Global modelling of non-equilibrium low-temperature plasmas

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Global (zero-dimensional) models are very popular in the modeling of low-temperature plasmas, especially when the focus is on plasma chemistry. This talk will briefly introduce the LisbOn Kinetics LoKI-B+C simulation tool, highlighting some of the most recent simulation results obtained with the code. We will underline the importance of validation activities, comparing modelling results with experimental measurements, to unfold the full potential of modelling as a predictive tool.

The field of low-temperature plasma (LTP) science and engineering is driven by a dual focus on both fundamental scientific exploration and practical applications aimed at societal advancements. Fundamental research endeavors to delve into the underlying principles governing these plasmas, playing a pivotal role in achieving the scientific breakthroughs necessary for successful applications.

Modelling activities are a fundamental component in any research domain, complementing and/or aiding experimental diagnostics; providing predictions on the behaviour of significant quantities, especially when experimental acess is limited; and contributing to a deeper understanding of the field‘s fundamental knowledge. Modelling and simulation of LTP have been considered as requirements for advancing the field, and model-based design for plasma equipment and processes has been identified as a critical capability realizing industrial objectives [1]. The guidance offered by LTP models proves particularly valuable given the inherent complexity of the medium (often characterized by different material phases), composed by charged particles (electrons and ions) and by neutral species in different excited states, intrinsically in non-equilibrium as result of collisional, radiative and electromagnetic interactions.

Global (zero-dimensional) models are very popular in the modeling of LTP, especially when the focus is on plasma chemistry [2]. In these models, the dynamics of the plasma species *s* is described by particle rate balance equations, composed by production and destruction terms as defined by chemical reactions, in addition to a loss term due to transport writen under an algebraic form

$$\frac{dn_s}{dt} = \sum_j \left\{ \left(a_{sj}^{(2)} - a_{sj}^{(1)} \right) k_j \prod_l n_l^{a_{lj}^{(1)}} \right\} - \nu_{transp_s} n_s \ . \qquad (1)$$

Here, n_s is the density of the species; $a_{sj}^{(1)}$ and $a_{sj}^{(2)}$, are the stoichiometric coefficients of species *s*, as they appear on the left- and right-hand sides of a reaction *j*, respectively; k_j is the rate coefficient of reaction *j*; and ν_{transp_s} is the spatial-averaged loss frequency due to transport to the walls. The set of chemical reactions defining the kinetic scheme of interest should include both volume and surface mechanisms. The extension to a surface kinetics can be easily done by considering a mesoscopic description [2], including for example physical adsorption/desorption, chemical adsorption, surface transport, and Eley-Rideal and Langmuir–Hinshelwood recombination processes. The rate coefficients for electron-induced processes, such as ionisation, excitation/de-excitation and dissociation, are obtained by averaging the corresponding energy-dependent cross sections over the electron energy distribution function (EEDF), and for other chemical reactions, e.g. between the neutral species or the ions, they are typically calculated from temperature-dependent Arrhenius equations, obtained from literature. In non-equilibrium LTP, the EEDF should be calculated by solving the electron Boltzmann equation coupled to the rate balance equations. In this case, there is no need to solve the electron-energy balance equation to close the model, since the electron Boltzmann equation makes it possible to obtain

the electron mean energy (or an equivalent electron kinetic temperature) for a given value of the reduced electric field E/N (where E is the electric field and N is the density of the gaseous mixture), to be determined self-consistently.

The transport of charged particles is key to identify the operating point of a gas discharge, defined through a Schottky-like condition [2,3] that balances the net creation rate of electrons and ions due to kinetic mechanisms in the volume, with their loss rate to the walls. Satisfying this condition allows self-consistently determining as eigenvalue the reduced electric field that maintains the plasma, consistent with the required net creation-rate of charged particles, for given discharge parameters (e.g. gas density and plasma dimensions) that define the corresponding particle losses. In the end, a direct effect of this eigenvalue on the plasma chemistry is expected, via the electron excitation and ionization frequencies influencing the kinetics.

