

Influence of the gas-flow on the thermodynamic equilibrium of atmospheric-pressure microwave plasmas

J. Martínez¹, C. Gonzalez-Gago¹, E. Castaños-Martínez¹, J. Muñoz¹, M.D. Calzada¹, R. Rincón¹

¹*Laboratory of Innovation in Plasmas (LIPs), Universidad de Córdoba, Córdoba (Spain)*

1. Introduction

Microwave plasmas sustained at atmospheric pressure can be applied in many fields due to the flexibility and high chemical reactivity that result from non-equilibrium operation conditions. However, the performance of a plasma in a specific technological application is determined by the density of active species and their characteristic temperatures, which are closely related to the thermodynamic equilibrium (TE) degree of the discharge. Though many studies have dealt with the impact of experimental conditions on TE, only a few of them have focused on the impact of gas-flow [1]. In the present study, the influence of gas-flow in the axial distribution of plasma parameters along an atmospheric-pressure microwave argon capillary plasma sustained using a surfaguide device [2] has been examined.

2. Experiment Setup

Figure 1 shows the main features of the experimental setup sustaining the plasma. The discharges were contained inside a quartz tube of 0.75 and 2.00 mm inner and outer radii open to the atmosphere using two different flows of 0.25 and 1.00 slm high-purity argon (99.999%), with the gas flowing from bottom to top of the tube. A microwave (2.45 GHz) power of 300 W was supplied in continuous mode by a SAIREM 12 kT/t generator and coupled as a surface-wave using a surfaguide equipped with a movable short-circuit and a triple stub.

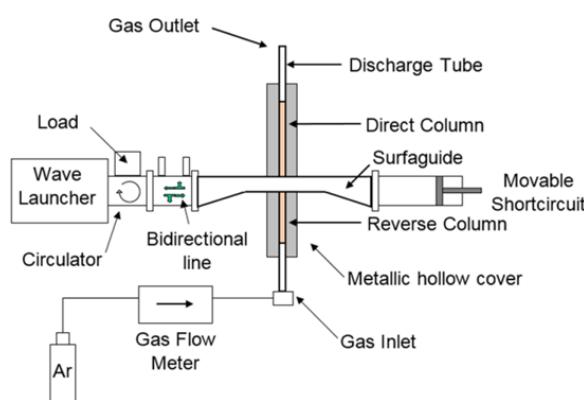


Figure 1. Experiment Setup.

The discharge extended to both sides of the wave-launching region of the surfaguide ($z = 0$), giving place to a direct column ($z > 0$) and reverse column ($z < 0$), depending on whether the gas flow and the surface-wave propagation take place in the same or opposite directions, respectively. Symmetry is henceforth referred to equal values of a given plasma parameter in both columns at the same $|z|$ position.

The parameters characterizing the discharge were studied using optical emission spectroscopy. The light emitted by the discharge at a given axial position was collected perpendicularly to it using an optical fibre and led to the entrance slit of a previously-calibrated 1 m Jobin-Yvon Horiba monochromator equipped with a 2400 grooves/mm diffraction grating and a R928P photomultiplier as detector. Gas temperature was measured from the OH ($A^2\Sigma^+, v = 0 \rightarrow X^2\Pi, v' = 0$) rovibrational band, appearing in the 306-312 nm spectral region [3], whereas electron density was calculated from the Stark broadening of the H_β Balmer line appearing at 486.1 nm [4]. Finally, the densities of Ar I excited atoms, whose values were used to determine the excitation temperature, were determined from the intensities of Ar atomic lines using the spectral response in intensity of the monochromator (absolute intensity calibration).

3. Results and Discussion

Figure 2 shows the axial profiles of gas temperature and electron density of the discharges. In microwave plasmas sustained at atmospheric pressure, electrons absorb the energy from the electromagnetic field and transfer it to the rest of the particles via elastic and inelastic collisions. Increasing the gas-flow results in a reduction of gas temperature which is more noticeable in the reverse column (Figure 2, left). Since the flow is laminar under those conditions, this decrease can be explained due to the lower residence time of the particles.

