Self–Consistent Modeling of Discharge: the Role of Superelastic Collisions

G. Colonna

PLASMI Lab CNR-NANOTEC CNR Bari (Italy)

Modeling chemistry in a gas discharge is a research field of growing interest, describing systems of increasing complexity such as CO_2 destruction [1], methane combustion [2] and ammonia synthesis [3]. These chemical models must include processes induced by electron impact, whose rate coefficients are determined from the electron energy distribution function (eedf), obtained by solving the Boltzmann equation for free electrons [4]. From the eedf it is possible to determine other fundamental quantities of the electron gas such as mobility, mean energy, diffusion (swarm data), needed for a complete characterization of the discharge [5]. To reduce computational time, rate coefficients and swarm data are tabulated as a function of E/N (reduced electric field) [6], namely *local field approximation (LFA)*, or to the mean electron energy [7], i.e. *local mean energy approximation* (LEA). These approaches are based on two assumptions [8]: 1) the eedf is stationary and 2) it depends only on E/N. As a consequence, the influence of the evolution of the plasma composition and of the population of excited states on the eedf is neglected and only transitions from the ground state are considered. These limits can only be overcome by using the self-consistent state-to-state (SC-StS) approach [9, 10, 11], which solves, at each time step, the Boltzmann equation for free electrons and the master equations for chemical species and level population (see Fig. 1), accounting for the influence of the excited states on the eedf. The SC-StS approach has been applied to nitrogen [13] and hydrogen [14] to evaluate the effects of using a complete sets of vibrationally-resolved cross sections in affecting the dissociation and ionization kinetics in different kind of discharges. In the last two years, a Round Robin [12] activity has been carried out for the verification of the plasma kinetic codes used by different research groups, trying to rationalize the discrepancies. During this activity, the relevance of superelastic collisions in affecting the eedf was highlighted, in turn reflecting also on the plasma kinetics. Superelastic collisions are processes where an electron gains energy by de-exciting an atom or a molecule. In this class of transitions we include also the reverse of chemical processes induced by electron collisions, such as dissociation and ionization, entering the Boltzmann equation as described in Ref. [4].

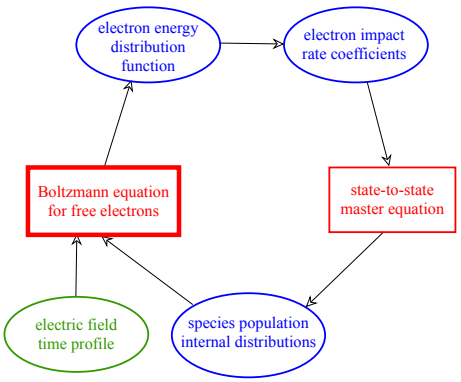

Figure 1: *Schematic view of SC-StS approach.*

As first test case, argon ionization kinetics was investigated, considering the metastable state $Ar^{\star}$ and the ion Ar^{+}. In Fig. 2, electron (e^{-}) and metastable state densities, together with reduced electric field E/N have been reported, comparing results obtained with the complete SC-StS approach with those neglecting the superelastic collisions in the Boltzmann equation (*NoSup*), but including them in the master equation, mimicking the local field approximation. The results were obtained feeding the discharge with a given power profile (see inset in Fig. 2) at pressure $p = 0.1$ bar and temperature $T = 300$ K, calculating the electric field from the relation $P = \vec{J} \cdot \vec{E} = N_e \mu_e E^2$ where N_e and μ_e are electron density and mobility respectively. Initially, $N_e = 1$ cm^{-3} while argon is in the ground state. The results show that, for $t < 0.2$ ms ($E/N > 15$ eV), including or neglecting superelastic collisions in the Boltzmann equation does not make any difference in discharge quantities. When $E/N > 15$ eV, superelastic collisions become relevant. The SC-StS model gives higher ionization and lower metastable density than NoSup. The increase of the ionization degree induces a further reduction in the electric field, making superelastic collisions even more important.

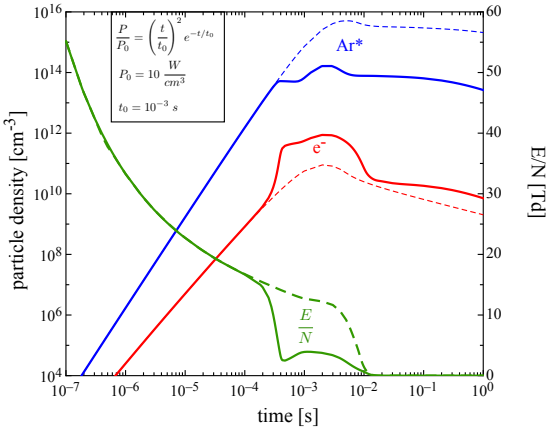

Figure 2: *Electric field profile, electron and argon metastable densities in SC-StS (continuous lines) and NoSup (dashed lines) cases.*

