Detailed and simplified kinetic mechanisms for high enthalpy flows
Application to the analysis of the Fire II flight experiment

* Marco Panesi*, Anne Bourdon†, Arnaud Bultel‡, Thierry Magin§

* Institute for Computational Engineering and Sciences, The University of Texas at Austin, U.S.A.
† CNRS Research Fellow, EM2C Laboratory
‡ CORIA, CNRS UMR 6614, Université de Rouen
§ von Karman Institute for Fluid Dynamics

Symposium in Honor of Prof Mario Capitelli
Outline

1. Introduction

2. Atomic and Molecular Energy Levels

3. Coupled Fluid & Collisional Radiative models
   - Kinetic Processes
   - Radiative Processes
   - Fluid Model and Radiation Transfer

4. Results
   - FIRE II: non-equilibrium ionization
   - EAST: Comparison with shock tube data.
   - Grouping of the levels

5. Conclusions
Motivations and Objectives of the Project

Goals

- Development of an accurate kinetic mechanism for earth entry applications.
- Determination of a reduced mechanism for CFD applications.

Bultel, A. et al., “Collisional-radiative model in air for earth re-entry problems”
Physics of Plasmas, 2006, 13, 11
Atomic Structure

Atomic chemical components: N, O, N⁺, O⁺

Nitrogen

- Nitrogen 46 lumped levels: Combination of real and lumped levels (NIST 381).
- Oxygen 40 lumped levels: Combination of real and lumped levels (NIST 614).
Molecular structure

- Molecular chemical components: $N_2$, NO, $O_2$, $N_2^+$, $NO^+$, $O_2^+$
- Electronic specific treatment of the electronic molecular systems (27 states).
- Boltzmann assumption for the ro-vibrational structure, except for $NO^+$.

$$T_{v,Me} = T_{v,N_2X} \quad T_{r,Me} = T_{r,N_2X}$$

Schwenke D. AIAA-2007-811
Kinetic Processes

⇒ Collisional excitation (/ionization) and de-excitation (heavy/light).

▶ Atomic processes:

\[ A(E_i) + C \leftrightarrow A^{(+)}(E_j) + C(+e) \quad C \in [e, \mathcal{H}] \]

▶ Molecular processes, (Averaged over the ro-vibrational structure)

\[ M(\bar{E}_i) + C \leftrightarrow M^{(+)}(\bar{E}_j) + C(+e) \quad C \in [e, \mathcal{H}] \]

⇒ Collisional dissociation (heavy/light)

⇒ Exchange reactions (Zeld’ovich reactions)

⇒ Charge exchange

⇒ Dissociative recombination / Associative ionization

▶ NO\(^+\)(X\(^1\Sigma^+\), v) + e \leftrightarrow N + O, Motapon et al.
▶ O\(_2\)\(^+\), N\(_2\)\(^+\), Boltzmann averaged values.
▶ (Not included in the present model)

⇒ Over 100 K elementary processes included

Bultel, A. et al., “Collisional-radiative model in air for earth re-entry problems”

Physics of Plasmas, 2006, 13, 11
Line radiation

The atomic bound-bound radiation

\[ N_i(v, E_i^0) + h\nu (n, d\Omega_\nu) \rightleftharpoons N_j(v, E_j^0) \]  \hspace{1cm} (1)

\[ N_j(v, E_j^0) + h\nu (n, d\Omega_\nu) \rightarrow N_i(v, E_i^0) + 2h\nu (n, d\Omega_\nu) \]  \hspace{1cm} (2)

Detailed balance

\[ B_{j,i}(\nu) = \frac{c^2}{8\pi h\nu^3} A_{j,i}(\nu) \hspace{1cm} g_j B_{j,i}(\nu) = g_i B_{i,j}(\nu) \]

The $B$ coefficients defined originally by Einstein, and still sometimes used in literature, differ from the Einstein-Milne coefficients by a factor $\left(\frac{c}{4\pi}\right)$.
Radiative Recombination and photo-ionization