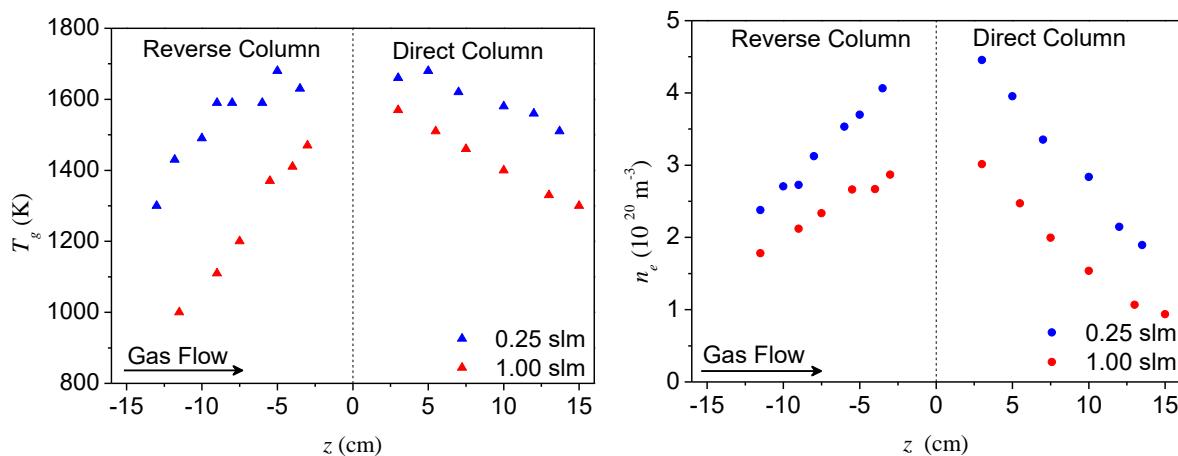
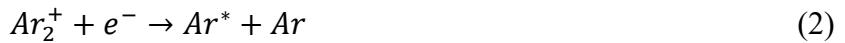


Figure 2. Axial profiles of gas temperature (left) and electron density (right) in the reverse and direct columns.

The lower residence time could also explain the decrease in electron density, which shows a more symmetric profile with lower values for the larger gas flow (Figure 2, right). Moreover, for gas temperatures below 1500 K the ions dynamics is significantly influenced by argon molecular ions, created by atomic ion conversion (1) and destroyed by dissociative recombination (2), resulting in a lower number of electrons for low gas temperatures [5].



Important asymmetries can also be detected in the axial distribution of excited states for the largest gas flow considered. The lower excited levels (4s) can be efficiently populated as a result of dissociative recombination (2), resulting in a significant input of Ar metastable and resonant atoms. This overpopulation propagates through the atomic system via stepwise excitation to the closest energy levels [6], resulting in the asymmetry shown by 4p levels (Figure 3, left), but disappears for higher levels (figure 3, right), whose population is controlled by inelastic collisions with electrons.

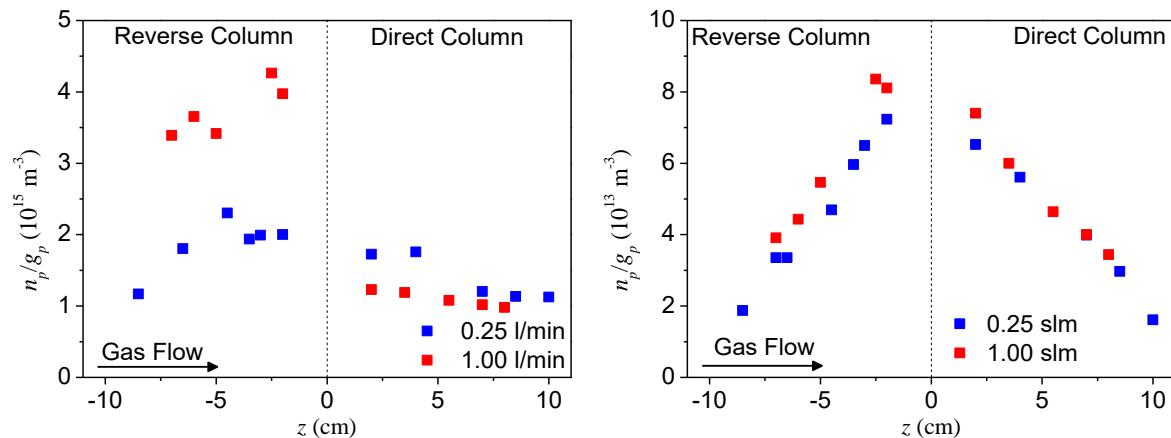


Figure 3. Axial profiles of Ar I 4p (left) and 5d (right) level densities in the reverse and direct columns.