Global models can be solved using codes available in the LTP community: ZDPlasKin, a freeware code developed by Pancheshnyi *et al.* [4]; GlobalKin, developed by Kushner *et al.* [5, 6] and available upon request; Quantemol-P, developed with a graphical user interface [7], corresponding to a commercial application that extends GlobalKin to the automatic generation of a plasma chemistry from a set of userdefined species; and the global model within the PLASIMO commercial software, developed by van Dijk *et al.* [8]. In this work, we will use the LisbOn KInetics LoKI-B+C [9], a simulation tool for plasma chemistry (to be relased as open-source code), which couples two main calculation blocks: a two-term Boltzmann solver (LoKI-B) [10,11] (released as open-source code licensed under the GNU GPL v3.0) and a Chemical solver (LoKI-C), developed / consolidated resorting to the well-grounded scientific foundations of the Portuguese group N-PRiME.

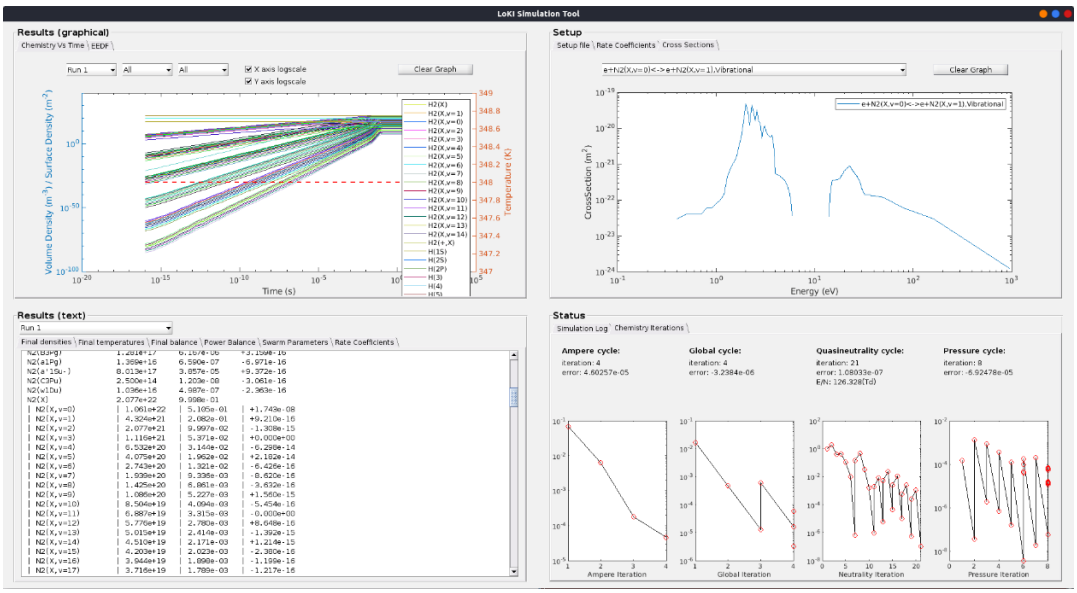

Fig. 1: Example of the Graphical User Interface display after a complete LoKI-B+C simulation.

LoKI-B+C has been developed to handle kinetic schemes in *any* complex gas mixture, describing *any* type of collisional encounter between *any* electron/neutral/ion species. In particular, LoKI-B considers first and second-kind electron collisions, including anisotropic effects for elastic and rotational collisions. The solution of LoKI-B+C follows a workflow embedding four iterative cycles: (i) over the initial mixture composition, to obtain the user-prescribed *pressure*; (ii) over the reduced electric field, to satisfy the plasma *neutrality*, for an user-prescribed electron density (or some equivalent parameter, see (iv)); (iii) over the densities of the most relevant excited states afecting the electron Boltzmann equation, to *globally* converge over the EEDF and the electron macroscopic parameters; and (iv) over the electron density, to obtain the user-prescribed *discharge current* (or *power density*). As output, LoKI-B+C self-consistently calculates the EEDF and the associated electron macroscopic parameters, the densities of species, the reaction creation/destruction rates, and the reduced electric field.

