The reaction kinetics of atmospheric pressure MW plasmas

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In order to study the reaction kinetics aspects of atmospheric MW plasma we constructed a collisional radiative model (CRM) that apart from atomic levels also takes the formation and destruction of the dimmer Ar_2^* and the molecular ions Ar_2^+ and Ar_3^+ into account. The CRM is coupled with a Boltzmann solver that calculates the electron energy distribution function (EEDF). The combination of the CRM and the EEDF-solver is combined with the balances for the electron density and energy. One of the striking results is that the increase of the power of an atmospheric plasma leads to a reduction of the electron temperature.

1. General

The enormous variety of applications of plasmas originates from their capability to produce large fluxes of photons and radicals. Plasmas can be efficient light sources and provide handy sources for surface treatment, surface modification etc [1–5]. However such high fluxes will bring the plasma into non-equilibrium conditions. And the prediction of the chemical composition and the plasma properties becomes difficult as they can no longer be described by the classical distribution laws of statistical physics. An adequate description of such plasmas requires a model, which accounts for the description of the configuration, transport and chemistry. Transport accounts for the transfer of particles, momentum and energy and is treated through balance equations. These depend on source terms and transport coefficients, which in turn strongly depend on chemical composition. Chemistry primarily deals with the creation and destruction of plasma species. Therefore it is treated through a set of reaction equations with corresponding rate coefficients. In the description of chemistry in non-equilibrium situation a *collisional–radiative model* (CRM) is a useful tool.

This study presents a CRM of argon. It is aimed for Ar plasmas operated at high pressure but can also be applied in low pressure conditions. Here we will use the model to prove the counter intuitive trend that increasing the power of atmospheric plasma leads to lower electron temperatures.

2. Model description

The first step in the construction of a CRM is to decide on how many species, i.e. atomic and molecular levels have to be taken into account. Figure 1 gives a sketch of the energy diagram of argon, chosen in a way to describe adequately the species constituting plasma at high pressure.

The accounted levels are argon in the ground state and seven blocks of excited states namely 4s, 4p, 3d, 5s, 5p, 4d and 6s. The singly ionized atomic ion and two- and three-atomic molecular ions are considered as well. In addition the excited molecule (dimmer) Ar_2^* is accounted for. The dimmer is formed by three-body collisions of Ar(4s) with two Ar atoms and at high pressures its density could be considerable. All excited states are treated as blocks of levels. This simplification is justified by the fact that the electron and the atomic densities are sufficiently high to ensure a strong collisional mixing between the populations in the levels of each block. A level-block b is characterised by the total number of states $g_b = \Sigma g_j$ and the mean energy

$$E_b = \Sigma g_j E_j / g_b \tag{1}$$

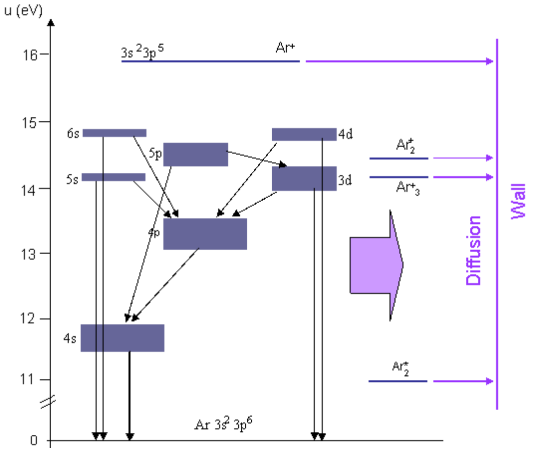

Figure 1. Energy level diagram of the argon atom, atomic and molecular ion and dimmer, illustrating all the effective levels (blocks) incorporated in the model. The arrows depict the radiative transitions and the diffusion.

where E_j is the energy of level j in the block b; the summation runs over the levels in the block..

The model handles 87 elementary processes. These are: elastic scattering, diffusion, excitation and deexcitation processes between the ground and excited Ar states, all allowed radiative transitions between the excited Ar states, ionization from the ground and the excited states, associative and Penning ionization, three-body and dissociative recombination and conversion to molecular ions. The condition for plasma quasi-neutrality is also assumed.