Additional information regarding the thermodynamic equilibrium degree of a plasma can be obtained calculating Griem's critical level, p_G , [4], which is a level such that any other level with an effective quantum number, $p = Z(E_H/E_p)^{1/2}$, larger than p_G , will have its population controlled by electron collisions, being Z the charge of the core atom, E_H the ionization energy of hydrogen and E_p the ionization energy of the p -th level. Furthermore, a quantum number p^* , such that those levels with an effective quantum number larger than p^* will be in partial Local Saha Equilibrium (pLSE) can be also defined. The calculation of both p_G and p^* require previous determination of n_e and the electron temperature, T_e . This later parameter was taken as the excitation temperature, T_{exc} , calculated from the Boltzman-plot of

the excited levels of Ar [6]. Further details on the calculation of p_G and p^* and can be found in [8] and references therein.

Figure 4 shows the phase diagram of Ar I system together with p_G and p^* values. A value of p_G close to 2 is determined for every condition, showing that 4s levels are always out of the collisional regime and far from TE due to the influence of dissociative recombination (2). Similarly, the 4p levels always fall out of the pLSE region. For the lower gas flow considered the pLSE limit is displaced to exclude 3d and 5s levels as we move away from the wave launcher ($|z| = 7$ cm) levels, whereas for the largest gas flow, lower 3d and 5p levels are also out of pLSE for $|z| = 2$ cm and $|z| = 7$ cm, respectively.

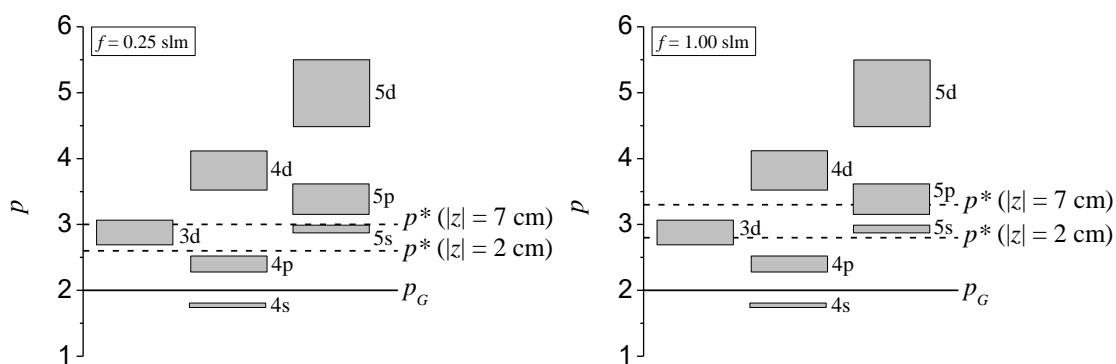


Figure 4. Level diagram of the Ar I system for a gas flow of 0.25 (left) and 1.00 (right) slm.

Acknowledgements

This work was supported by XXII-XXIII Programa Propio de Fomento de la Investigación de la Universidad de Córdoba (Spain) (MOD 4.1 PP2017-2018). The contract of Dr. C. González-Gago was supported by XXI Programa Propio de Fomento de la Investigación de la Universidad de Córdoba (Spain) (MOD 5.2 PP2016).

References

- [1] Martínez J, Castaños-Martínez E, González-Gago C, Rincón R, Calzada MD Muñoz J, *Plasmas Sources Sci. Technol.* 27 (2018) 077001.
- [2] Moisan M, Etemadi E, Rostaing JC (1998) French Patent No 2 762 748; European Patent No EP 0874537A1.
- [3] Mermet J, *Inductively coupled plasmas emission spectrometry*, in Boumans PWJM (Ed.), Wiley-Interscience, New York (1987).
- [4] Griem HR, *Plasma Spectroscopy*, McGraw-Hill, New York (1964).
- [5] Kabouzi Y, Graves DB, Castaños-Martínez E and Moisan M, *Phys. Rev. E* 75 (2007) 016402.
- [6] Castaños-Martínez E and Moisan M, *Spectrochim. Acta B* 65 (2010) 199-209.
- [7] M.D. Calzada, M. Moisan, A. Gamero and A. Sola, *J. Appl. Phys.* 80 (1996) 46.
- [8] Calzada MD, Rodero A, Sola A, Gamero A, *J. Phys. Soc. Jpn.* 65 (1996) 948-954.