# 17. NONEQUILIBRIUM KINETICS AND SIMULATION OF DISCHARGES, AFTERGLOW PLASMAS AND HIGH-SPEED PLANETARY ENTRIES

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## 17.1. INTRODUCTION

The research work carried out by this team in 2005 falls into the following main fields of investigation:

- Kinetics of the nitrogen afterglow;
- Plasma sterilization at reduced gas pressure and low temperature;
- Nonequilibrium processes and plasma radiation in high-speed spacecraft planetary entries;
- Microwave discharges in N2-CH4 for metal nitrocarburizing and chemistry studies of Titan's atmosphere;
- Modeling of surface atomic recombination

## 17.2. KINETICS OF THE NITROGEN AFTERGLOW[1]

The study of the electron and heavy-particle kinetics in nitrogen post-discharges has been continued. The theoretical study involves two separate modules, one for the discharge (I) and another for the post-discharge (II). The stationary solutions from I are the initial conditions for module II. The electron energy distribution function (EEDF), the vibrational distribution function (VDF) of ground-state $N_2(X,v)$ molecules, and the concentrations of the most important neutral and ionic species are obtained from the coupled solutions to the electron Boltzmann equation and a system of rate-balance equations for the heavy-particles.

The purpose of this investigation is *to understand the behavior of the pink afterglow,* characterized by a raise in the emission of the first negative system bands, corresponding to transitions between the ionic states $N_2^+(B\rightarrow X)$, after a dark zone downstream from the end of a flowing discharge. The concentration of several other species, both radiative and metastable, exhibit a similar profile. In particular, it is very striking to verify an increase in the population of $N_2(A)$ and $N_2(a)$ metastables, taking place in the field-free post-discharge.

It has been shown that an equilibrium between the vibrational distribution of ground-stated $N_2(X,v)$ molecules is established and that collisions of highly vibrationally excited molecules with N atoms are in the origin of a maximum in the electron density, occurring downstream from the discharge. It is concluded that there must be a local production of $N_2(A)$ molecules, which has been shown to be due to near resonant vibration-vibration (V-V) energy exchanges, followed by electronic-vibration (V-E) exchanges. The later can be induced by collisions of highly vibrationally excited $N_2(X,v)$ molecules with both N atoms and electrons. Once the $N_2(A)$ state is created, it starts transferring energy to other states and to ionization. Therefore, many other excited states, as well as electrons and positive ions, have a similar profile during the afterglow (Figure 17.1).

In spite of the general good agreement between the available experimental results and the theoretical predictions, a global explanation for the ionization processes taking place in the nitrogen afterglow is still missing. As a matter of fact, recent experiments made in Grenoble, France, show that the role of singlet metastables in the ionization during the afterglow has been overestimated. That being so, the present-day description of the afterglow underestimates ionization, and new ionization mechanisms have to be investigated.

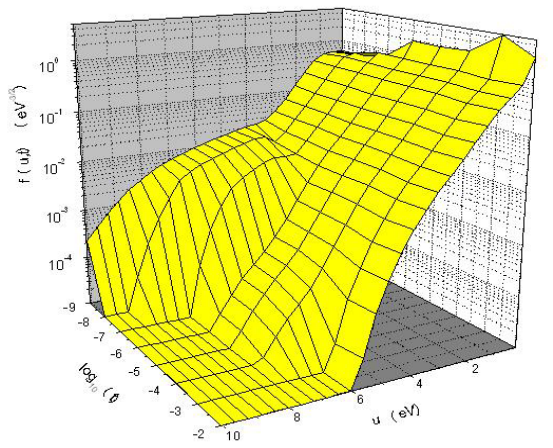


*Figure 17.1 - Time evolution of the EEDF in the nitrogen afterglow.*

## 17.3. PLASMA STERILIZATION AT REDUCED GAS PRESSURE AND LOW TEMPERATURE[2]

Gas plasma sterilization in hospitals has appeared a very promising alternative to conventional sterilization processes. Because of materials that are thermosensitive are increasingly being used in the composition of medical

[1] Work carried out in collaboration with Université des Sciences et Technologies de Lille (France) and Université Joseph Fourier de Grenoble (France).