Superelastic collisions create plateaux in the eedf (see Fig. 3), increasing the ionization rates, and depopulating the metastable level. In practice, the energy stored in the metastable state during the discharge is transferred to ionization, by means of electrons, when the electric field is not sufficient to sustain the discharge. A deeper view to the evolution of the eedf in the two cases (Fig. 3) will clarify these aspects. Up to $t = 10$ μs, the eedf's in the two cases evolves in the same way, while at $t = 100$ μs, the distribution tail in the SC-StS case presents a plateau, while in the NoSup case it still decreases exponentially, slowly cooling up to $t = 1$ ms. On the other hand, in this time interval, the SC-StS distribution in the middle energy range decreases much faster than in NoSup case, because superelastic collisions

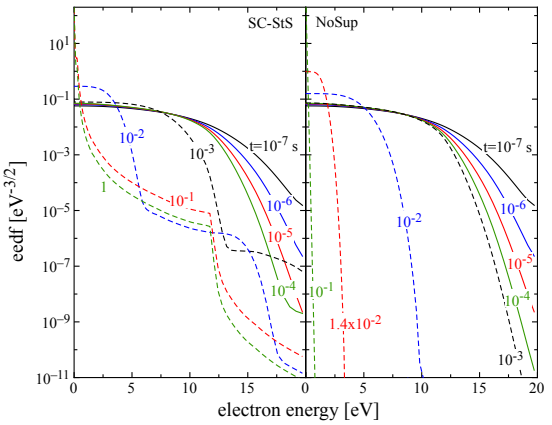

Figure 3: *Time evolution of the eedf calculated in SC-StS and NoSup cases.*

contribute to the cooling of low energy electrons. Nevertheless, the eedf tail, produced by superelastic collisions of electrons with energy around 10 eV with $Ar^\star$, grows of about a factor 40.

Between 1 and 10 ms, the distribution in the middle energy range is depleted, however, in the SC-StS case, a plateau is produced by the three-body recombination ($2e^-+Ar^+ \rightarrow e^-+Ar$). After $t = 10$ ms, the electric field is practically null. In the NoSup case, the distributions are rapidly cooling, reaching the equilibrium with the gas temperature at $t = 0.1$ s. In SC-StS case, the eedf cools down more slowly. After $t = 0.1$ s, the plateau is produced by superelastic collisions of cold electrons and relaxation of the distribution is very slow. It should be noted that electron mobility is a function not only of the electric field, but also of the metastable density, a behavior already demonstrated for helium [15].

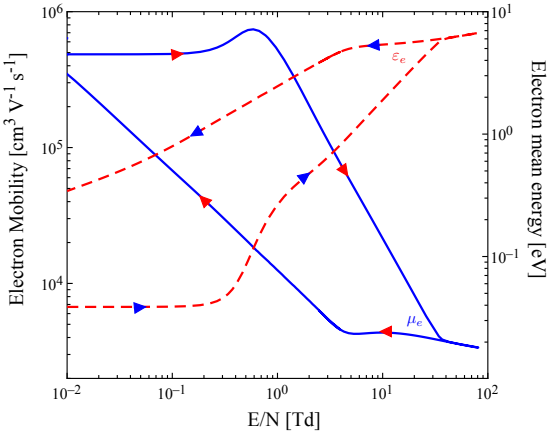

Figure 4: *Electron mobility (μ_e) and mean energy (ε_e) as a function of the reduced electric field in the SC-StS. The arrows indicates the direction of time.*

As a consequence, electron mobility, as well as electron mean energy (see Fig. 4), are not a monotonic function of the applied electric field, except for $E/N > 30$ Td. In the rest of the interval it presents and hysteresis loop, related to the growing/depletion of ionization degree and excited state density. This behavior poses doubts about the validity of the local field and local mean energy approximations for small electric fields. Argon has been chosen because is a very simple case. However, the presence of high energy metastable state makes the effects of superelastic collisions very large. Let us consider a pure nitrogen discharge, as a paradigm for molecular systems. The power supply provides a pulse (see inset of Fig. 5, $p = 1$ bar, $T = 300$ K) connected to parallel plate electrodes with gap d and section S, including a resistor R to limit the plasma current [16], giving for the plasma field $E_p = E - N_e \mu_e \tilde{R} E_p$. The electric field time evolution is reported in Fig. 5. The model includes 60 N_2 vibrational and levels and 4 electronically excited states, 6 states for N, N_2^+ and N^+ ions. In this case, the cross section set includes processes starting from

