Modelling of microwave sustained capillary plasma columns at atmospheric pressure

M Pencheva¹, Ts Petrova², E Benova³ and I Zhelyazkov¹

¹ Faculty of Physics, Sofia University, 5 James Bourchier Blvd., BG-1164 Sofia, Bulgaria
² Berkeley Research Associate, Inc., Beltsville MD 20705, USA
³ Department of Language Learning, Sofia University, 27 Kosta Loulchev Street, BG-1111 Sofia, Bulgaria

¹E-mail: m_pencheva@deo.uni-sofia.bg

Abstract. In this work we present a model of argon microwave sustained discharge at high pressure (1 atm), which includes two self-consistently linked parts – electrodynamic and kinetic ones. The model is based on a steady-state Boltzmann equation in an effective field approximation coupled with a collisional-radiative model for high-pressure argon discharge numerically solved together with Maxwell’s equation for an azimuthally symmetric TM surface wave and wave energy balance equation. It is applied for the purpose of theoretical description of the discharge in a stationary state. The phase diagram, the electron energy distribution function as well as the dependences of the electron and heavy particles densities and the mean input power per electron on the electron number density and wave number are presented.

1. Introduction

The discharges sustained by travelling waves at atmospheric pressure attract an increasing interest because of the great variety of scientific and technological applications - in mass spectrometry for the analytical determination of substances, in surface treatment, lasers, lighting, etc [1-4]. Moreover, they have specific advantages over the other microwave plasmas. For example, as excitation sources in atomic emission spectroscopy an important advantage is the efficient excitation of halogens and other non-metals, which are not readily accessible for detection [5]. Another advantage in comparison with other electrodeless discharges is the higher electron plasma density at a given input power. In addition, they are effective sources of chemically active particles – ions and excited atoms and molecules.

Electrical discharges are observed to contract when sustained at sufficiently high pressure, typically higher than 10 Torr in rare gases. The onset of contraction is found to depend also on the applied power, the discharge vessel, and the nature of the gas. To achieve a stable stationary discharge without contraction for an argon plasma column sustained by surface electromagnetic wave with frequency \( f = 2.45 \text{ GHz} \) at gas pressure \( p = 1 \text{ atm} \) the tube radius must be in order of some millimeters [6]. Despite of the broad theoretical investigations on the microwave-sustained atmospheric pressure discharges, the modelling of these is much less advanced than at reduced pressure because of the greater
complexity of the mechanisms involved. Our goal is to build a self-consistent axial model of surface-wave produced argon discharge at atmospheric pressure in stationary state. We will present our results for the abovementioned experimental conditions: the EEDF and the mean electron energy, the axial electric field and the mean power required for sustaining an electron-ion pair, the effective electron-neutral collision frequency as well as the wave phase diagrams.

2. General Conditions
In our study we use the approach developed by Petrova and Benova [7, 8] for the modelling of microwave-sustained plasmas at low and intermediate pressures. This approach includes two aspects. The first one is based on the electrodynamics and permits a full description of the wave propagation. The second one is based on a kinetic description, and enables studying plasmas at different discharge conditions. The key relation providing the connection between the two separate parts of the model is the electron energy balance equation.

2.1. Kinetic part
As it is well known, the detailed modelling of surface wave plasma requires the knowledge of the electron energy distribution function (EEDF), which determines the electron transport parameters, the rates of elementary processes, and several other important quantities as the effective electron-neutral collision frequency.

### Table 1. Elementary processes

| Charged particles creative processes | \( \text{Ar} + e \rightarrow \text{Ar}^+ + e + e \) |
|-------------------------------------|-----------------------------------------------|
| Direct ionization                   |                                               |
| Stepwise ionization                 | \( \text{Ar}^+_j + e \rightarrow \text{Ar}^{+j} + e + e \) |
| Penning ionization                  | \( \text{Ar}^+ + \text{Ar}^+ \rightarrow \text{Ar}^{+2} + \text{Ar} \) |
| Associative ionization              | \( \text{Ar}^+ + \text{Ar}^+ \rightarrow \text{Ar}^{+2} + \text{Ar} \) |
| Conversion to molecular ions        | \( \text{Ar}^+ + \text{Ar} + \text{Ar} \rightarrow \text{Ar}^{+2} + \text{Ar} \) |