When describing cool plasma one can assume that the heavy particles are static due to their high mass and low mobility, while the electrons move and trigger the interactions in the discharge. A refined description of this phenomenon demands for the computation of the electron energy distribution function (EEDF). This distribution results from the field acceleration and the particle randomization of electron motion due to collisions with discharge constituents. In order to obtain the EEDF the Boltzmann equation is required. In addition, a detailed kinetic description requires the calculation of the electron energy balance equation. It provides information on how the energy gained by the electrons from the field is expended on different interactions sustaining the plasma. Calculation of the particle balance equation for electrons is also needed. Further elaboration of the modelling includes solving the particle balance equation for each of the relevant species. In this way the number density of all the species of the plasma can be obtained as well as all the plasma characteristics. However, in this paper we only present the energetic characteristics of the discharge such as the EEDF, the partial distributions of the different processes θj in the energy (power) balance, and the mean electron energy $<\varepsilon>$.

In order to obtain the EEDF $f(\varepsilon)$ the electron Boltzmann equation is solved using the two-term Legendre polynomials expansion giving

$$f(<\varepsilon>) = f_0(<\varepsilon>) + \mathbf{f}_1(<\varepsilon>) \cos\chi \exp(i\omega t) \qquad (2)$$

where $f_0(\varepsilon)$ is the isotropic component of the EEDF which is independent of time, $\mathbf{f}_1(\varepsilon)$ is the anisotropic component while χ is the angle with respect to the field. Apart from the inelastic collisions we also consider elastic collisions of the type electron–electron, electron-atom and electron–ion elastic collisions [6]:

The energy balance for electrons (eEB) can be conveniently written down in terms of power density per electron θ. It yields detailed information on how the power absorbed by electron (the left-hand side of equation (3)) is dissipated in collisions (the right-hand side):

$$\theta \equiv \theta^{elast} + \theta^{exc} + \theta_0^{ion} + \theta^{ion} + \theta^{diff} + \theta^{rec} - \theta^{Pen} \qquad (3)$$

The superscripts refer to the processes, respectively elastic collisions, excitation, direct and stepwise ionization, diffusion, dissociative and three-body recombination and Penning ionization.

For a fully self-consistent model the gas thermal balance equation (TBE) should be considered as well. It gives the local gas temperature. Yet in this study we do not calculate the TBE and use a fixed value for the gas temperature obtained from experiments.

3. Results and discussion

The calculations have been done for an argon plasma column at 1.01×10^5 Pa sustained by electromagnetic field with frequency 2.45 GHz, gas temperature 1500K and plasma radius 0.05 cm. The results are given for the broad interval of $3\times10^{11} < n_e < 3\times10^{15}$ cm^{-3}. This is an interval of plasma densities typical for different types of atmospheric pressure discharges.

Figure 2 presents the mean electron energy $<\varepsilon>$ as function of n_e. The figures show that generally $<\varepsilon>$ decreases with the increase of n_e with a variable slope. It is the steepest for low n_e values and the most gentle for $n_e > 1\times10^{14}$ cm^{-3}. The tendency is in agreement with the experimental observations [7,8]: as the ionization ratio $\alpha = n_e / N$ increases the $<\varepsilon>$ value goes down, just as figure 2 depicts. Note that high α values are obtained for higher powers and as $<\varepsilon> = 2/3\ T_e$ is related to the electron temperature, we find the counter intuitive trends that an atmospheric plasmas driven by a higher power have lower electron temperatures.

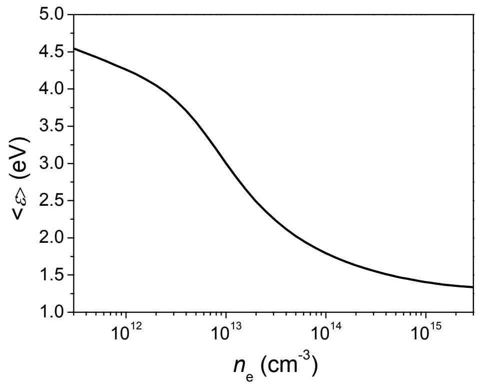

Figure 2. Mean electron energy versus electron density.