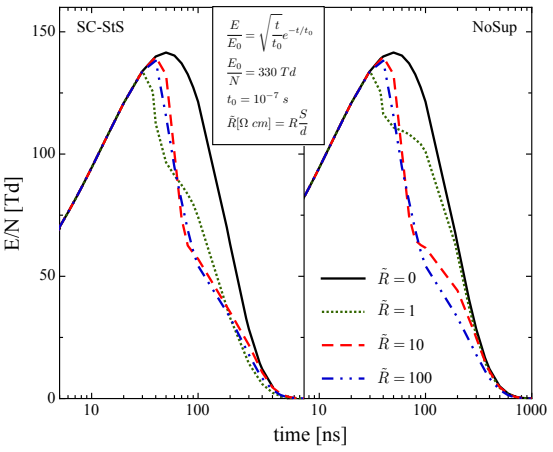

Figure 5: *Reduced electric field in N_2 discharge for different values of the reduced resistance $\tilde{R}$ in SC-StS and NoSup cases.*

all vibrational levels. Therefore, vibrational superelastic collisions are considered.

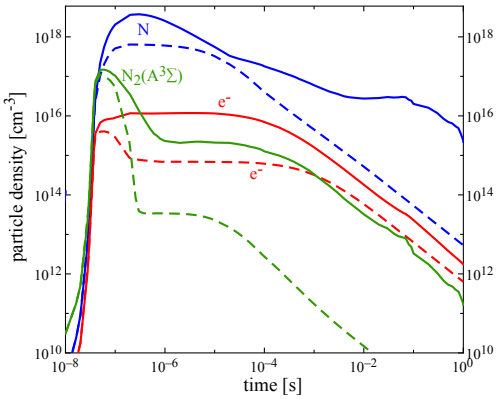

Figure 6: *Comparison of e^-, N and $N_2(A^3\Sigma)$ densities in SC-StS (continuous lines) and NoSup (dashed lines) for $\tilde{R} = 1\ \Omega$ cm.*

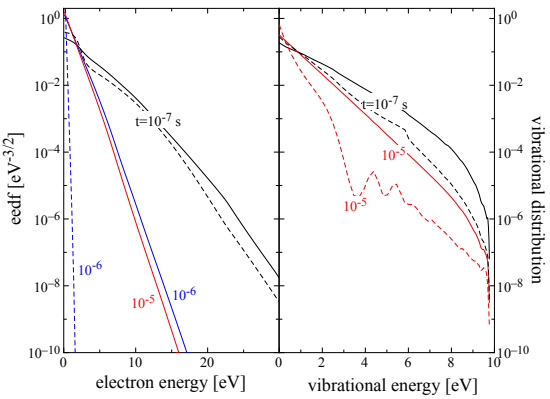

Figure 7: *Comparison of vibrational distributions and eedf in SC-StS (continuous lines) and NoSup (dashed lines) for $\tilde{R} = 1\ \Omega$ cm.*

The SC-StS predicts higher concentration of electrons, atoms and electronically excited states (see Fig. 6) than the NoSup case. Both electron and vibrational distributions (see Fig. 7) are more energetic in the SC-StS case. The eedf relaxes more rapidly in the NoSup case, reaching equilibrium after $t = 1\ \mu$s, while at $t = 10\ \mu$s, the SC-StS eedf is still far from equilibrium.

The present results, showing important differences between SC-StS and NoSup approaches, put in evidence the importance of a self-consistent solution of the Boltzmann and master equations in modeling discharges, especially in the post discharge conditions.

References

[1] M. Capitelli et al:Plasma Sources Science and Technology **26** 055009 (2017)
[2] G. Colonna et al:Plasma Sources Science and Technology **26** 025008 (2017)
[3] J. Hong et al:Journal of Physics D: Applied Physics **50** 154005 (2017)
[4] G. Colonna, A. D'Angola (Ed), Plasma Modeling: Methods and Applications, IOP (2017)
[5] Z. Petrović et al: Plasma Processes and Polymers **14** 1600124 (2017)
[6] S. Rassou et al:Physics of Plasmas **24** 100704 (2017)
[7] X. Chen et al: Journal of Physics D: Applied Physics **50** 395202 (2017)
[8] L. Alves et al: Plasma Sources Science and Technology **27** 023002 (20178)
[9] M. Capitelli et al: Plasma Chemistry and Plasma Processing **32** 427 (2012)
[10] M. Capitelli et al: Plasma Sources Science and Technology **16** S30 (2012)
[11] M. Capitelli et. al, Fundamental Aspects of Plasma Chemical-Physics: Kinetics (2016)
[12] L. Pitchford et al: Plasma Chemistry Round Robin, GT1.00063, 70th Annual GEC, 2017.
[13] G. Colonna et al: Plasma Sources Science and Technology **24** 035004 (2015)
[14] G. Colonna et al: Plasma Sources Science and Technology **25** 054001 (2016)
[15] G. Capriati et al: Plasma Chemistry and Plasma Processing **12** 2037 (1992)
[16] G. Neretti et al:Plasma Sources Science and Technology **28** 015013 (2016)