Influence of the operating conditions on Ar microwave plasma characteristics: modelling and experiment

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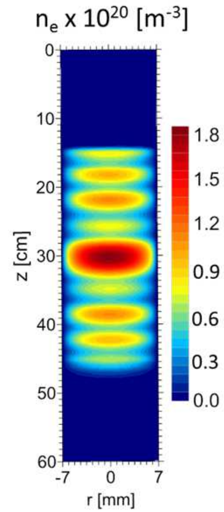


Outline

- Motivation
- Surfaguide system
- 2D model description
- Spatial profiles
- OES for determination of n_e, T_e and n_{Ar4s}
- Influence of applied pressure and power
- Summary

Motivation

- Microwave sustained plasmas:
  - High-density plasmas over a wide pressure range: *10^{-3} – 10^{5} Pa*.
  - High degree of non-equilibrium $T_e >> T_{ion}$
  - Energetically efficient: electrons absorbed almost entirely the applied energy.
- We apply ***MW*** at intermediate pressure for:
  - CO_2 or CO_2/H_2O dissociation.
  - activation of catalysts.

TL-17: Plasma-assisted catalysis for conversion of CO_2 and H_2O over supported nickel catalysts. ***Guoxing Chen*** ULB-UMONS

- Importance of plasma characteristics for control of dissociation process.

Surface-wave sustained plasma*

- *Surface waves*: propagating at the interface between two dielectrics with positive and negative permittivity
- Plasma can have negative permittivity

$$\epsilon_p = 1 - {\omega_p}^2/{\omega_{applied}}^2$$

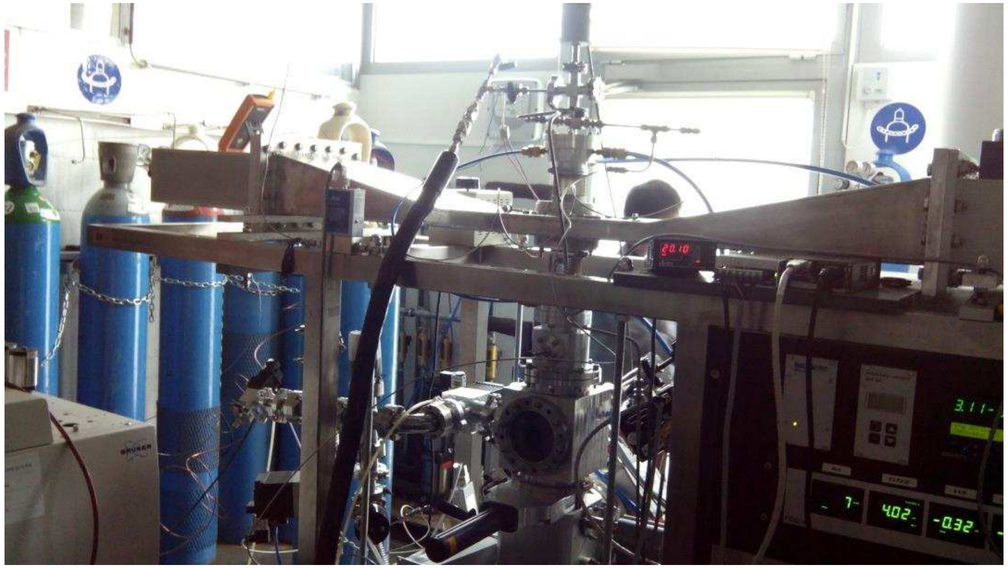
- Pure surface waves: propagating on both sides of the plasma-dielectric boundary when $|\epsilon_p| > \epsilon_d$
- *Symmetric surface waves:* TM mode and m=0

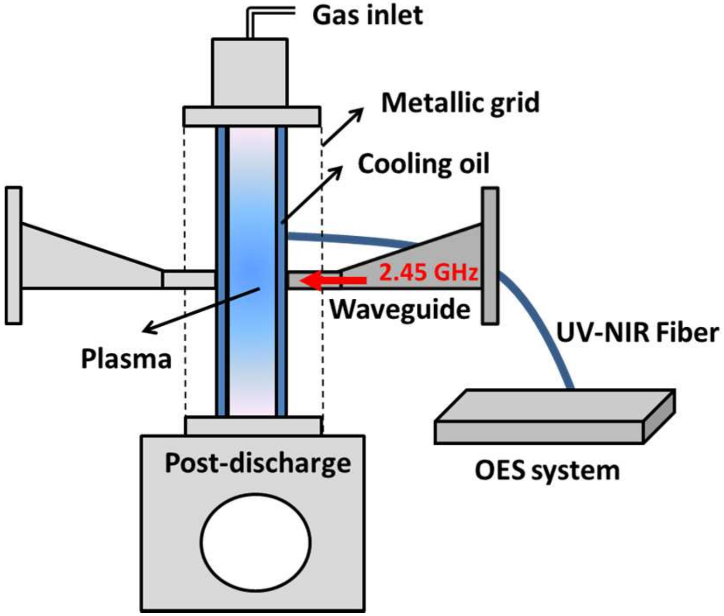
*M. Moissan, A. Shivarova, and A.W Trivelpiece, *Plasma Phys,* **24,** 1331 (1982).