| Loss of charged particles processes | \( \text{Ar}^{+j} + e \rightarrow \text{Ar}^{+} + \text{Ar} \), \( j = 2, 3 \) |
|------------------------------------|----------------------------------------------------------------------------|
| Dissociative recombination         | \( \text{Ar}^{+j} + \text{Ar} + \text{Ar} \rightarrow \text{Ar}^{+} + \text{Ar} \), \( j = 1, 2, 3 \) |
| Three-body recombination           | \( \text{Ar}^{+j} + e + e \rightarrow \text{Ar}^{+} + e \), \( j = 1, 2, 3 \) |
| Diffusion                          | \( \text{Ar} (4s), e, \text{Ar}^{+} \rightarrow \text{wall} \), \( j = 1, 2, 3 \) |

| Exchanging energy processes        |                                               |
|------------------------------------|----------------------------------------------------------------------------|
| Elastic scattering                 | \( e + e \rightarrow e + e \) |
| Excitation processes               | \( \text{Ar} + e \rightarrow \text{Ar}^{+j} + e \), \( j = 1, 2, 3 \) |
| Deexcitation processes             | \( \text{Ar}^{+j} + e \rightarrow \text{Ar}^{+} + e \) |
| Radiative transitions             | \( \text{Ar}^{+i} + \text{Ar} \rightarrow \text{Ar}^{+} + \text{Ar} \), \( k = i - 1 \) |
|                                    | \( \text{Ar}^{+i} + \text{Ar} + \text{Ar} \rightarrow \text{Ar}^{+} + \text{Ar} + \text{Ar} \), \( k = i - 1 \) |
|                                    | \( \text{Ar}^{+i} + e \rightarrow \text{quenching} \) |
|                                    | \( \text{Ar}^{+i} \rightarrow \text{Ar} + hf \) |
|                                    | \( \text{Ar}^{+i} \rightarrow \text{Ar}^{+} + hf \) |
collision frequency for momentum transfer $\nu_{\text{eff}}$ and the mean power $\theta$ required for sustaining an electron-ion pair in the discharge. The EEDF is derived from the electron Boltzmann equation, solved using the two-term expansion in Legendre polynomials.

The species considered in the model are Ar (ground state atoms), Ar(4s), Ar(4p), Ar(3d), Ar(5s), Ar(5p), Ar(4d), Ar(6s) (excited atoms), Ar$_2^*$ (excited dimers), Ar$^+$, Ar$_2^+$ and Ar$_3^+$ (atomic and molecular ions), assuming all excited states as blocks of levels with effective energy corresponding to the energy of the center. The elementary processes taken into account are listed in table 1.

The obtained EEDF satisfies the energy and particle balance equations for the electrons as well as the balance equations for the heavy particles.

The parameter $\theta$, namely the mean power per electron can be obtained from the electron energy balance equation with the determined EEDF. The heavy particle kinetics coupled with the electron kinetics allows us to determine the atomic and molecular ion number densities, the populations of the excited states as well as $\theta$ and $\nu_{\text{eff}}$ as a function of the electron number density.

2.2. Electrodynamic part

The electrodynamic part of the model considers Maxwell’s equation for an azimuthally symmetric TM surface wave with angular frequency $\omega$ propagating along a small capillary plasma cylinder with given radius surrounded by vacuum. The plasma permittivity $\varepsilon_p$ is

$$\varepsilon_p = 1 - \frac{\omega_p^2}{\omega (\omega + i\nu_{\text{eff}})} = 1 - \frac{\varepsilon_{\text{pl}}^2}{\omega^2} \left( 1 + \frac{\nu_{\text{eff}}^2}{\omega^2} \right)^{-1} + i \frac{\nu_{\text{eff}}^2}{\omega^2} \left( 1 + \frac{\nu_{\text{eff}}^2}{\omega^2} \right)^{-1}$$

Here $\omega_0 = \sqrt{4\pi e^2 n_{\text{eff}}/m}$ is the electron plasma frequency, $n_{\text{eff}}$ is the effective electron density, and $\nu_{\text{eff}}$ is the effective electron-collision frequency for momentum transfer [7].