[2] Work performed in collaboration with the Physics Department of the University of Montreal (Canada), the Laboratoire de Science et Génie des Surfaces de l' École des Mines de Nancy (France), the Department of Physical Electronics of the Faculty of Science of the Masaryk University of Brno (Czech Republic), and Prof. P.J. Coelho (Department of Mechanical Engineering, IST).

and dental devices, the possibility of the various active species created in a plasma medium may be used for sterilization has been considered. Further, this possibility should be also explored due to the necessity of inactivating new types of pathogenic agents. *Plasma sterilization reactors operating in the afterglow of a gas discharge* is the most interesting new device to be used, since it fulfill the two conditions of much lower gas temperature than in the discharge itself and the absence of charged species which could damage the material to be sterilized.

Investigations realized by the group of Plasma Physics in the Physics Department of the University of Montreal has shown that almost total inactivation of an initial prion spore population can be achieved using the afterglow of a microwave $N_2$-$O_2$ discharge, with small $O_2$ addition of the order of 0.2-2%, as a result of a synergistic effect between UV photons emitted by $NO(B^2\Pi)$ molecules and $O(^3P)$ atoms. With the aim of giving an insight into the the kinetics of a low pressure microwave flowing post-discharge in $N_2$-$O_2$, and thus determining the optimal operating conditions, investigations have been conducted in CFP by developing a fully self-consistent model for the kinetics of electrons and heavy-neutral and charged species in a flowing microwave discharge. Once the concentrations of active species produced in the discharge are determined, the afterglow is modeled by considering both a short-lived afterglow, at the end of the discharge, and the long-lived afterglow in the sterilization vessel of much larger dimension, where the objects to be sterilized will be placed. In the afterglow a complex interplay kinetics between active neutral species still continues to take place leading to the creation of some species and to the destruction of others.

Work has been performed on the kinetics of charged and heavy-species in a $N_2$-$O_2$ microwave discharge, with a model for the short-lived afterglow downstream from the discharge tube. Furthermore, a comparison between measured and predicted populations in the afterglow of a $N_2$-$O_2$ microwave discharge was also conducted.

This work has been pursued by considering a 3-D Navier-Stokes model for the post-discharge chamber, based on the coupled solutions to the set of equations for mass conservation of different species, total mass conservation, momentum transfer, and energy conservation. With this hydrodynamic model the concentrations of the various species, such as the molecules responsible by UV emission and oxygen atoms, may be followed up to the farthest remote zones of the reactor (Figure 17.2).

Finally, the study of $O_2$ and $O_2$-$N_2$ microwave discharges and post-discharges has been also conducted with the purpose of application to surface treatments, namely in the study of the oxygen plasma surface interaction in treatments of polyolefines and of the modification of hexatriacontane by $O_2$-$N_2$ microwave post-discharges (Figure 17.3).

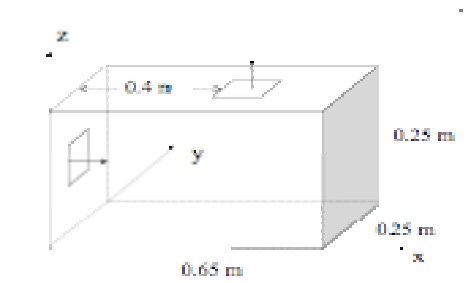


*Figure 17.2 - The post-discharge chamber used in the modulation is shown in this figure. The active species created in a $N_2$-$O_2$ flowing microwave discharge after passing through a short afterglow region are introduced into the large vessel. The entrance and the outlet have a length and width of 2.6 cm and are situated in the middle of the planes giving symmetry to the chamber.*