Surfaguide system

ChIPS, University of Mons, Materia Nova Research Center

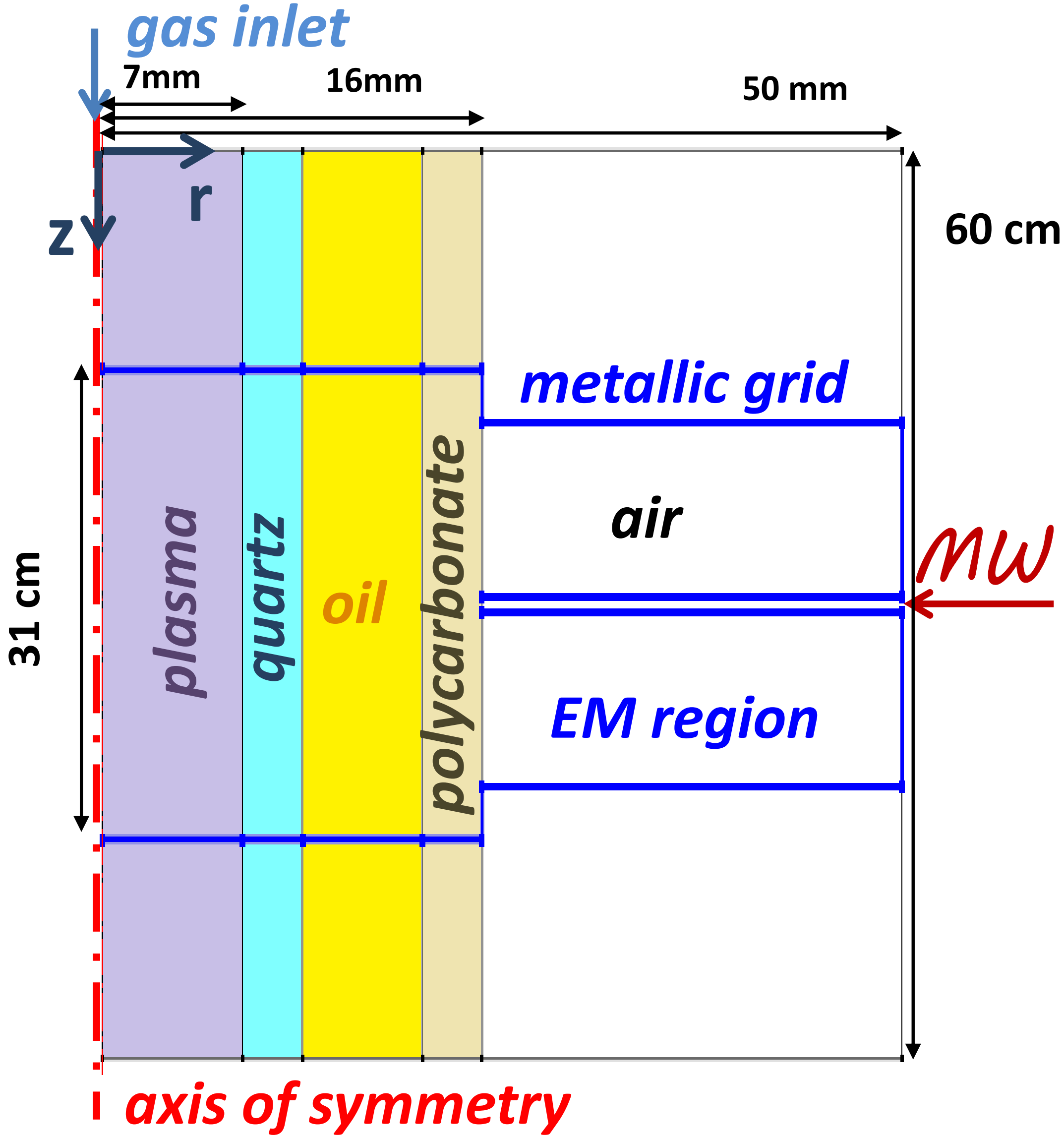
Surfaguide launcher at **2.45 GHz/ 915 MHz** in continuous or pulsed regime
Pressure: **0.5 - 40 Torr** Power: **50 - 500 W**





G. Chen, T. Silva, V. Georgieva, T. Godfroid, N. Britun, R. Snyders, M.-P. Delplancke-Ogletree
Int. J. Hydrogen Energy, 2015, **40**, 3789.

Simulation region



Fluid + EM equation set

- ***Fluid*** description of plasma
  - Heavy species density balance
  - Electron density from quasi-neutrality assumption
  - Heavy particle energy balance
  - Electron energy balance
  - Gas flow is calculated based on
    - Mass continuity equation for plasma bulk
    - Momentum and energy balance for plasma bulk
- ***EM*** model: surface waves in **TM** mode, **m=0**
  - Maxwell-Faraday equation for harmonic fields
  - Maxwell-Ampere equation for harmonic fields

Equation set

$$\nabla \cdot (n_s \vec{v}_b) - \nabla \cdot (D_s \nabla n_s) = S_s.$$

$$n_e = \sum_i n_i$$

$$\nabla \cdot (C_{p,h} T_h \vec{v}_b) + \nabla \cdot \vec{q}_h = Q_{eh}^{elas} + Q_{h^*h}^{inel} + \tau : \nabla \vec{v}_b + \vec{v}_b \cdot \nabla p_h$$

$$\nabla \cdot (C_{p,e} T_e \vec{v}_b) + \nabla \cdot \vec{q}_e = Q_{Ohm} - Q_{eh}^{elas} - Q_{eh}^{inel} + \vec{v}_b \cdot \nabla p_e - Q_{rad}$$

$$\nabla \cdot (\rho_b \vec{v}_b) = 0$$

$$\nabla \cdot (\rho_b \vec{v}_b \vec{v}_b) = -\nabla p + \nabla \cdot \tau$$

$$\nabla \times \vec{E} + i\omega\mu_0 \vec{H} = 0$$

$$\nabla \times \vec{H} - i\omega\epsilon_r \vec{E} = \vec{J}$$

$E_z, E_r, H_\varphi \neq 0$

Jimenez-Diaz M., et al, *J Phys. D: Appl. Phys.*, **45**, 335204 (2012)