This talk will briefly introduce LoKI-B+C and its workflow. We will focus on the formulation used to describe electron anisotropic scattering in LoKI-B, and the flexibility of the code to parse I/O data,

adopting the standards of the future platform LXCat 3.0 [12]. And we will attempt to illustrate a simulation example (see Fig. 1), before highlighting some of our most recent simulation results obtained using LoKI-B+C.

The literature proposes several formulations to describe the transport of charged particles in the global modeling of LTP, and we will analyze the influence of several of these formulations using as testbeds DC discharges in oxygen and microwave discharges in helium [13].

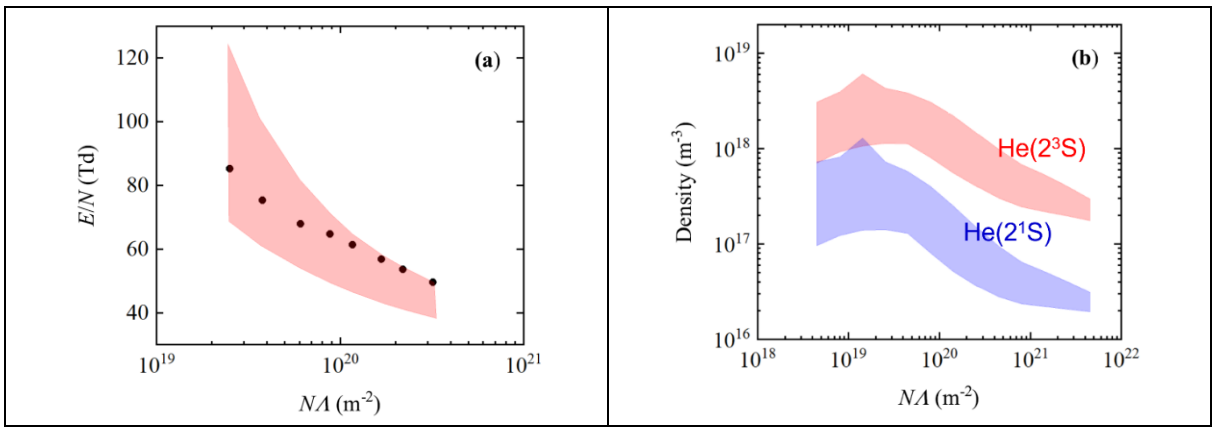

Fig. 2: Measurements (points) and calculations (bands), adopting various charged-particle transport models, of: (a) discharge characteristics of E/N vs. $N\Lambda$ in oxygen, for cylindrical DC discharges (1 cm radius and 52.5 cm length) at 10 mA current; (b) densities of metastables in helium, as a function of $N\Lambda$, for cylindrical microwave discharges (0.3 cm radius), at 2.45 GHz frequency, $5\text{x}10^{18}$ m^{-3} electron density, and 1000 K gas temperature.

Results show that (see Fig. 2) using different charged-particle transport models can result in uncertainties of 20% – 60% and 8% – 115% in the discharge characteristics of oxygen and helium, respectively, with larger dispersion at low pressure and low electron density. The spreading in the results is observed also in the densities of the main plasma species, corresponding to uncertainties up to 60% and within 50% – 150% in oxygen and helium, respectively.

The development of kinetics schemes for plasma chemistry is only meaningful when these schemes are validated by comparing simulation predictions with experimental measurements. The LTP community has been following this path for many years, but it is suggested that it should adopt a higher paradigm, defining *reaction mechanisms* validated against *benchmark experiments* [14]. The concept of reaction mechanism was introduced by the combustion community, and it corresponds to a set of experimentally validated reactions and corresponding rate coefficients. And in the present context, benchmark experiments represent a significant ensemble of experimental data, intended (or suited) for model validation, obtained in well defined and reproducible conditions, using established diagnostics, and assessing multiple quantities.