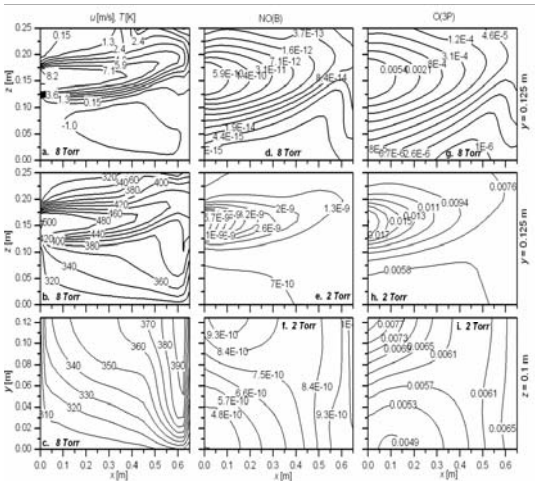

*Figure 17.3 - Distribution of velocity (a), temperature (b, c), relative mass density of $NO(B^2\Pi)$ molecules (d, e, f) and of $O(^3P)$ atoms (g, h, i), in the entrance plane y = 0.125 m (figures a, b, d, e, g, h) and in the x-y plane at z = 0.1 m height (figures c, f, i). The results are presented for two discharge conditions: (i) p = 8 Torr, f = 915 MHz (figures a, b, c, d, g); and (ii) p = 2 Torr, f = 2.45 GHz (figures e, f, h, i). Here, the results are for a $N_2$-2%$O_2$ mixture composition and gas flow of $2\times10^3$ sccm but the influence of these parameters is investigated. The gas temperature at the inlet and in the wall is assumed to be 500 K and 300 K, respectively.*

## 17.4. NONEQUILIBRIUM PROCESSES AND PLASMA RADIATION IN HIGH-SPEED SPACECRAFT PLANETARY ENTRIES

During an atmospheric entry of a space vehicle at hypersonic speeds (>5 km/s), a strong shock-wave is created in front of the spacecraft forebody. Immediately behind the shock-wave, the translational temperature of the flow reaches temperatures usually in large excess of 10,000 K. For interplanetary missions, the flight pattern is hyperbolic, and the entry velocities and translational temperatures may exceed 10 km/s and 100,000 K

respectively. After the excitation of the flow translational mode through the shock front, excitation of vibrational levels of the gas then follows through redistribution of energy from the translational mode to the vibrational mode. Dissociation and ionization of the gas species then follow until a plasma state is reached. Two issues arise in this case. The dissociation and ionization channels need to be known, in order to accurately describe the evolution of the flow macroscopic parameters (species concentrations and temperatures). This has a large impact on the determination of the convective heat transfer endured by the spacecraft thermal protections. Moreover, nonequilibrium excitation processes of neutral and ionised flow species need to be accurately known in order to determine the radiation from the plasma and to evaluate the radiative fluxes endured by the spacecraft thermal protections.

### 17.4.1. Analysis of shock-induced dissociation processes

A numerical model based on the Forced Harmonic Oscillator (FHO) theory has been developed for the *simulation of atom-diatom and diatom-diatom Vibration-Translation (V-T) processes.* This model is advantageous compared to First Order Perturbation Theory (SSH models) as it allows the simulation of multiquantum transitions and provides accurate results at very high temperatures (up to 100,000 K). Good agreement has been reached between this model and quasi-classical calculations for $N_2$ and $O_2$ molecules. The influence of multiquantum transitions on the global dissociation rates of molecular nitrogen has also been evidenced.

Currently, the influence of molecular rotation on V-T processes is being studied through the development of additional models. Vibration-Electronic (V-E) transfer processes are scheduled to being studied shortly. Future studies will also focus on ionization processes such as associative ionization ($A+B \rightarrow AB^+ + e^-$) or Penning ionization ($AB^*+AB^* \rightarrow AB^+ + e^-$). Long term objectives include the development of a full collisonal-radiative model for Earth, Mars and Titan high speed atmospheric entries.

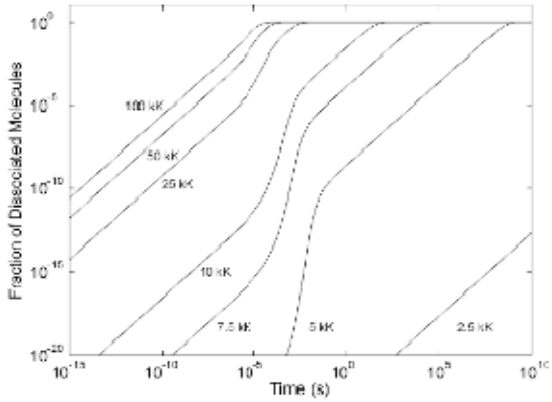


*Figure 17.4 - Dissociation times for different post-shock translational temperatures, at a 76 km altitude, and for a pre-shock temperature of 195 K.*

A collaboration program has also been established with the Université de Provence in Marseilles, France, where the shock-tube TCM2 is located. This facility is operated in the frame of the ESA-sponsored AURORA program for the simulation of shock-waves typical of Earth, Mars, and Titan atmospheric entries. The established working plan has scheduled a series of visits from researchers from the two institutions, in order to carry an interpretation and a numerical reproduction of spectra measured in Titan and Martian-type mixtures.

