Boltzmann-Chemistry global models: status and future challenges

L.L. Alves and A. Tejero-del-Caz

Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

Modeling and simulation (M&S) activities in low-temperature plasmas (LPT) 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 usually 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 [1]

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

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

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

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. 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. The gas temperature can also be calculated by solving the power balance equation for the heavy-species.

The LTP community benefits from several implementations of global models, such as ZDPlaskin [2], GlobalKin [3,4], for which a commercial application with a GUI was developed [5], and the tool within PLASIMO [6]. 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 [7,8] 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 [9].

Despite the investment of the community in developing such models and tools, with considerable predictive performance, there are still several open issues that require further attention and may pose some challenges. Examples of those issues are: revisiting 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; bringing global models into hydrodynamic codes; updating the description of radiation; the critical evaluation of data; strategies for the Boltzmann-Chemistry coupling, namely in view of self-consistent time-dependent calculations. On this last issue, a recent analysis for the simple case of the 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 [10].

References

[1] L.L. Alves *et al*, Plasma Sources Sci. Technol. **27**, 023002 (2018).
[2] S. Pancheshnyi *et al*, http://zdplaskin.laplace.univ-tlse.fr (2008).
[3] R. Dorai and M.J. Kushner, J. Phys. D **36**, 1075 (2003).
[4] D.S. Stafford and M.J. Kushner, J. Appl. Phys. **96**, 2451 (2004).
[5] J.J. Munro and J. Tennyson, J. Vac Sci. Technol. A **26**, 865 (2008)
[6] J. van Dijk *et al*, J. Phys. D **42**, 194012 (2009).
[7] A. Tejero-del-Caz *et al*, Plasma Sources Sci. Technol., submitted (2018).
[8] P. Coche *et al*, J. Phys. D **49**, 235207 (2016).
[9] V. Guerra *et al*, Plasma Sources Sci. Technol., submitted (2018).
[10] A Tejero-del-Caz *et al*, in FLTP-Simulations (2019).

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