The local wave dispersion relation is obtained by means of applying the assumption for radially averaged electron and excited atoms densities and using the continuity of the azimuthal wave field components at the plasma-vacuum interface as boundary conditions.

$$\frac{\varepsilon_p}{\omega_p} I_1(a_p) + \frac{1}{a_p} K_1(a_p) = 0$$

with $a_p^2 = k^2 - \sigma^2 \varepsilon_p$ and $a_v^2 = k^2 - \sigma^2$, where $k = k_\rho R + ik_\rho R$ is the dimensionless complex wave number, $\sigma = \omega R/c$ and $I_0, I_1, K_0, K_1$ are the modified Bessel functions of zeroth and first order.

The energy flux along the plasma column is the sum of the axial components of Poynting’s vectors averaged over the wave period and integrated over the plane normal to the plasma column:

$$S(z) = 2\pi \int_0^1 d\rho \rho S^\rho_z + 2\pi \int_1^\infty d\rho \rho S^\rho$$

which in this particular case reads:

$$S = \frac{1}{4} \omega R^2 E^2 \text{Re} \left[ \frac{k \varepsilon_p}{a_p^2 - a_p^2} \left( \frac{1}{a_p} I_1(a_p) - \frac{1}{a_v} I_1(a_v) \right) \right]$$

$$+ \frac{1}{4} \omega R^2 E^2 \text{Re} \left[ \frac{k}{a_v^2 - a_v^2} \left( \frac{1}{a_v} K_1(a_v) - \frac{1}{a_v} K_1(a_v) \right) \right]$$

with $k = k_\rho R + ik_\rho R$. The modified Bessel functions are evaluated at their arguments.
The wave power dissipated per unit length is given by the relation:

\[ Q(z) = 2\pi \int_0^R dr \int \rho E^2 \frac{1}{a_p^2 - a_p} \left[ k^2 \frac{R^2}{k^2 R^2} \left( \frac{1}{a_p I_0(a_p)} - \frac{1}{a_p I_0(a_p)} \right) + a_p I_0(a_p) - a_p I_0(a_p) \right] \]  

and is equal to:

\[ Q = \frac{\omega}{4} \text{Im}(\varepsilon_p) R^2 E^2 \left( \frac{1}{a_p I_0(a_p)} - \frac{1}{a_p I_0(a_p)} \right) + a_p I_0(a_p) - a_p I_0(a_p) \]  

On the other hand, Q is the power expended by electrons in elastic and inelastic collisions and it can be presented in the this form

\[ Q = \pi R^2 n_e \theta \]  

The values of Q derived from the kinetic and the electrodynamic parts of the model must be equal, for ensuring a self-consistency of the model.

The relation between S and Q is given by the wave energy balance equation

\[ \frac{d}{dz} S = -Q \]  

The local dispersion relation yields the electron density for a given wave number, and the solution of the wave energy balance equation provides the dependence of the electron density on the axial position \( n_e(z) \). Having obtained the axial dependence of the electron density, the kinetic part is recalculated again for appropriate axial position. This provides the spatial distribution of the discharge characteristics.

### 3. Results

The numerical calculations have been done for an argon plasma column investigated experimentally by Garcia, Rodero, Sola and Gamero [9] – an electromagnetic wave with frequency \( \omega/2\pi = 2.45 \text{ GHz} \), wave power: 110 W, gas pressure: 1 atm, gas temperature: 1000 K, discharge length 14 cm, tube radius: 0.5 mm, electron plasma density \( 1 \times 10^{15} \) and \( 1 \times 10^{14} \text{ cm}^{-3} \) at the launcher and at the column end, respectively.

In Figure 1 the EEDF calculated for the two electron densities, corresponding to that at the launcher and at the end of the discharge, is plotted. The calculations confirm that the function is Maxwellian (solid line) for the entire column length except at the end (dashed line).