The atomic photoionisation corresponds to:

\[ N_i(v, E_i^0) + h\nu (n, d\Omega_\nu) \leftrightarrow N_j^+ (v, E_j^+) + e^- (v_e, d^3v_e) \]  \hspace{1cm} (3)

\[ Q_{i,j,(\nu)}^{(0,+)} = 2 \left( \frac{g_j^+}{g_i^0} \right) \frac{m_e}{(h\nu)^2} c^2 E_e Q_{j,i,(E_e)}^{(+,0)} \]

We define the cross section for induced free-bound processes as follows

\[ \frac{\tilde{Q}_{j,i,(v_e)}^{(0,+)}}{Q_{j,i,(v_e)}^{(0,+)}} = \left( \frac{c^2}{2h\nu^3} \right) \]
Transition Rates

Bound-Bound rates

\[
\frac{dn_{(i,s)}}{dt} = \sum_{j > i} \left[ A_{j,i} n_{s,j} - (B_{i,j} n_{s,i} - B_{j,i} n_{s,j}) \int_0^\infty G_\nu \Phi_{\nu}^{i,j} d\nu \right] - \sum_{i > j} \left[ A_{i,j} n_{s,i} - (B_{j,i} n_{s,j} - B_{i,j} n_{s,i}) \int_0^\infty G_\nu \Phi_{\nu}^{i,j} d\nu \right]
\] (4)

Bound-Free rates

\[
\frac{dn_{(i,s)}}{dt}^+ = n_{(j,s)}^+ n_e \bar{v}_e \int_0^\infty Q_{j,i,(\epsilon_e)}^{(0,+)} \epsilon_e \exp(-\epsilon_e) d\epsilon_e + n_{(j,s)}^+ n_e \bar{v}_e \int_0^\infty G_\nu \tilde{Q}_{j,i,(\epsilon_e)}^{(0,+)} \epsilon_e \exp(-\epsilon_e) d\epsilon_e
\]

\[
\frac{dn_{(i,s)}}{dt}^- = n_{(i,s)} \int_0^\infty \frac{G_\nu}{h\nu} Q_{i,j,(\nu)}^{(0,+)} d\nu
\]
Coupled Fluid & Collisional Radiative models

Radiative Transfer Equation

\[ \mu \frac{dI_\lambda(\tau, \mu)}{d\tau_\lambda} + I_\lambda(\tau_\lambda, \mu) = \frac{\eta_\lambda}{\kappa_\lambda}(\tau_\lambda) = S_\lambda(\tau_\lambda) \]  

Incident Intensity:

\[ G_\lambda(\tau) = 2\pi \left[ I_\lambda^+(\tau_\lambda, b) E_2(\tau_\lambda) + I_\lambda^-(\tau_\lambda, s) E_2(\tau_\lambda, s - \tau_\lambda) + \int_{\tau_b}^{\tau} S_\lambda E_1(\tau_\lambda - \tau'_\lambda) d\tau'_\lambda \right] + \int_{\tau}^{\tau_s} S_\lambda E_1(\tau'_\lambda - \tau_\lambda) d\tau'_\lambda \]

Radiative heating and its divergence

\[ q_\lambda(\tau) = 2\pi \left[ I_\lambda^+(\tau_\lambda, b) E_3(\tau_\lambda) + \int_{\tau_b}^{\tau} S_\lambda E_2(\tau_\lambda - \tau'_\lambda) d\tau'_\lambda \right] - I_\lambda^-(\tau_\lambda, s) E_3(\tau_\lambda, s - \tau_\lambda) - \int_{\tau}^{\tau_s} S_\lambda E_2(\tau'_\lambda - \tau_\lambda) d\tau'_\lambda \]
Modeling of non-equilibrium flows

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

\[
\frac{d}{dt} \begin{pmatrix} \rho_i \\ \rho u \\ \rho E \end{pmatrix} + \frac{d}{dx} \begin{pmatrix} \rho_i u \\ \rho u^2 + p \\ \rho u H \end{pmatrix} = \begin{pmatrix} M_i \omega_i \\ 0 \\ -\nabla \cdot \mathbf{q}_{rad} \end{pmatrix}
\]

