Electron kinetics in atmospheric-pressure discharges of helium mixtures with N$_2$ and O$_2$

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1. Introduction. In last years, helium and helium-based plasmas at atmospheric-pressure and room-temperature have received considerable interest due to their potential for biomedical applications. They can lead to the production of energetic species when interacting with open air, or to the generation of reactive radicals and ions when admixed with a molecular gas. Recently, different experiments have been carried out to study the dynamics of these plasmas in long capillary tubes used for the development of medical devices [1,2]. To optimize these applications one needs to identify and to understand the elementary processes controlling the global behavior of the discharge and the kinetics of the main charged and neutral species in the plasma, which are usually produced using mixtures of helium with small quantities of nitrogen, oxygen or synthesized air (80%N$_2$-20%O$_2$). The modelling of the plasma propagation can also be used for comparison with experiments and to gain physical insight into various phenomena.

2. Model. In this work, the tool IST-LoKI (LisbOn KInetics) is adapted and used to study electron-impact reactions in the aforementioned conditions. IST-LoKI is a self-consistent numerical code that solves the two-term electron Boltzmann equation (EBE) together with a system of rate balance equations describing the creation and loss processes of the dominant plasma species. The present study focuses on the electron energy distribution function (EEDF) of helium-containing plasmas, calculated for several values of the stationary reduced electric field (*E/N*), analyzing the effects of small admixtures of N$_2$, O$_2$ and synthesized air, as well as the influence of He metastables involved in stepwise inelastic and superelastic collisions. From the EEDF it is possible to determine the electron kinetic mean energy and all the electron transport parameters and rate coefficients, as a function of *E/N* [3].

3. Solution for Helium plasmas. The electron-neutral scattering cross sections used for the calculations in Helium include the following mechanisms [4]: elastic collisions; direct and stepwise excitation and ionization collisions, with ground-state He(1^1S) and with metastable

excited states He(2^3S) and He(2^1S), respectively; de-excitation collisions with metastables He(2^3S) and He(2^1S) (these states have long lifetimes and relevant relative densities, between 10^{-9} and 10^{-5} in a steady-state discharge [4]). For the latter de-excitation mechanisms, the superelastic cross sections are deduced from the corresponding inelastic cross sections, using the Klein-Rosseland relation.

The influence of He metastables on the EEDF is noted mostly at low reduced electric fields. The left figure 1 shows results for 1Td, when the relative density of He(2^3S) increases from 0 to 10^{-4}. It is seen that electron-He(2^3S) superelastic collisions turn the EEDF more energetic, creating a plateau up to the He(2^3S) threshold at 19.82 eV, corresponding to the energy gained by one electron in a superelastic collision. At very low energies (0-1 eV) the EEDF is very high, presenting a deep fall until $\approx$ 3 eV, the region where the electron-He(2^3S) inelastic collisions matter the most. After the plateau, the EEDF drops again due to the inelastic collisions with both He(1^1S) and He(2^3S), the fall increasing with the metastable density. Similar effects are obtained by introducing He(2^1S) instead of He(2^3S), or both metastable states with equal densities. At higher E/N values, e.g. between 10 Td and 50 Td, the EEDFs have less energetic bodies and more energetic tails, even in the presence of stepwise-inelastic / superelastic collisions with metastable states that lose importance in this case.
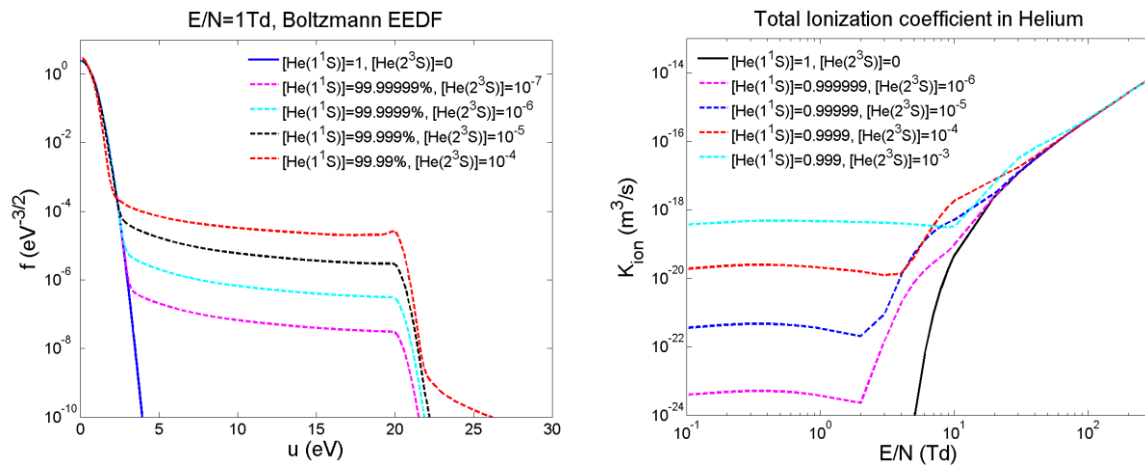

Figure 1: EEDFs at E/N = 1 Td (left) and electron-impact ionization rate coefficients as function of E/N (right), for different relative densities of He(1^1S) and He(2^3S).

