PLASMAKIN: A CHEMICAL KINETICS LIBRARY FOR PLASMA PHYSICS MODELLING

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Abstract

PLASMAKIN is a software library to handle physical and chemical data and to compute kinetics data from the reactions taking place in the gas or at the surfaces – particle generation and loss rates, photon emission and energy exchange rates. PLASMAKIN supports a large number of species properties and reaction types, doesn't impose any limit on the number of species and reactions, is independent of problem dimensions and can be used on a large range of conditions.

The interaction of the user with the library is limited to the preparation of an input file characterizing the interacting species and reactions, accessing the data or the chemical kinetics results through a reduced number of procedure calls.

An auxiliary library BOLTZKIN solving the homogeneous electron Boltzmann equation and build on top of PLASMAKIN, allows coupling the electron, vibrational and chemical kinetics permitting a solution of a significant number of problems.

As an example a program has been prepared to evaluate the maintenance field, equilibrium populations, relative contribution of each reaction, photon emission spectra and the energy losses rates on the positive column region of a discharge in electropositive gases. Results are shown for a neon discharge.

PLASMAKIN is written in Fortran 95 and is published under the GNU Open Software licence terms.

Introduction

A large number of problems in plasma physics involve the consideration of several chemical species and reactions. The solution of such problems invariably requires the ability to read, classify, sort and manipulate particles and reactions and the evaluation of source terms in conservation equations. The study of the discharge processes also requires the evaluation of the energy transferred in collisions, the gas heating or the photon emission spectra.

The handling of these data frequently represents a significant fraction of codes, development and maintenance time and is a source of errors. It would clearly be advantageous to have a package able to deal with that data independently of the number or nature of the species and chemical reactions involved, of the problem being solved or the method used. Such a package could be used as a "black box" moving the description of particles and reactions from code to a data file, allowing the user to concentrate on the physical problem and on the algorithm to solve it. Once the code developed, it would allow an easy and fast modification and testing of chemical models.

The need of a "language" to write chemical reactions and the computation of kinetic terms in a generic way is a subject of very broad application and several approaches have been developed. Packages have been published that are directed to specific fields – plasma physics [1]; atmospheric chemistry [2,3] – or to general-purpose chemistry [4]. However only the last one evaluates the energy exchange rates; the first one does not include surface reactions, the atmospheric chemistry codes do not cover the needs of plasma physics and the last, although
quite complete, is a proprietary, commercial product. Some of these packages have been
designed as closed programs and are not readily adapted to other problems.
To address these limitations *PLASMAKIN* was designed as a library to be linked with an user's
programs and providing a standard framework to handle particle properties, reaction data and
the kinetic terms needed for plasma physics modelling. In order to be as general as possible,
*PLASMAKIN* is independent of the number of space dimensions, has no limits on the number of
species or reactions and can be used both in stationary and time-dependent problems. At the
same time it was decided not to include any ODE or PDE solver, leaving the choice of the
algorithm to the user. These design options allow *PLASMAKIN* to be used in rather different
problems, with a large range of codes – Boltzmann equation solvers, collisional-radiative
codes, fluid and hybrid codes. Monte Carlo or PIC codes.
Finally, in discharges where superelastic collisions are important (particularly in molecular
gases) the electron energy distribution depends on the population of vibrational and electronic
level and the electron Boltzmann equation must be solved together with the master equations
for these levels. To facilitate this coupling the library *BOLTZKIN* has been developed to solve
the homogeneous electron Boltzmann equation in DC or HF electrical fields based on the
two-term expansion in velocity space and using the data handling capabilities of *PLASMAKIN*.
The following sections give an overview of the capabilities of these two libraries; a discussion
of the architectural design; an example of usage of the library, finishing with a discussion of
future developments.

**Species properties and chemical reactions**
Species taking part on the discharge and the values of several properties must be listed on an
input file. The value of some properties allows the library to perform "clever guesses" about
the values of other species or reactions properties. Together with the use of default values for
all properties this reduce the amount of data the must be written in the input file and the
possibility of errors.
The list of properties include the name; whether the concentration is constant; the charge state
$q$; the mass $M_e$; the level degeneracy $g_i$; the excitation or ionisation energy $E_i$ or the standard
molar formation enthalpy $H^F_i$; the specific heat capacity $C_p$ or $C_v$; the thermal conductivity
$K_i$; the vibrational quantum number $v$; the vibrational frequency $\omega$; and temperature $T_i$; the
anharmonicity parameter $\zeta_i$; the rotational constant; the dipolar or quadrupolar momentum;
the initial concentration; an index identifying a used defined numerical scheme for the
the corresponding conservation equations; whether the species is to be considered a cascade level;
and a data structure allowing the reading of other properties in an auxiliary file.
*PLASMAKIN* is able to evaluate the species forming a vibrational series from the properties of
the corresponding electronic level and the limiting values of $v$. In this case the initial relative
population of vibrational levels is estimated using a Gordets-Treanor distribution [5].

