Numerical simulation tools for plasma chemistry

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Global models are the most popular choice for the modelling and simulation of low-temperature plasmas, when the focus is on the plasma-enhanced production of reactive species, and the analysis of the corresponding chemical reaction pathways for defining a reaction mechanism, a subject often referred as "plasma chemistry". There has been considerable investment in the development of global models and the implementation of numerical tools for their solution, but despite this effort some challenging issues remain open and require further attention. The talk will review the usual formulation of global models, present several well-known numerical tools available for plasma chemistry, and propose some topics where the community could concentrate additional efforts.

1. Introduction

Modelling and simulation (M&S) activities in low-temperature plasmas (LPT) have been considered as key requirements for the progress in the field, and model-based design for plasma equipment and processes has been identified as a necessary capability to achieve industrial goals [1,2]. However, the M&S of LPTs obtained from gas discharges can be challenging due to the nature of these media, composed by charged particles (electrons and ions) and by neutral species in different excited states, intrinsically in non-equilibrium as the result of collisional, radiative and electromagnetic interactions.

When developing plasma-driven applications (e.g. material processing, plasma medicine, environmental control, energy storage, etc), the focus is often on the plasma-enhanced production of reactive species, and the analysis of the corresponding chemical reaction pathways for defining a reaction mechanism, a subject often referred as "plasma chemistry". In this case, global models are the most logical choice for the M&S of gas/plasma systems, since they allow describing the detailed plasma chemistry in complex gas mixtures, with little computational effort.

Essentially, global models solve the rate balance equations of the various gas/plasma *k*-species [3]

$$\frac{dn_k}{dt} = \sum_j \left\{ \left[a_{kj}^{(2)} - a_{kj}^{(1)} \right] k_j \prod_l n_l^{a_{kj}^{(1)}} \right\} - \frac{D_k}{\Lambda_k^2} n_k \quad (1)$$

where n_k is the density of the *k*-species; $a_{kj}^{(1)}$ and $a_{kj}^{(2)}$ are the stoichiometric coefficients of the *k*-species, as they appear on the left- and right-hand sides of reaction *j*, respectively; D_k and Λ_k are the corresponding diffusion coefficient and diffusion length, respectively, eventually obtained by considering multicomponent transport and addressing also the reactivity at the walls; and k_j is the rate coefficient of the *j*-reaction. In the case of electron-induced mechanisms, the latter writes

$$k_j = \left(\frac{2}{m_e}\right)^{1/2} \int_0^\infty u \sigma_j(u) f(u) du \quad (2)$$

where m_e and u are the electron mass and kinetic-energy, respectively, $\sigma_j(u)$ is the cross section of the *j*-reaction and $f(u)$ is the electron energy distribution function (EEDF). Under non-equilibrium conditions, typical of LTPs, the EEDF should be calculated with a Boltzmann solver, often integrated in the global model. The rate coefficients of the chemical reactions resulting from collisions between heavy species (neutrals and/or ions), are typically calculated from Arrhenius-type equations that depend on the gas temperature, using data adopted from the literature.

Usually, the closure of the model corresponds to the self-consistent calculation of the power required to sustain the plasma, or any related quantity such as the reduced electric field. Often, this closure is implemented by adopting the *local energy approximation*, which solves the power balance equation for the electrons, accounting for the power gained from the electric field and the power lost in transport and collisions. Alternatively, the closure can adopt the *local field approximation*, either by solving a simplified form of the power balance equation (where the losses due to transport are neglected), or by using directly the electron Boltzmann equation to evaluate the reduced electric field that satisfies the condition of quasi-neutrality.

The gas temperature T_g can also be calculated, by solving the power balance equation for the heavy-species, assumed thermalized. For an ideal gas of density $N = \sum_k n_k = p/(k_B T_g)$ (with p the gas pressure and k_B the Boltzmann constant), producing plasma under isobaric conditions within a cylinder of radius R and wall temperature T_w, this equation writes

$$\frac{1}{N}\sum_k n_k m_k C_{p,k}\frac{dT_g}{dt} = \frac{8\lambda(T_g - T_w)}{R^2} + \Theta_{el} + \sum_j R_j \Delta H_j \qquad (3)$$

where m_k and $C_{p,k}$ are the mass and the specific heat at constant pressure of the k-species, respectively; λ is the gas thermal conductivity; Θ_{el} is the power transferred from the electrons to the heavy particles by elastic collisions; R_j is the rate of the j-reaction; and ΔH_j is the net enthalpy transferred in the j-reaction into the translational mode of the gas.

2. Tools and challenges

The LTP community benefits from several implementations of global models, such as ZDPlaskin [4], GlobalKin [5,6], for which a commercial application with a GUI was developed [7], and the tool within PLASIMO [8]. The reduction of reaction mechanisms can also be done by using the post-processing tool PumpKin [9]. Recently, the N-PRiME group with IPFN has also implemented a global model, using flexible and upgradable object-oriented programming under MATLAB®. The LisbOn KInetics (LoKI) simulation tool [10,11] embeds a Chemistry solver and a Boltzmann solver, the latter to be released soon as open source. The development of this platform was also used as an opportunity to critically review and update several reaction mechanisms, namely in rare gases (Ar, He) and in N_2-O_2 mixtures [12].

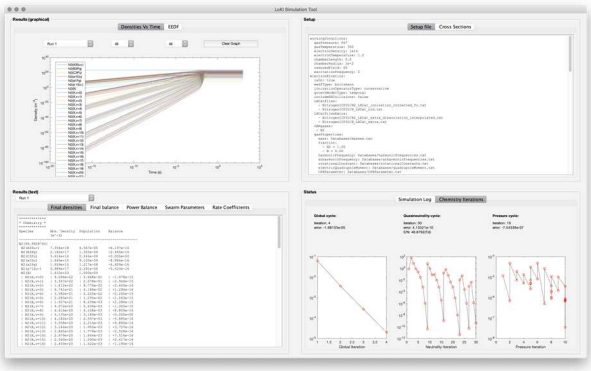

Fig. 1. GUI output of the LoKI simulation tool.

The investment of the community in developing such models, and implementing the numerical tools for their solution, has increased considerably the quality of M&S predictions relative to the "plasma chemistry". However, there are still several open issues that require further attention and may pose some challenges. Examples of those issues are: revisit the transport models for the neutral and the charged species, considering ambipolar effects according to the working pressure, and taking multicomponent diffusion (including wall reactions) for the heavy-species; bring global models into hydrodynamic codes; update the simplified description of radiation imprisonment, adopted in most codes; perform a critical evaluation of data; discuss strategies for the coupling between Chemistry and Boltzmann solvers, namely in view of self-consistent time-dependent calculations (also for the EEDF). On this last issue, a recent test-case analysis of the time-evolution of the electron kinetics, when excited by a μs-duration electric-field pulse, shows that results depend on the implementation adopted when solving the electron Boltzmann equation [13].

3. Final remarks

Global models are formidable modelling tools for understanding and predicting the behaviour of LTPs, when the focus is "plasma chemistry". The main difficulties in the formulation of these models are with (i) defining a kinetic scheme and the corresponding elementary kinetic data; (ii) describing the transport of species, according to the pressure regime. Verification and validation procedures [14] are key to assess the prediction capability of these tools, in terms of both the correctness of the numerical implementation and the relevance of the results obtained.

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Acknowledgments

This work was funded by Portuguese FCT, under projects UID/FIS/50010/2013 and PTDC/FISPLA/1243/2014 (KIT-PLASMEBA).