Lotz [11]. Therefore, this model has been adopted, except when experimental data exist. We have then used the rate coefficients compiled by Capitelli *et al* [12] and Kossyi *et al* [13]. For direct dissociation by molecular impact, the rate coefficients of Park et al. [14] are computed at the average temperature $\sqrt{TT_v}$ and the simple vibration-dissociation coupling firstly proposed by Candler have been adopted.

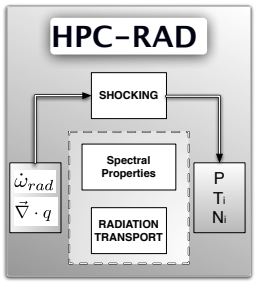
RADIATIVE PROCESSES AND RADIATIVE TRANSPORT

The treatment of the radiative processes drastically differs for atomic and molecular species. While the atomic species radiation signature is obtained as a solution of the Radiative Transfer Equation (RTE), the possible re-absorption of molecular radiation is estimated by making use of escape factors [18]. It is assumed here that an optically thin medium is associated with an escape factor equal to 1, whereas for an optically thick medium, the escape factor is set to 0.

When modeling atomic line radiation three mechanisms have to be considered: spontaneous emission, absorption, and stimulated emission. These processes require the knowledge of one of the three Einstein coefficients: $\mathscr{A}_{ul}$, $\mathscr{B}_{lu}$ and $\mathscr{B}_{ul}$. A comprehensive list of atomic line data for nitrogen and oxygen is provided by the NIST atomic line database [15] and have been used in this work. When the gas cannot be considered optically thin an accurate modeling of the spectral line shape is also important. In this work we account for Doppler, natural and collisional broadening as discussed in Ref.[17].

As far as molecules are concerned, some states of species considered in our mixture of gases strongly radiate. The β ($B^2\Pi \rightarrow X^2\Pi$) and γ ($A^2\Sigma^+ \rightarrow X^2\Pi$) systems of NO, as well as the first positive ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) and second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) systems of N_2, and the first negative system ($B^3\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) of N_2^+ have been considered. Since a vibrational equilibrium is assumed at the species vibrational temperature T_v, the equivalent transition probabilities A_{ij} have been calculated by fitting the data calculated by Laux and Kruger [16], averaging over the vibrational structure.

Radiative transport



Particular care is paid to the modeling of the radiative processes and the interaction between the radiation field and matter. For this purpose the RTE equation, within the approximation of tangent slab, is solved together with the modified set of Euler equations (1-3), by coupling a recently developed radiation code (HPC-RAD) to the flow solver SHOCKING. The output from the flow calculation in terms of flow quantities, i.e. pressure, temperature, electron density and the population of the electronic states of the atomic species is used to compute the spectral dependent emission and adsorption coefficients. The spectral properties are used in Eq. (3) to calculate the intensity at each location of the domain. in Eqs. (1-2). The knowledge of the radiative intensity allows for the estimation of the energy source terms, thus accounting for the radiative power emitted or adsorbed by the gas. This term is simply obtained by computing the divergence of the radiative heat-flux. The other output from the radiation calculation is the rate of change of the number densities of the chemical component s in the quantum electronic state i.

This term is modeled as follows:

$$\dot{\omega}_{s,i}^{rad} = \sum_{j>i} \left[\mathscr{A}_{j,i} n_{s,j} - \int_{\lambda_{min}}^{\lambda_{max}} \left(\mathscr{B}_{i,j} n_{s,i} - \mathscr{B}_{j,i} n_{s,j} \right) \rho_{e,\lambda} \Phi_\lambda d\lambda \right]$$

$$- \sum_{i>j} \left[\mathscr{A}_{i,j} n_{s,i} - \int_{\lambda_{min}}^{\lambda_{max}} \left(\mathscr{B}_{j,i} n_{s,j} - \mathscr{B}_{i,j} n_{s,i} \right) \rho_{e,\lambda} \Phi_\lambda d\lambda \right] \tag{4}$$

where the spectral radiant energy density $\rho_{e,\lambda}$ is defined as:

$$\rho_{e,\lambda} = \frac{1}{c} \int_{4\pi} I(\lambda, \theta) d\theta \tag{5}$$

The explicit coupling of the codes is obtained by iteratively alternating a flow and a radiation solve until convergence is reached.

RESULTS: FIRE II EXPERIMENTS

We investigate the behavior of the electronic energy level populations of the atoms for the trajectory point of the FIRE II experiment at 1634s. The set of operating conditions for the corresponding shock-tube problem are: u_1 = 11 360 m/s; p_1 = 2 Pa; T_1 = 195 K.