Boundary conditions

$$\frac{\partial \Psi}{\partial z} = 0$$

$$v_{z0} = \frac{2\Phi}{\pi R_1^2}\left[1 - \left(\frac{r}{R_1}\right)^2\right]$$

$$\frac{\partial^2 p}{\partial z^2} = 0$$

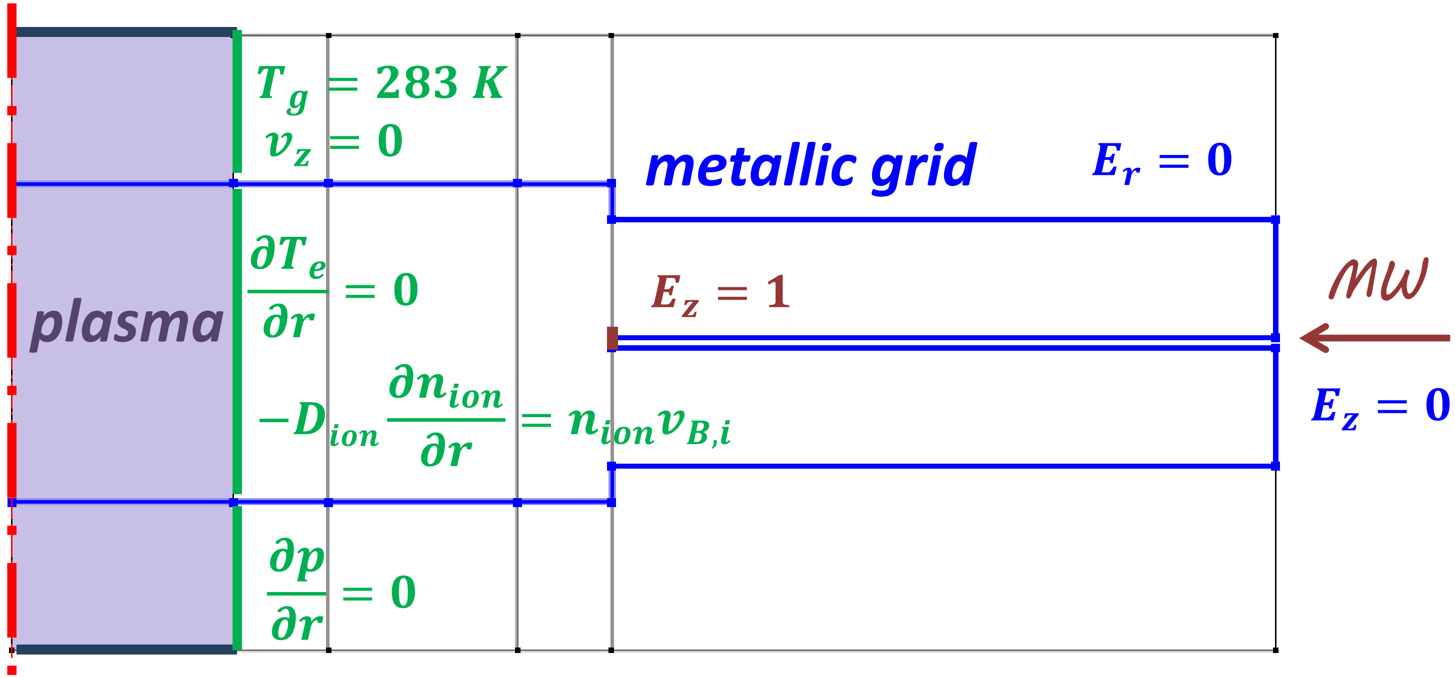
$$\Psi \equiv n_i, T_e, T_g$$

$$\frac{\partial E_z}{\partial r} = 0$$

$$\frac{\partial \Psi}{\partial r} = 0$$

$$\frac{\partial v_z}{\partial r} = 0$$

$$\frac{\partial p}{\partial r} = 0$$



$$\frac{\partial \Psi}{\partial z} = 0$$

$$\frac{\partial v_z}{\partial z} = 0$$

$$p_{out} = p_{pump}$$

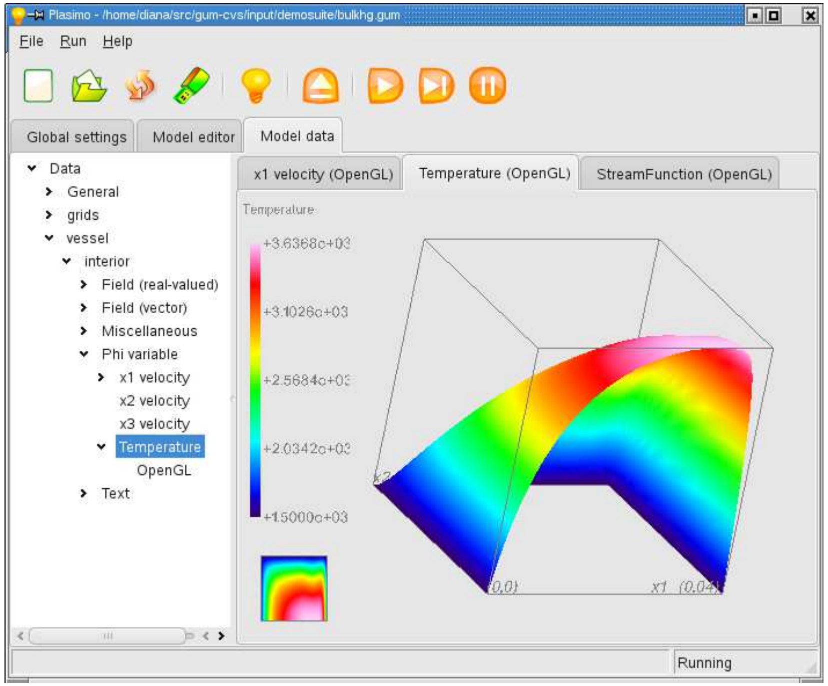
Species and reactions

- **6** species: Ar , e^-, Ar^+, Ar_2^+, Ar(4s) , Ar(4p)
- Rate coefficients
  - Electron-neutral (in ground or excited state) collisions (**11**) – calculated using cross-section data + BOLSIG+
  - Heavy species reactions (**9**)
  - Electron-ion recombination (**3**)
  - Electron-ion impact (**1**)
- Radiative transitions (**2**): transition probablity
  - Ar(4s) → Ar + hν
  - Ar(4p) → Ar (4s) + hν