The numerical calculations in the kinetic part of the model allow us to obtain the dependence of the wave and plasma characteristics on the plasma density, presented in Figure 2. One can see from Figures 2a,c that the wave field \( E_0 \) and the mean power for sustaining an electron-ion pair \( \theta \) have similar behaviour and decrease with increasing of \( n_e \) at low plasma densities \( (n_e \leq 2 \times 10^{14} \text{ cm}^{-3}) \). For \( n_e \geq 2 \times 10^{14} \text{ cm}^{-3} \) both \( E_0 \) and \( \theta \) increase monotonously. In the same time the mean electron energy (Fig. 2b) decreases with \( n_e \) and respectively the electron temperature (Fig. 2d), defined as \( T_e = \frac{2}{3} u \), also decreases from 1.3 to 1 eV, which is higher than the experimental values 0.7 eV.

Figure 3a presents the phase diagrams for electron-neutral collision frequency equal to 1.52 and 2.39 \( \times 10^{11} \text{ s}^{-1} \), referring to the column end and near the exciter, and the
part of the phase diagram (Fig. 3b) corresponding to the electron densities under consideration. For comparison, the phase diagram for collisionless plasma is introduced too (dotted curve). One can see that the phase diagrams for the two $\nu$ are close. So it is applicable in this instance to use an average value of $\sim 2 \times 10^{11}$ s$^{-1}$. But the account of the collision frequency is necessary because of the great difference with respect to the collisionless case.

In Figure 4 the axial distribution of the electron density and wave energy flux is plotted. It can be seen that the theoretical wave power value at the launcher is 80 W which is close to the experimental one of 110 W.

Figure 5 presents the axial distributions of the wave electric field, the mean electron energy, the mean power required for sustaining an electron–ion pair and the electron temperature. In contrast to the results at low and intermediate pressure [7] where $E_0$ and the $\theta$ increase from the launcher to the column end, at atmospheric pressure these quantities decrease along the column except at its end (Figure 5a,c). The mean electron energy is almost constant along the column at low and intermediate pressure [7] while it increases with $z$ at atmospheric pressure, which means that the assumption for infinite electron thermal conductivity is no longer valid at these conditions.

4. Conclusions
The numerical results of the model at atmospheric pressure compared with those at low and intermediate pressure show that the account of

![Figure 2](image2.png)

**Figure 2.** Axial electric field (a), mean electron energy (b), mean power required for sustaining an electron-ion pair (c) and electron temperature (d) versus electron density

![Figure 3](image3.png)

**Figure 3.** Phase diagram for the electron-neutral collision frequency at the launcher and at the column end (a), and the phase diagram corresponding to the considered electron densities (b)

![Figure 4](image4.png)

**Figure 4.** Axial distribution of the electron density (a) and wave energy flux (b)
collisions is important. Therefore, the approximation of collisionless plasma is not applicable in this case.

The axial profiles of the wave and plasma characteristics are obtained. The theoretical results are in good agreement with the available experimental data.

5. Acknowledgements
This work was supported by the Fund for Research of Sofia University under Grant 124/05.

![Figure 5. Axial electric field (a), mean electron energy (b), mean power required for sustaining an electron-ion pair (c) and electron temperature (d) versus the axial coordinate](image)

References
[1] Moisan M, Hubert J, Margot J and Zakrzewski Z 1999 Advanced Technologies Based on Wave and Beam Generated Plasmas, NATO ASI Partnership Subseries 3 edited by H. Schluter and A. Shivarova (Amsterdam: Kluwer, Academic Publisher) 23–64
[2] Moisan M, Barbeau C, Claude R, Ferreira C M, Margot J, Paraszczak J, Sá A B, Sauvé G and Wertheimer M R 1991 J. Vac. Sci. Technol. B 9 8
[3] Moisan M, Sauvé G, Zakrzewski Z and Hubert J 1994 Plasma Sources Sci. Technol. 3 584
[4] Gamero A 1995 Phenomena in Ionized Gases eds K. H. Becker, W. E. Carr and E. E. Kunhardt (Woodbury, New York: AIP PRESS) 257
[5] Tran K C, Lauzon U, Sing R and Hubert H 1997 J. Anal. At. Spectrom. 13 507
[6] Petrov G M and Ferreira C M 1999 Physical Review E 59 3571–82
[7] Petrova Ts, Benova E, Petrov G and Zhelyazkov I 1999 Physical Review E 60 875–86
[8] Benova E and Petrova Ts 2000 Bulg. Journal of Phys. 27 25–9
[9] García M C, Rodero A, Sola A and Gamero A 2000 Spectrochimica Acta B 55 1733–45