### 17.4.2. Analysis of atmospheric entry radiative processes

A detailed investigation of the *high temperature radiative processes encountered during an atmospheric entry* is also carried in the research group. Currently, two different numerical tools have been developed and made available to the atmospheric entry research community:

*i)* The line-by-line code SPARTAN (**S**imulation of **P**lasma **R**adiation in **T**hermodyn**A**mic **N**onequilibrium) for the simulation of plasma radiation from air and $CO_2$-$N_2$ plasmas has been developped and is freely made available to the general scientific community. The numerical code is capable of simulating over 50 different bound, bound-free, and free transitions (Figure 17.5). More informations on the numerical code can be found in the following electronic adress: http://cfp.ist.utl.pt/geg/radiation/SPARTAN/. Currently, the code is being used by three different european research teams (two in France and one in Italy).

*ii)* An electronic database gathering factual information on radiative transitions of diatomic molecules of interest for planetary atmospheric entries has been developed and put online at the following electronic adress: http://cfp.ist.utl.pt/geg/radiation/GPRD/. Future versions of this database are scheduled to be added to the electronic databases provided by the European Space Agency, acting as the database of reference for providing spectral coefficients for the calculation of atmospheric entries radiation.

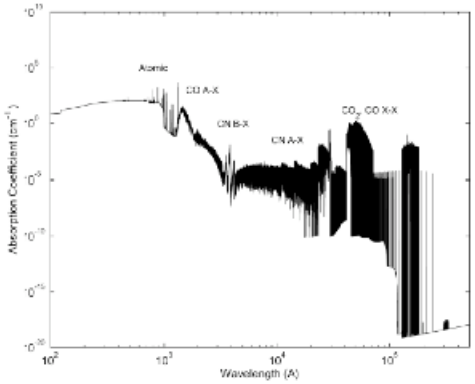


*Figure 17.5 - Sample calculation of the spectral-dependent absorption coefficient for a 97% $CO_2$ – 3% $N_2$ plasma at 1bar, 5000K, and in thermodynamic equilibrium*

The group maintains a collaboration with the Laboratoire Arc Electrique et Plasmas Thermiques in Clermont-Ferrand, France. An analysis of the thermodynamics and radiative properties of a Martian-type $CO_2$-$N_2$ plasma produced in a Inductively Coupled Plasma torch at atmospheric pressure is being carried in the scope of this collaboration. Also, the group is currently involved in the expertise and further development of the ESA line-by-line code PARADE (Fluid Gravity Eng. Contract with M. Dudeck, U. Paris VI).

### 17.4.3. Analysis of Born-Oppenheimer hypothesis in polyatomic molecules

A working group has been recently set-up to focus on the Born-Oppenheimer hypothesis breakdown and it's impact on aerothermodynamics. We are participating in this working group whose task is to meet at regular schedules and to analyse the consequences of using the Born-Oppenheimer hypothesis in the majority of all the classical to quantum molecular models developped by the scientific community. The working group task also includes examining the possibility of developping further methods who do not require this assumption, and defining a roadmap for future investigations.

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## 17.5. MICROWAVE DISCHARGES IN N2-CH4 FOR METAL NITROCARBURIZING AND CHEMISTRY STUDIES OF TITAN'S ATMOSPHERE[3]

The study of a $N_2$-$CH_4$ afterglow has an actual interest due to the large number of applications in different fields, such as the detoxification of gases, metal surface nitrocarburizing and the study of the atmospheric chemistry of Titan.

In the case nitrocarburizing, the afterglow resulting from a nitrogen-methane flowing microwave discharge can be very efficient in metal surface treatments, due to the importance of the presence of N and C atoms in the formation of carbonitrides $\varepsilon$-$Fe_{2-3}$ (C, N) and $\gamma$-$Fe_4$(C,N) in metal nitrocarburizing processes. Further, this treatment can be improved with the presence of H atoms.