BOLSIG + http://www.bolsig.laplace.univ-tlse.fr/

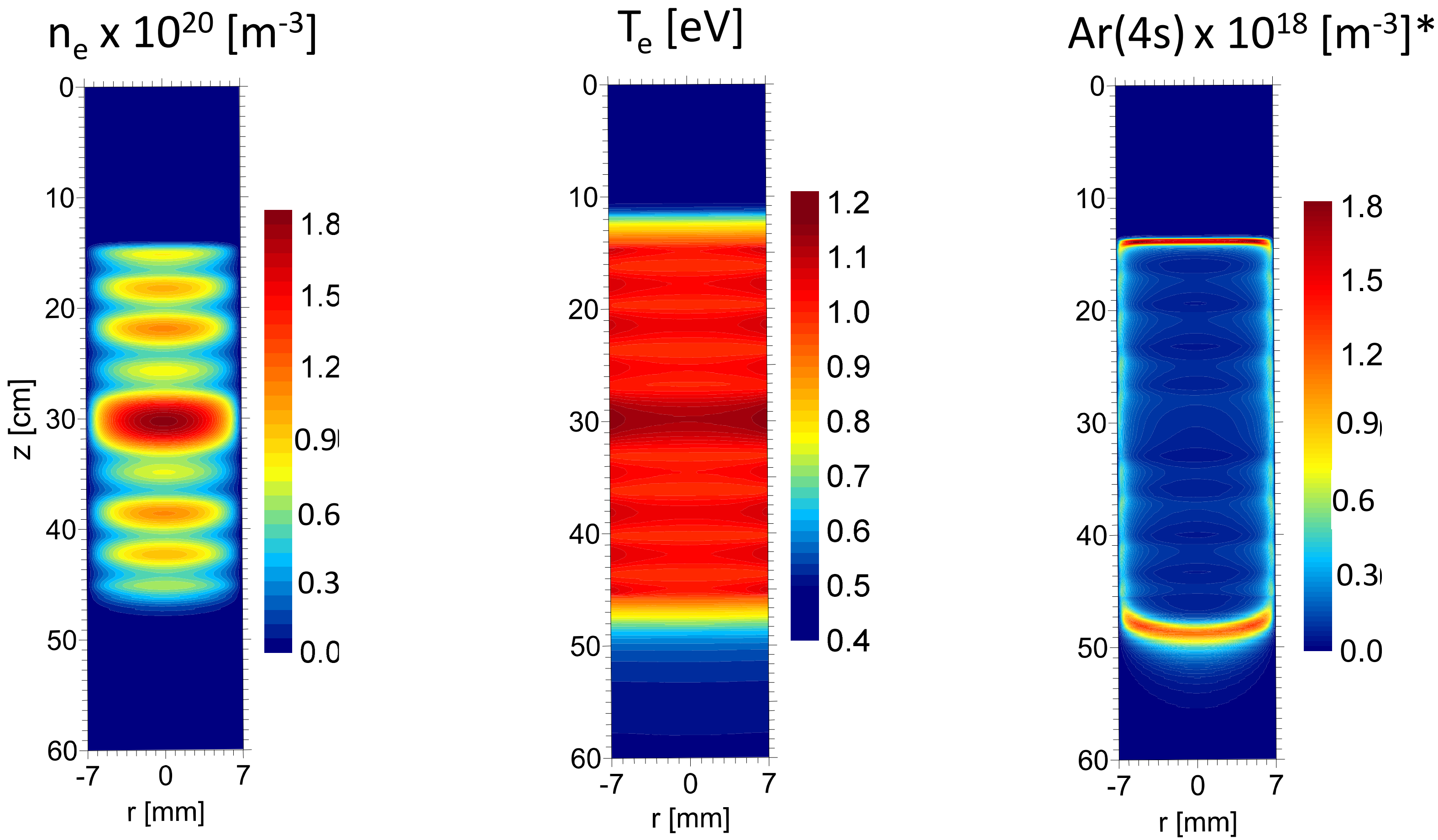
PLASIMO

EPG, Eindhoven University of Technology https://plasimo.phys.tue.nl/



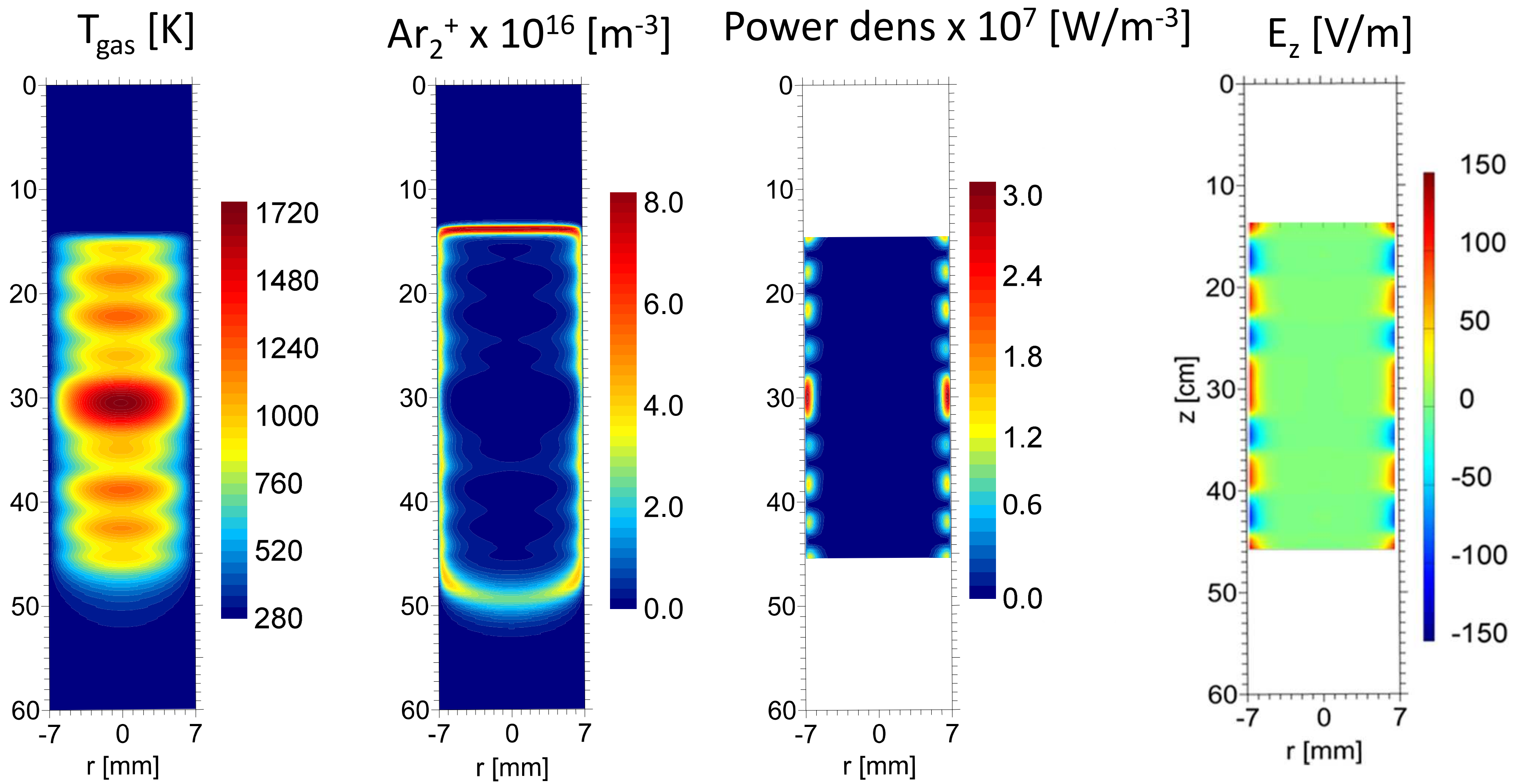
Spatial profiles

Power **100W** Pressure **7.5 Torr** (1000 Pa) Flow rate **250 sccm**



*C. Lao, et al, J. Appl. Phys. **87**, 7652 (2000); S. Hubner, et al, J. Appl. Phys. **113**, 143306(2013)

Spatial profiles



Benchmarking

- Good agreement with a model solving the electron density balance equation (7.5 Torr, i.e. 1000 Pa)