Both unimolecular, bimolecular and termolecular reactions can be included.

*Optical emission and absorption* are examples of unimolecular reactions important in plasma
physics. Radiation imprisonment can be accounted including a constant or radial dependent
escape factor [6].

*Cascade levels* (influencing the population of lower levels by spontaneous emission but
whose density is not followed) are supported and the corresponding branching ratios are
automatically evaluated.

*Rate coefficients* - A large number of rate coefficients have an Arrhenius temperature
dependence. However reactions in plasma can have more complex temperature dependencies
or, as is the case for electron collision reactions, depend on the electron temperature. To
accommodate this, rate coefficients with a power series dependence on temperature in the exponential term can be used in PLASMAKIN:

$$k_i = \alpha_i T^{\gamma_i} \exp\left(\sum_{j=1}^{5} \alpha_{ij} T^{\beta_i j}\right)$$

where $T$ is the electron temperature for electron collision reactions and the gas temperature for other cases. The initial temperature is read in the data file and can be changed during program execution.

A large number of reactions with vibrational levels are formally identical, the only difference being the vibrational number(s). To avoid the need of writing all this reactions PLASMAKIN is able to read a description of a group of vibrational reactions, create the corresponding individual reactions and compute the rate coefficients.

Finally, to compute rate coefficients known as a function of the reduced field $E/N$ or mean energy $\epsilon$ (as is frequently the case for electron rate coefficients), rate coefficients depending on vibrational quantum numbers or other expressions, a user supplied routine can be used.

**Reverse reactions** - As the rate coefficient for forward and reverse reactions are related by the principle of detailed balancing, PLASMAKIN automatically evaluates the reverse rates from the corresponding forward rates.

**Termolecular Reactions** - Two types of pressure-dependent reactions are included: recombination reactions and chemically activated bimolecular reactions. Reaction rates are calculated using the Lindemann [7] and Troe [8] formulation. In both cases the 3rd body concentration can be set proportional to the total pressure of to the partial pressure of a selected gas species.

**Surface Reaction** can be included and adsorbed atoms with different efficiencies in promoting the reaction can be accounted. The indication of a surface name allows differentiating between surfaces.

**Energy losses** - The energy exchanged in reactions is calculated from the values of the formation enthalpy at the gas temperature. As the gas temperature in cold plasmas is within a few hundred degrees $T_0$, the formation enthalpy at gas temperature is not much higher than the standard value and is approximated by $H_f(T_0) = H_f^0(T_0) + C_p \Delta T$.

**Electron kinetics**

In discharge regions with a homogeneous electrical field and for low $E/N$ values, the classical two-term expansion of the electron velocity distribution function in velocity space can be used and when associated with a sparse matrix solver, allows a fast computation of the eedf on DC or HF fields.

The library BOLTZKIN extends PLASMAKIN with the capability of handling electron collision cross sections for forward and superelastic processes (the superelastic cross sections are automatically evaluated); calculation of the electron energy distribution function, eedf, an the evaluation of transport parameters and electron collision rate coefficients.

**Architectural design**

PLASMAKIN has been influenced by the application of object-oriented methodologies to Fortran [9]. The programming paradigms of abstraction, information hiding, data encapsulation and function overloading were followed as guidelines for the design of data types and routines and simplify future development and use with other languages.

Fig. 1 represents the relationships between PLASMAKIN and other routines. The library is a Fortran 90/95 module unit with public and private data and procedures. However although PLASMAKIN is build on modern programming concepts and structures, for compatibility with existing code all public data and procedures are compliant with FORTRAN 77 conventions.
The module reads data from an input file and can call a user-supplied routine SetRate to evaluate complex reaction rates, but is otherwise, self-contained.

Three categories of procedures are available:

a) Data reading, input file parsing, data allocation and destruction;

b) Data inquiring - particle or reaction properties and kinetic data;

c) Data modification

PLASMAGIN can be obtained through C.P.C. Program Library and a throughout description of the library procedures and data of can be found in [10].

![Diagram](image)

**Figure 1 - Relationship between and Other program units and data files**

**Example of usage - the positive column region in a neon discharge**

As an example of the library usage a program to study the positive column in electropositive gases was prepared.

The condition for a steady-state discharge, i.e., the discharge "maintenance" condition can be written [11]:

$$\frac{N D_{ii}}{(N \Lambda_i)^2} = G_i / \Lambda_i \cdot I_i, \quad i = 1, \ldots, N_s - 1$$

where $N$ is the gas density, $N_s$ the number of species, $D_{ii}$ a diffusion coefficient, $\Lambda_i$ the diffusion length, $\Lambda_i = \bar{\Delta_i}/N$ the radial averaged relative concentration of species $i$ and $N$, the number of species and it is assumed that the rate coefficients and transport parameters are independent of the radius. For ions $D_i$ is the ambipolar diffusion coefficient and for electrons $D_e$ is an effective diffusion coefficient ranging from the space charge free diffusion coefficient to the ambipolar diffusion coefficient [12]. The diffusion and electron rate coefficients are functions of $E/N$. Imposing a discharge current, the above non-linear system can be solved together with the charge conservation condition, to evaluate the maintenance field, the relative concentrations, $\Delta_i$, and the contribution of each reaction to these populations. The collision terms $G$ and $L$ are evaluated by PLASMAGIN allowing the program to be independent of the gas mixture.