Characterization of the physico-chemical state of the plasma in the shock layer requires the knowledge of the chemical composition as well as the determination of the energy stored into the internal modes. Figure 1 shows the evolution of the rotational and translational temperature and the vibrational free-electron temperature. After a sudden increase of the rotational and translation temperature, across the shock the two temperatures relax reaching the equilibrium value. It is important to mention that the extent of thermal non-equilibrium (i.e. $T \neq T_V$) depends on the modeling of the free-electron energy removed by the excitation and ionization of atomic species.

The influence of the optical thickness of the gas on the results is clear when observing the electron density profiles, shown in Fig. 1. When the medium is assumed optically thick all the radiation emitted is immediately self-absorbed and the electron density reaches its equilibrium value. The other extreme corresponds to the optically thin gas case. In this case the density plot exhibits a maximum and is monotonically decreasing due to the radiative energy losses. The coupled calculation sits in the middle among the two curves, stressing the importance of the correct modeling of the radiative processes and their interaction with matter.

To characterize non-equilibrium of the populations, the number density of the electronic states of atomic nitrogen and oxygen are compared in Fig. 2 with the Boltzmann distribution (T_e) in the post-shock area. The strong depletion of the excited states was previously discussed in [1]-[2] and it is strongly dependent on the optical thickness of

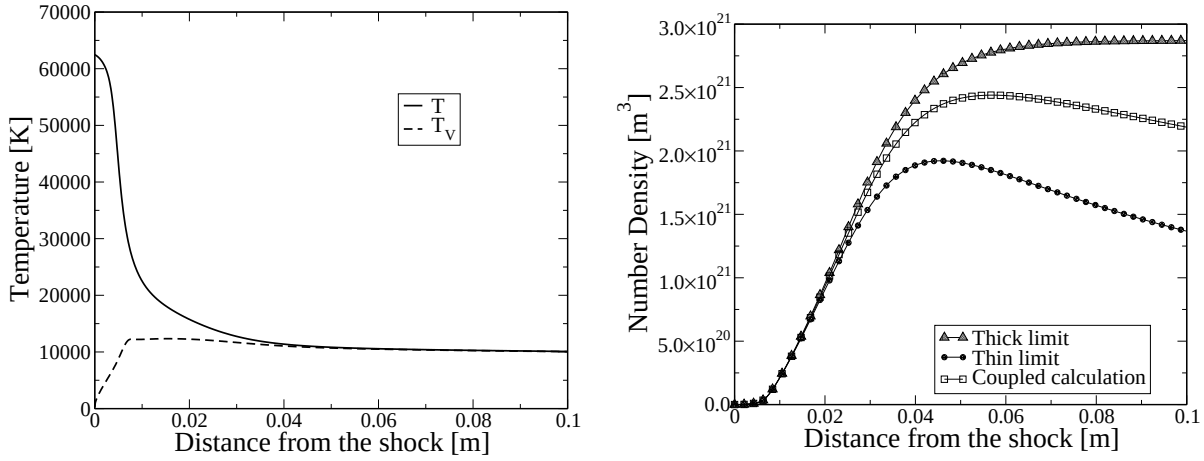


FIGURE 1. Post-shock temperature (*left*) and electron number density (*right*) profiles for a fluid particle as a function of the distance from the shock