***TL-6*: Antonin Berthelot,** *University of Antwerp*

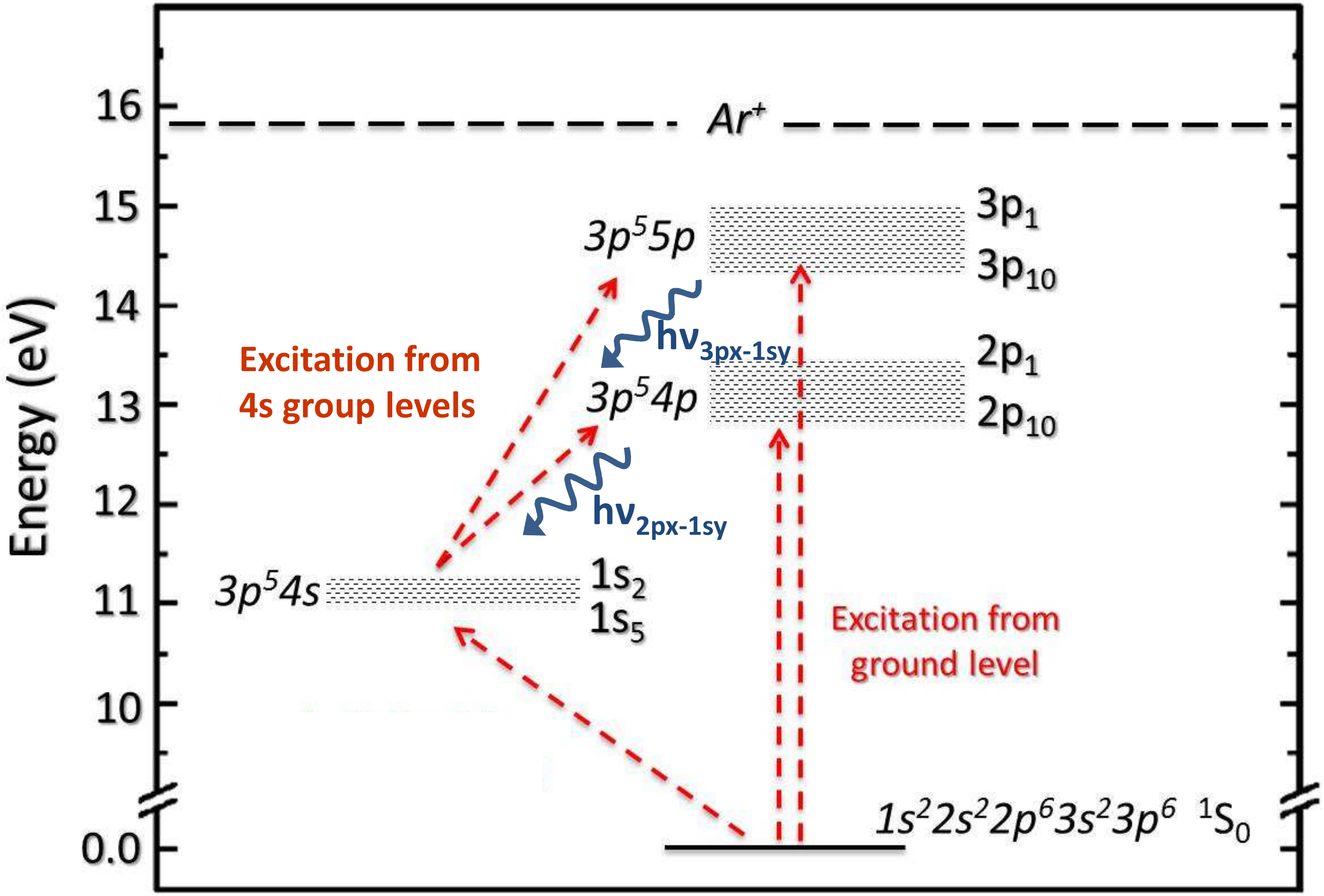
- Good agreement with experimental measurements of electron density (10 Torr, i.e. 1300 Pa) from literature: $n_e = 1x10^{20}\ m^{-3}$

C Boisse-Laporte, et al , *J. Phys. D: Appl. Phys.* **20** ,197 (1987)

- With experimental measurements in the lab of *University of Mons* and *Materia Nova Research Center*

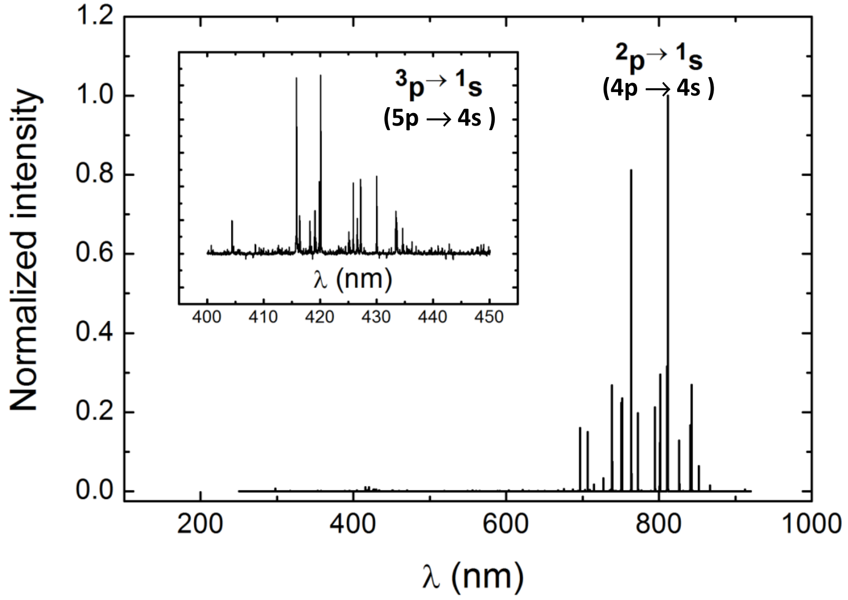
In the next slides

Background for OES measurements



Self-absorption method*

Ar emission spectrum

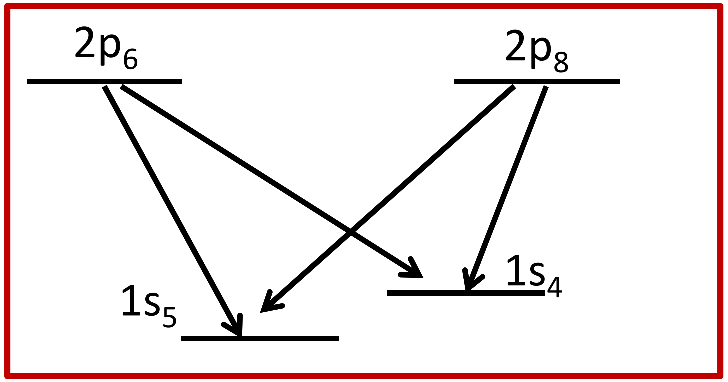


Emission line formula

$$I(2p,1s) \sim n(2p)\boldsymbol{\gamma_{2p1s}}$$

$$\boldsymbol{\gamma_{2p1s}} = f(n_{1s})$$

Example of optical transitions



Density of Ar(4s) is determined using emission lines from transitions $2p_y \rightarrow 1s_x$

*John B Boffard, R O Jung, Chun C Lin and A E Wendt, *Plasma Sources Sci. Technol.*, **19,** 065001 (2010).