Ionization is obtained for electron energies above 3.97 eV for collisions with He(2^1S), 4.77 eV for collisions with He(2^3S) and 24.59 eV for collisions with He(1^1S). Therefore, the presence of metastables, with relative densities similar to the ones in figure 1, has a noticeable effect also in the calculated electron rate coefficients, particularly in the ionization coefficient at low E/N. The right figure 1 shows this effect for several relative concentrations of He(1^1S) and

He(2^3S), plotting the total ionization coefficient over a range of E/N between 0.1 Td and 300 Td. The results demonstrate the influence of stepwise ionization reactions for reduced fields below 20 Td. In particular, for $E/N < 1$ Td the total ionization coefficient clearly increases with the metastable density, due to the very-low energy thresholds associated with stepwise ionization. The EEDF plateau-effect and the influence of stepwise ionization on the total ionization rate coefficient have been previously reported [3,5].

4. Solution for He-N$_2$-O$_2$ mixtures. The addition of air constituents to He affects also the EEDF. Helium presents a much more energetic EEDF than molecular gases, such as nitrogen and oxygen. The excited states of He have much higher energy thresholds than the low-energy excited states of N_2 and O_2, which leads to a depletion of the EEDF tail when they are admixed. The addition of molecular gases to helium, in percentages as small as 1%, is sufficient to produce significant changes in the EEDF, as reported in [6], especially at low fields ($E/N\sim1$ Td) where low-energy-threshold collisions are dominant. Notice that the description of the electron kinetics in He-N$_2$-O$_2$ plasmas considers the following additional electron-neutral scattering cross sections: elastic, rotational excitation, vibrational excitation (first energy threshold 0.29 eV), electronic excitation (6.17 eV) and ionization (15.5 eV) with N_2; and elastic, rotational excitation, vibrational excitation (0.19 eV), electronic excitation (0.98 eV), ionization (12.1 eV) and attachment with O_2.

The changes in the EEDF induce differences also in the calculated rate coefficients, particularly in the total electron-impact ionization rate coefficient. The left figure 2 presents this coefficient for several He-N$_2$ mixture compositions, for $E/N = 1$-100 Td. As expected, the less energetic N_2 EEDF leads to an ionization coefficient much lower in pure N_2 than in pure He. For the conditions of figure 2, a large decrease in the ionization coefficient is observed above 10% N_2, although this quantity presents a maximum for an admixture of only 0.1% N_2 at fields below 20 Td (for which the EEDF is not significantly changed), due to the lower N_2 ionization-threshold. This means that the rate coefficients for electron-He reactions always decrease by admixing N_2 but, on the contrary, the contribution of N_2 for direct ionization presents a maximum as a function of its percentage in the mixture. The overall result obtained for He-N$_2$ plasmas suggests that a small admixture of a molecular gas to helium may contribute to create and maintain the discharge.
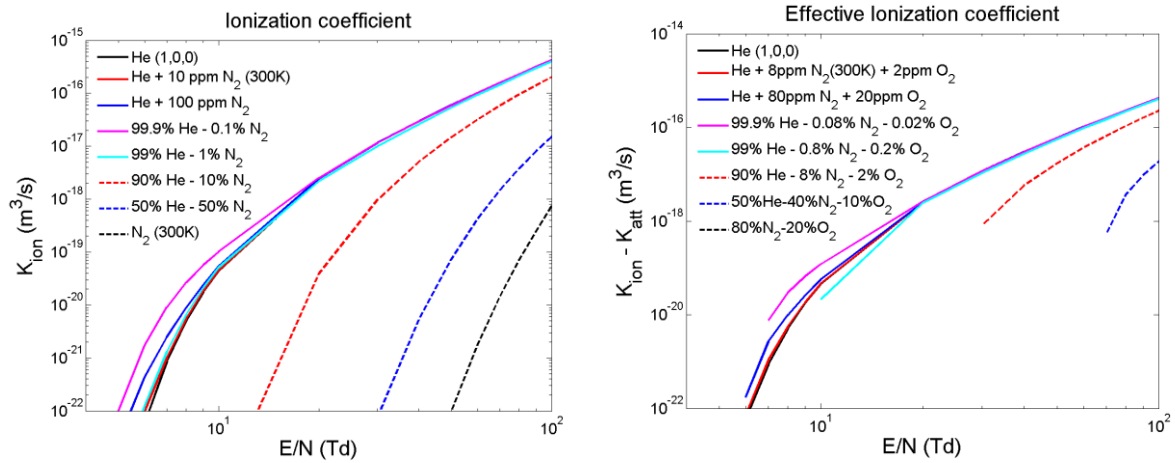
Figure 2: Ionization rate coefficients for different relative densities of He(1^1S) and N$_2$ (left) and effective ionization rate coefficients for different relative densities of He(1^1S) and dry air (right), as function of E/N.

The admixture of O$_2$ to He produces similar changes on the EEDF, but the electronegativity of O$_2$ is shown to have an important additional effect on the plasma behaviour, due to the presence of the electron attachment process, e$^-$ + O$_2$ → O$^-$ + O. The right figure 2 presents calculation results of the effective ionization rate coefficient, defined as the difference between the rate coefficients for electron-impact ionization and attachment, obtained for several mixtures of He with dry air, in the range E/N = 1-100 Td. One observes that the addition of O$_2$ is responsible for the appearance of negative values in the effective ionization rate coefficient (due to the attachment mechanism), for low reduced electric fields and low He concentration (see the interrupted curves in figure 2), which suggests enhanced difficulties in the breakdown of oxygen-containing plasmas.

6. References

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