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

\[
\frac{d}{dt} (\rho e_m) + \frac{d}{dx} (\rho u e_m) = \Omega^m - \nabla \cdot \mathbf{q}^m_{rad} + \cdots
\]

⇒ **Radiation transport models**

\[
\mu \frac{dI_\lambda(\tau, \mu)}{d\tau_\lambda} + I_\lambda(\tau_\lambda, \mu) = S_\lambda(\tau_\lambda)
\]
Radiation Coupling

Loosely coupled (explicit coupling) strategy

- Flow quantities SHOCKING
  \[ \bar{U} = [N_i, T_i, p]^T \]

- Spectral quantities HPC-RAD
  \[ I_\lambda = I_\lambda (\epsilon_\lambda, \kappa_\lambda) \]

- Divergence and Intensity
  \[ \bar{I} = [\dot{\omega}_{rad}, \vec{\nabla} \cdot q] \]
Results

- Fire II - Fully coupled
- EAST - Comparison with experiments
- Fire II - Reduction of the model

References:

Journal of Thermophysics an Transfer, 2009, 23, 236-248

Journal of Thermophysics an Transfer, 2011, accepted

Panesi, M. et al. “Non-equilibrium ionization phenomena behind shock waves”
27th International Symposium on Rarefied Gas Dynamics, 2010
FIRE II

Objective

• Study the behavior of the electronically excited states of atomic and molecular species in the post shock area.
• Investigate the validity of the Q.S.S. assumption.
• Characterization of the ionization process.

<table>
<thead>
<tr>
<th>Time [s]</th>
<th>1634</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_1$ [Pa]</td>
<td>2.0</td>
</tr>
<tr>
<td>$T_1$ [K]</td>
<td>195</td>
</tr>
<tr>
<td>$u_1$ [m/s]</td>
<td>11 360</td>
</tr>
<tr>
<td>$p_2$ [Pa]</td>
<td>3827</td>
</tr>
<tr>
<td>$T_2$ [K]</td>
<td>62 377</td>
</tr>
<tr>
<td>$u_2$ [m/s]</td>
<td>1899</td>
</tr>
</tbody>
</table>

Flow characteristic quantities

Figure 1. Project FIRE II Launch on May 22, 1965.
Flowfield quantities

Figure: Post-shock temperature (*left*) and electron number density (*right*) profiles for a fluid particle as a function of the distance from the shock.
Internal distribution functions

Figure: Electronic energy distribution function for atomic nitrogen (left) and oxygen (right) at 1 cm from the shock front
Atomic spectra

Figure: Atomic spectra: non-equilibrium (left) and equilibrium (right) atomic line radiation at 1 cm from the shock front
EAST experiment: Simplified radiation

\[ P = 13 \text{ [Pa]} \quad \text{and} \quad V_s = 9.165 \text{ Km.s}^{-1} \]

Absolute Measurement

Boltzmann results over-predict the radiative peak by a factor 4

Relative Measurement
Grouping of the high-lying excited states

**GROUPING STRATEGY**

**COMPARISON REDUCED/FULL MODEL**
Acknowledgments

The author want to acknowledge:

NASA Ames Research Center, USA

- Richard Jaffe
- Winifred Huo
- Yen Liu
- David Schwenke
- Alan Wray
- Duane Carbon

for the very insightful discussions.
**Conclusions:**

We have studied the departures of the electronic energy populations from Boltzmann distribution for one-dimensional air flows obtained in a shock-tube.

⇒ Validation and improvement of the model is obtained comparing our results with shock tube experiments.

⇒ The atomic (and molecular) excited species distribution are found to depart from Boltzmann.

⇒ Importance of self-consistent coupling of collisional and radiative processes.

**Future Work:**

⇒ Improvement of dissociation model: Bin model ($N_2$).

⇒ Modeling of diatomic and triatomic molecular radiation.

⇒ Non-Boltzmann treatment of the free electrons (Colonna).
Happy Birthday !!!

The Abba Group