T_e determination

T_e : by the balance of creation/loss of **$3p_1$** (425.9 nm) and **$2p_1$** (750.4 nm) and using the line intensity ratio **I_{426}/I_{750}**

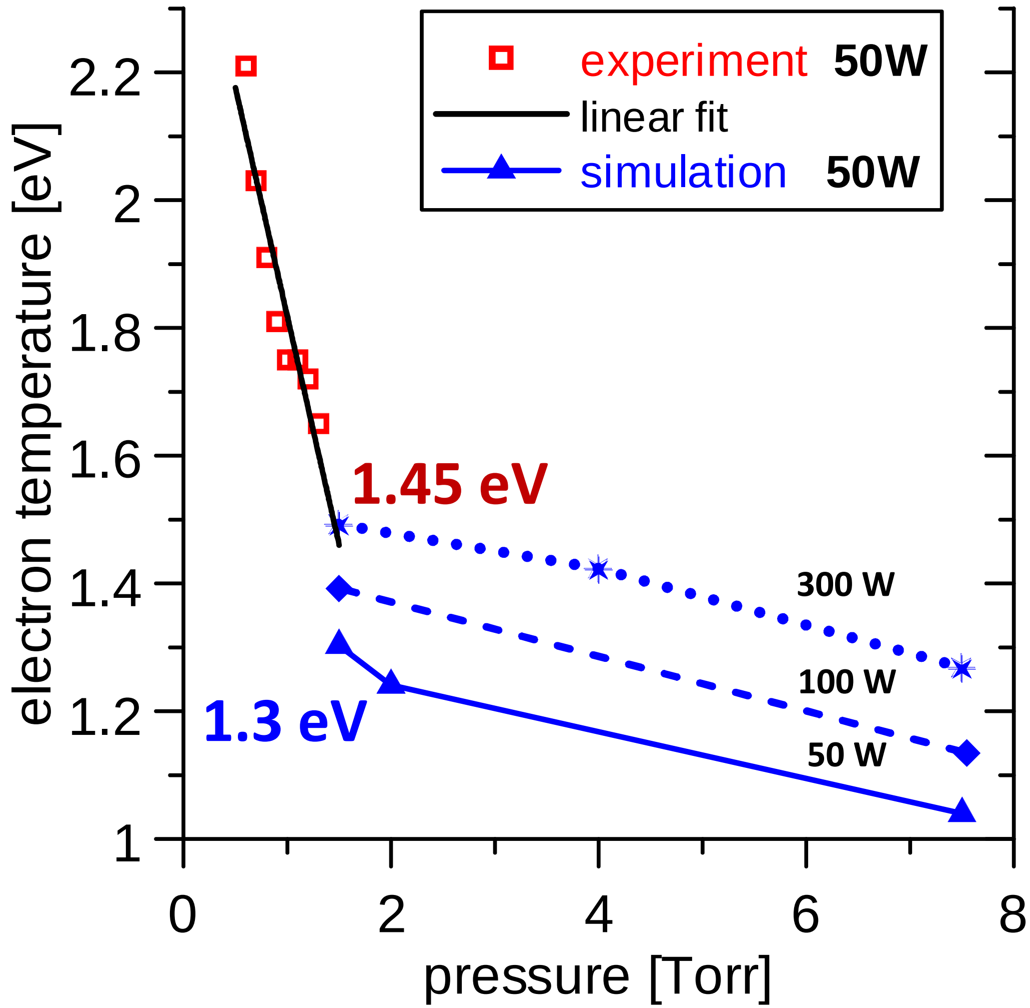
$$n_e \sum_{l=4s,3p^6} n(l) k_l^p(T_e) = n(p) \sum_{l=4s,3p^6} \gamma_{pl} A(p,l)$$

n_e determination

n_e : by the balance of creation/loss of the metastable **$1s_5$**, measured **$1s_x$** densities and calculated ***T_e***

$$n_e n_g k(g, 1s_5) + n_e \sum_x n(1s_x)\, k(1s_x, 1s_5) + \sum_y n(2p_y)\, A(2p_y, 1s_5)$$
$$+ \sum_z n(3p_z)\, A(3p_z, 1s_5) = n_e\, n(1s_5) \sum_q k(1s_5, q)$$

T_e : simulation - experiment



Power: **50 W**
Flow: **125-200 sccm**

Experiment limit:
max pressure **1.3 Torr**
due to decrease in Ar4s group density with pressure, i. e. weak optical signal above max pressure

Simulation limit:
min pressure: **1.5 Torr**
due to low particle densities, i.e. fluid plasma description is not valid below min pressure