A recent effort in this direction involved the comparison of simulations made by the N-PRiME group in Lisbon with measurements made in benchmark experiments by a group from the *Laboratoire de Physique des Plasmas* (LPP) in Paris, in collaboration with a team from the Lomonosov Moscow State University (MSU), regarding oxygen plasmas produced by DC glow discharges for gas pressures of 30 – 1000 Pa and currents of 10 – 40 mA. The study comprised the densities of the main species in the discharge, $O_2(X^3\Delta_g^-)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_{g+})$ and $O(^3P)$, and also the reduced electric field and the gas temperature, and it revealed new mechanisms for the creation / destruction of these species [14].

Figure 3(left) shows simulation results and measurements of the $O(^3P)$ density, as a function of pressure, for a discharge current of 30 mA. Measurements were obtained from radially averaged vacuum ultraviolet (VUV) and actinometry diagnostics, and from on-axis cavity ringdown spectroscopy (CRDS). There is good agreement between model and experiment, which is greatly due to the values used for the recombination probability, taken from experiment. The effect of the discharge current on the $O_2(a^1\Delta_g)$ density is shown in Fig. 3(right), for gas pressures of 50 and 400 Pa. As expected, an increase in current/electron density leads to larger densities of the metastable, which again agree well with VUV and optical emission spectroscopy (OES) measurements.

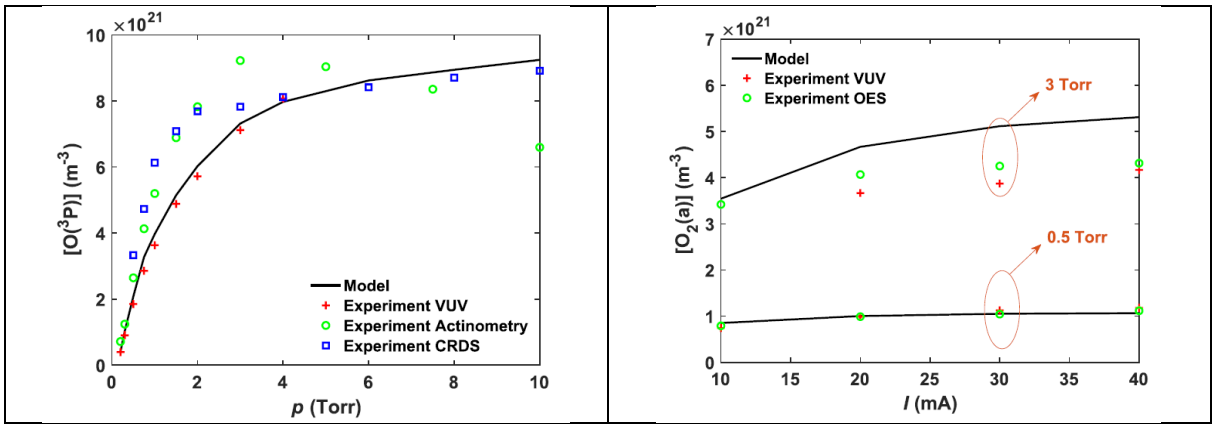

Fig. 3: Measurements (points) and calculations (curves) for cylindrical DC discharges in oxygen (1 cm radius and 52.5 cm length; wall temperature of 323.15 K): left, $O(^3P)$ density, as a function of pressure for 30 mA current; right, $O_2(a^1\Delta_g)$ density, as a function of discharge current, for 0.5 and 3 Torr gas pressures.

We will conclude presenting the results of our current efforts to model nitrogen-hydrogen plasmas produced in DC glow discharges with borosilicate glass walls [15], with low H_2 concentrations (< 5%), at 5 sccm continuous flow, 50 – 500 Pa pressures and 10 – 40 mA discharge currents. This involves a critical review of the rate coefficients adopted in the kinetic scheme, with a special focus on the wall reactions, the reactions leading to the production/destruction of mixed H/N species, and the electron-impact reactions that will mostly affect the trends as a function of current [16].

Modelling activities in the field of LTP are an essential and widely embraced research component for investigating fundamental processes, providing quantitative predictions on the behaviour of systems, guiding the design of experiments and diagnostics, and optimising devices. The potential of modelling as a predictive tool can only be achieved after a validation process, by comparing modelling results with experimental measurements, a step that requires an intense collaborative work within the community.

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