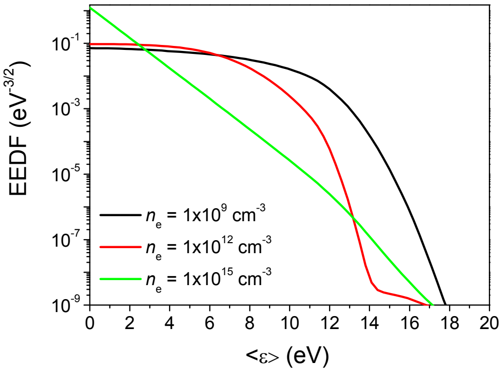

Figure 3. Electron energy distribution functions at different n_e values. The discharge radius – R = 0.05 cm

This tendency can be explained with a study of the EEDF shape as a function of α. In figure 3 the EEDF calculated for several electron densities is shown. The calculations confirm that the function is close to Maxwellian for high (~ 10^{15} cm^{-3}) electron densities but deviations from the Maxwell distribution are found going toward lower ionization ratios n_e / N. Under these conditions the electron–electron collisions are apparently not frequent enough to restore the departure from equilibrium induced by inelastic electron–atom collisions.

This increase of <ε> for decreasing α values can be understood with the help of the electron particle balance. Basically this balance sets a demand for the electron energy. In case of Maxwellian electron gas high losses, for instance due to diffusion, require for high <ε> value. However, if the EEDF has a depleted tail even higher <ε> values are needed since a depleted-tail EEDF needs to increase its bulk temperature in order to achieve the same electron–ion production. And it is the bulk that mostly determines the mean energy.

Figure 4 present the partial contributions θj in terms of power of the different processes in which an electron participates in the discharge. Generally θj increases with the increase of n_e. The steepest is the gradient of the power spent on recombination processes followed by those spent on ionization and excitation. In the whole range of n_e the main are the elastic collisions. They "scatter" the anisotropy and ensure the two-term expansion of the EEDF. For electron densities below 10^{13} cm^{-3} the elastic processes are an order higher than the main inelastic process, excitation. Ionization is also a magnitude higher then recombination for these values of n_e.

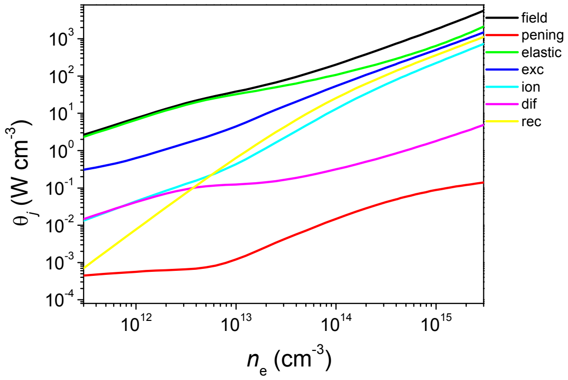

Figure 4. Partial distributions of the different elementary processes in the eEB as function of n_e.

However for higher n_e the inelastic processes increase quickly and for n_e > 10^{14} cm^{-3} the excitation, ionization and recombination become of the same degree as the elastic collisions and compete with each other. Thus we see that different regimes of functioning of atmospheric pressure discharges occur for low (< 10^{13} cm^{-3}) n_e values and for high (> 10^{14} cm^{-3}) n_e values and a transition regime happens for the intermediate n_e values.

In conclusion, the theoretical study of the reaction kinetics of argon atmospheric pressure MW discharge shows a decrease of the electron temperature with the increase of the electron density. Two regimes of functioning of these discharges are observed elastic processes dominated kinetics for $n_e < 10^{13}$ cm^{-3} and predomination of the inelastic processes for $n_e > 10^{14}$ cm^{-3}.

3. References

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