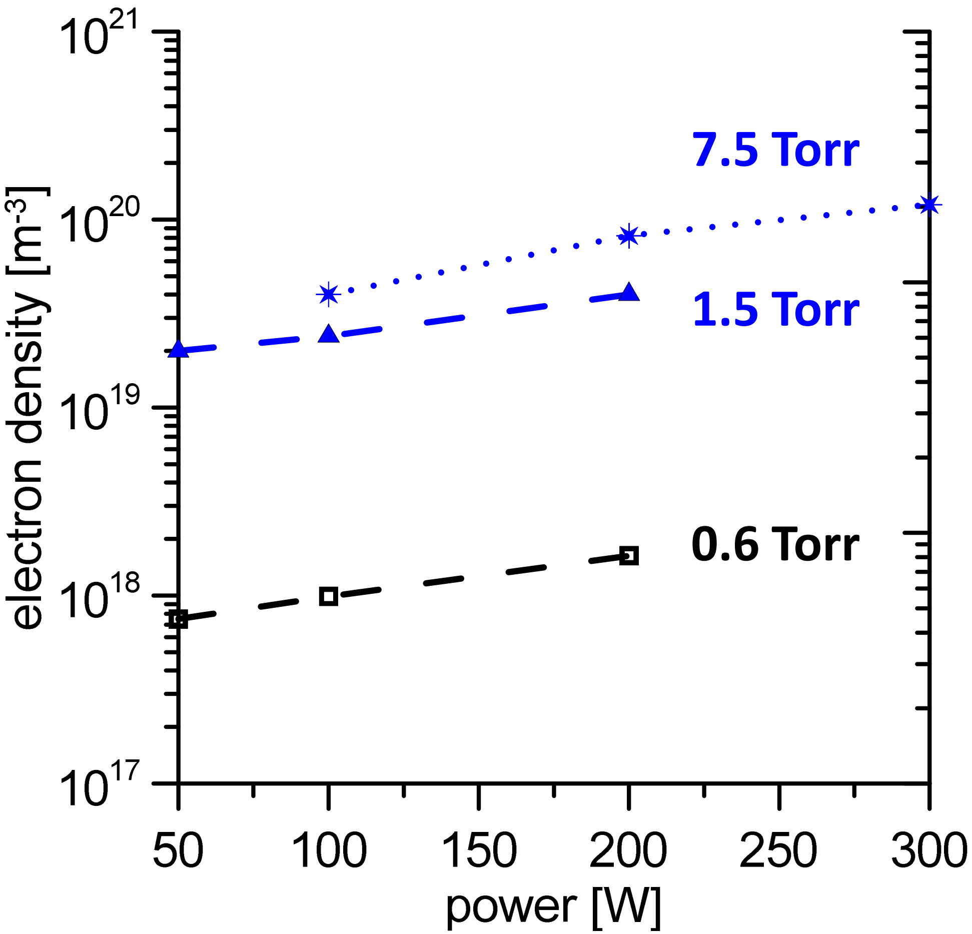
Simulation-experiment comparison

Radially averaged simulated plasma characteristics and OES measurements at **4cm** above the discharge center. Power: **50 W**

	T_e [eV]	n_e [m^{-3}]	T_{gas} [K]	Ar4s [m^{-3}]
Modelling **1.5 Torr**	**1.3**	**2.0×10^{19}**	**422**	**2.2×10^{17}**
Experiment **1.3 Torr**	**1.65**	**0.2×10^{19}**	**-**	**2.8×10^{17}**

- ***Good agreement*** in T_e and Ar4s group density
- 1 order of magnitude difference in n_e ; possible reasons
  - Different reaction rate coefficients in experimental and simulation models
  - Quasi-neutrality assumption, i.e. lower fluxes to the wall
  - Difference in the absorbed power in the experiment and in the simulation (measurement of T_{gas} is foreseen)

n_e : power influence



Power: **50 W**
Flow: **25-125 sccm**
Blue lines **– simulation**
Black line - **experiment**

Linear relation between the electron density and the applied power in agreement with theoretical and experimental studies previously reported.[1,2]

[1] M. Moissan and J. Pelletier, *Microwave excited plasmas,* 1992 (Elsevier)
[2] S. Rahimi, et al *J. Phys. D: Appl. Phys*. **47,** 125204 (2014) .

Benchmarking

Radially averaged plasma characteristics in the discharge center
pressure **7.5 Torr**
power **100 W**
flow rate **500 sccm**

	T_e [eV]	n_e [m^{-3}]	T_{gas} [K]	Ar4s [m^{-3}]	Ar_2^+ [m^{-3}]
$(1) n_e = \sum_i n_i$	**1.1**	**1.0×10^{20}**	**1025**	**1.7×10^{17}**	**1.0×10^{16}**
(2) n_e balance	**1.2**	**0.5×10^{20}**	**886**	**5.5×10^{17}**	**0.5×10^{16}**

- Good agreement in plasma characteristics profiles and in T_e and power density deposition values ➡ thin sheaths , i.e. validation of quasi-neutrality assumption.
- n_e , Ar^+ and Ar_2^+ densities: difference by factor of 2 : different equations solved for n_e ; thin sheaths and weak E in (1) , i.e. underestimated ion flux at the walls.

Summary

- A 2D quasi-neutral model of Ar surface wave sustained discharge at *intermediate pressure* was developed.
- Comparison with experimental measurements of Ar(4s) density, electron density and electron temperature: *reasonably good agreement* taking into account the simulation and measurement limitations .
- Electron temperature decreases with pressure and increases slightly with power
- Electron density increases with power and with pressure.

Acknowledgments

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- Antonin Berthelot University of Antwerp
- Stanimir Kolev Sofia University

- The work is done in the framework of

Plasma **S**urface **I**nteractions (**IAP,** phase **VII)**

https://psi-iap7.ulb.ac.be

Thank you for your attention !