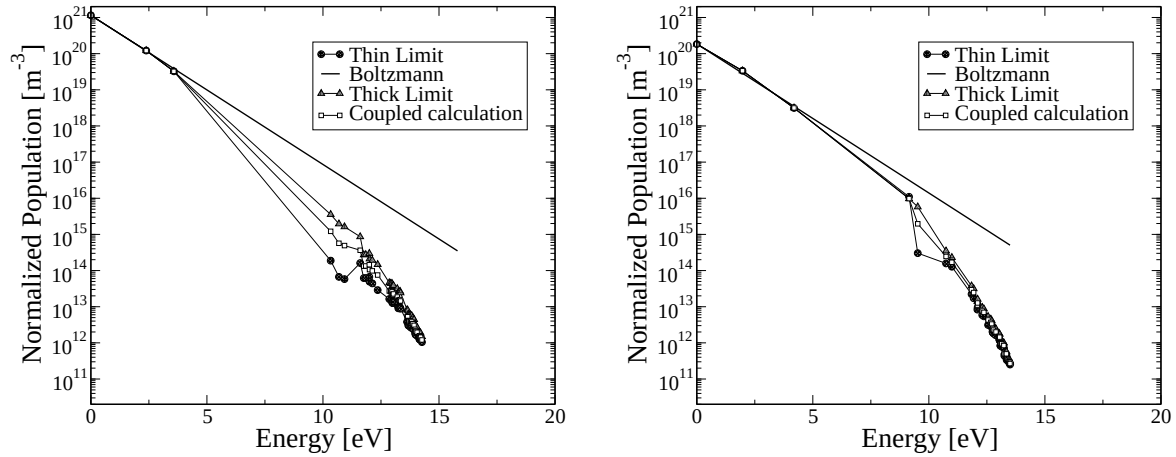


FIGURE 2. Electronic energy distribution function for atomic nitrogen (*left*) and oxygen (*right*) at 1 cm from the shock front

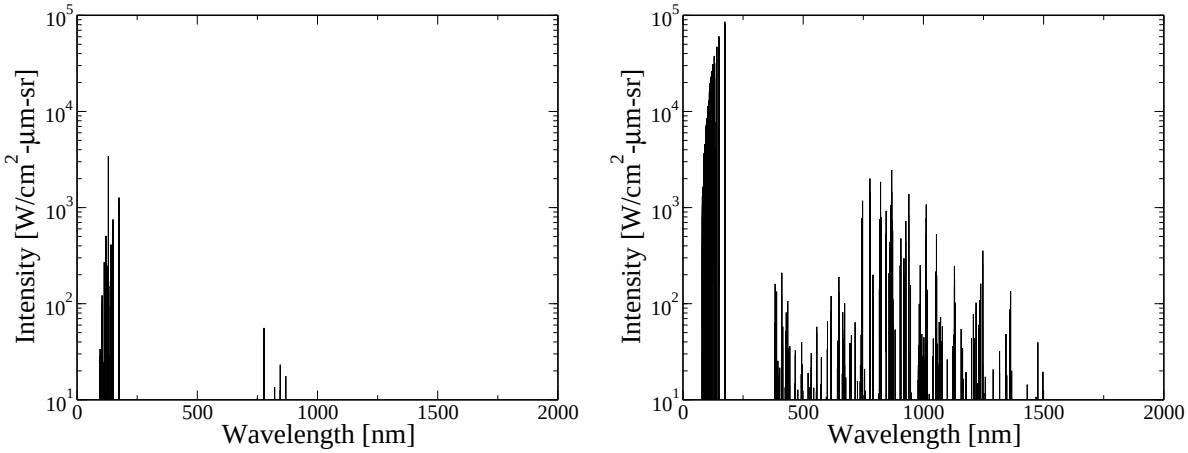


FIGURE 3. Atomic spectra: non-equilibrium (*left*) and equilibrium (*right*) atomic line radiation at 1 cm from the shock front

the medium. In particular the population of the low lying Rydberg states seems to be strongly influenced by the assumptions made on the optical thickness, since they radiate strongly in the VUV part of the spectrum, as shown in Fig. 3. In order to quantify the extent of this non-equilibrium effect, we compared the spectrum obtained by means of the collisional radiative mode with the one based on Boltzmann distributions Fig. 3. The large differences observed in the radiative signature of the gas are justified by the large overestimation of the population densities of the excited states when assuming Maxwell-Boltzmann equilibrium distribution.

CONCLUSIONS

In this work, we have studied the behavior of the excited electronic states of atoms and molecules in the relaxation zone of one-dimensional air flows obtained in shock-tube facilities. In our model the electronic states of atoms and molecules are treated as separate species, allowing for non-Boltzmann distributions of their populations. In the rapidly ionizing regime behind strong shock waves, the electronic energy level populations depart from Boltzmann distributions since the high lying bound electronic states are depleted. In order to quantify the extent of this non-equilibrium effect, we compared the results obtained by means of the collisional radiative model with those based on Boltzmann distributions.

Moreover, we have discussed the shortcomings of simplified approaches relying of escape factors for the treatment of radiative processes showing the impact that the wrong choices made when selecting the values of these parameters may have on the thermo-physical properties of the gas in terms of: electron density, populations of the electronic states and finally radiation. Furthermore, we have proposed a physically consistent model, where the optical thickness of the medium is a result of the calculation and not a result of choices made a priori. In this model the solution of the radiative transport equation is fully coupled to the solution of the flow-field equations by means of energy source terms in the energy and in the species continuity equations governing the population of the excited states of the atoms.

In the future, we propose to extend the physically consistent treatment of radiation to the molecular species.

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