Two situations have been investigated in a flowing $N_2$-$CH_4$ afterglow of a microwave discharge: i) methane is added to $N_2$ in the downstream afterglow; ii) methane is added to the discharge. In both cases the $CH_4$ addition is always smaller than ~ 0.5-1%. The discharge is produced using a surfatron device connected to a microwave generator at 2.45 GHz and the post-discharge is analysed at about 200 mm downstream from the discharge. Optical Emission Spectroscopy (OES) is carried out in the post-discharge. The densities of N and C atoms in the late post-discharge can be inferred from OES measurements of the first positive system of $N_2$ , emission of the $N_2(B^3\Pi_g,11) \rightarrow N_2(A^3\Sigma_u^+,7)$ transition, and of the CN violet band $CN(B^2\Sigma,7) \rightarrow CN(X^2\Sigma,7)$, respectively, by assuming simple kinetic models for the long-lived afterglow, and using absolute calibration by NO titration. On the other hand, the kinetic model considers the self-consistent determination of the active species concentrations in the discharge and consequent time-relaxation in the afterglow. In situation i), where a small methane percentage is introduced into the post-discharge at 250 mm downstream from the end of the discharge, methane dissociation ($CH_3$, $CH_2$, etc.) occurs in the afterglow in the presence of active nitrogen, together with several other reactions leading to formation of HCN, $CN(X^2\Sigma)$, $CN(B^2\Sigma)$, etc. The C atoms are then formed as a result of a complex kinetics.

Discharges in $N_2$-$CH_4$ have been also studied with the aim of understanding the organic chemistry of Titan's atmosphere, in particular the conditions for formation of organic aerosols, also termed "tholins", that are observed in Titan.

## 17.6. MODELING OF SURFACE ATOMIC RECOMBINATION:

The study of the surface kinetics of atomic species, such as N and O atoms, and in particular of the elementary processes leading to heterogeneous recombination, is nowadays an important subject of research in various problems of rarefied gas dynamics, such as the aerodynamics of space vehicles moving in rarefied gases. On the other hand, many of the characteristics of plasma reactors are in practice controlled by wall reactions. Therefore, there is a need to address the questions of the *role of surface processes in the overall behavior of different gas discharges.*

Many theoretical works have been done recently in order to investigate surface recombination of atoms. For instance, phenomenological models and Monte Carlo models have been developed. All these models provide important physical insight into the various elementary mechanisms occurring at the surface and, particularly for the case of the Monte Carlo, allow to perform quite complete and detailed simulations. The purpose of the present investigation is to follow a different approach, by obtaining asymptotic analytic solutions for the recombination probability. It is shown that the approximate analytic solutions describe the system with very high accuracy (Figure 17.6). Thus, for the system under analysis, the recombination probability can be readily evaluated from a simple expression, with no need for any numeric treatment. As a consequence, the dependence of the recombination probability on different surface parameters, such as the activation energies of the various processes and the wall temperature, can be fully understood.

The probability for surface atomic recombination of a single gas is theoretically investigated, for a system that takes into account atomic adsorption in physisorption and chemisorption sites, surface desorption, surface diffusion,

[3] Work carried out in collaboration with the Laboratoire de Science et Génie des Surfaces de l' École des Mines de Nancy (France) and the Service d' Aéronomie de l' Université de Paris VII and Versailles/Saint Quentin (France).

and both Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) recombination mechanisms.

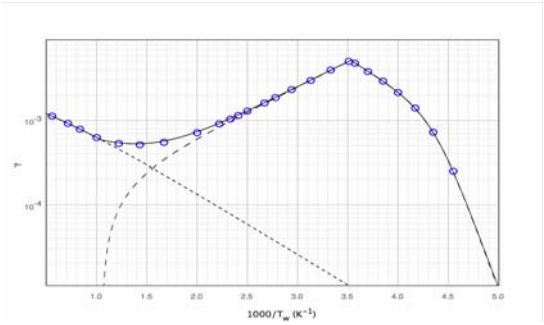


*Figure 17.6 - Numerical (blue circles) and asymptotic analytical solutions (full line) for the recombination probability of nitrogen in silica. The contribution of L-H (dashed line) and E-R (dotted line) recombination mechanisms to the total recombination probability is also shown.*