This model was applied to a neon discharge using a kinetic model similar to that used in [13] for argon. The species and reactions considered in the model are indicated in Table 1 and include electron excitation of the four 3s levels; excitation to two representative 3p levels and a upper level representing higher levels; cascade transitions from the 3p to the 3s levels; electron-impact-induced excitation transfer between the 3s levels; ionisation from the 3s levels; Penning ionisation between the 3s levels; radiative transitions for the resonance levels with radiation imprisonment; diffusion to the wall; formation of the neon molecular ion in Penning and 3-body collisions. Radiation imprisonment is accounted by an averaged escape factor [18] adapted to a Voigt line profile in the high opacity approximation.
Table 1 - Collisional and radiative processes included in the kinetic model for neon

<table>
<thead>
<tr>
<th>Process</th>
<th>Value</th>
<th>Reaction index</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne + e → Ne + e</td>
<td>Boltzmann</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ne + e → Ne(3s) + e</td>
<td>Boltzmann</td>
<td>2 - 5</td>
<td></td>
</tr>
<tr>
<td>Ne + e → Ne(3p) + e</td>
<td>Boltzmann</td>
<td>6 - 7</td>
<td></td>
</tr>
<tr>
<td>Ne + e → Ne(4s) + e</td>
<td>Boltzmann</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Ne + e → Ne^+ + 2e</td>
<td>Boltzmann</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Ne(3s) + e → Ne^+ + 2e</td>
<td>Boltzmann</td>
<td>10 - 13</td>
<td></td>
</tr>
<tr>
<td>Ne(3s) + e → Ne(3s) + e</td>
<td>Arrhenius</td>
<td>14 - 25</td>
<td>[14]</td>
</tr>
<tr>
<td>Ne(3s) + e → Ne + γ_k</td>
<td>j = 2, 4</td>
<td>30 - 31; 33 - 34</td>
<td>[15]</td>
</tr>
<tr>
<td>Ne(3p) + Ne(3s) + γ_k</td>
<td>cascade trans</td>
<td>36 - 45</td>
<td></td>
</tr>
<tr>
<td>Ne(3s) + Ne(3s) + 2e</td>
<td>3.2 x 10^{16} cm(^{-3}) s(^{-1})</td>
<td>46 - 55</td>
<td>[16]</td>
</tr>
<tr>
<td>Ne(3s) + Ne(3s) + Ne^+ + e</td>
<td>3.2 x 10^{16} cm(^{-3}) s(^{-1})</td>
<td>56 - 65</td>
<td>[16]</td>
</tr>
<tr>
<td>Ne^+ + 2M → Ne + M</td>
<td>2.5 x 10^{11} cm(^{-3}) s(^{-1})</td>
<td>66</td>
<td>[17]</td>
</tr>
</tbody>
</table>

This model although simple allows an approximate description of the discharge and is used here mainly as an example of the flexibility introduced by PLASMakin.

PLASMakin allows to obtain a large amount of information on the discharge. The following figures are a selection of the different results available:

Figure 2 shows the predicted discharge characteristics for three values of discharge current. As discussed in [13], for low values of the product NR, the discharge characteristics follows a similarity law of type $E/N = f(NR, I/R)$; Figure 3 shows the predicted relative concentration

![Figure 2](image1.png)  ![Figure 3](image2.png)

**Figure 2** - Characteristics of $E/N$ vs $NR$ for the neon positive column for three values of $I/R$.

**Figure 3** - Relative populations vs $I$ at $p = 0.5$ mbar and $R = 1$ cm.

for selected conditions; Figure 4 shows the photon emission spectra for $p = 1$ mbar and $I = 10$ mA. As we have considered the 3p and 4s levels grouped, the lines below 3 eV and corresponding to emission from these grouped levels are shown only for illustration; finally Figure 5 shows the relative contribution of selected reactions, including elastic collisions, to the electron energy losses for three current values. The labels refer to the reaction index in Table 1.
Figure 4 - Simulated photon emission spectra at $p = 0.1$ mbar, $R = 1$ cm and $I = 10$ mA. (See text for comments)

Figure 5 - Relative contribution of selected reactions to the electron energy loss term, at $p = 1$ mbar and $R = 1$ cm

Future developments

Although in the present version PLASMakin already supports a large number of gas properties and reaction processes, several improvements are being considered. Namely, support for ionic excited states; the support for surface reactions with different adsorbed atoms and evaluation of several physical properties such as the surface coverage and sticking coefficient, and several other thermodynamic properties.

References