Investigation of local thermodynamic equilibrium in laser-induced argon plasma using optical emission spectroscopy and Thomson scattering

A.Farah-Sougueh[1,2], A.Mendys[2], T.Pięta[2], K.Dzierzęga[2], S.Pellerin[1], B.Pokrzywka[3], J.Hermann[4] and D.G. Astanei[1,5]

[1] *GREMI Laboratory, Orleans University/CNRS, BP 4043, F-18028 Bourges cedex, France*
[2] *Marian Smoluchowski Institut of Physics, Jagellonian University, Krakow, Poland*
[3] *Obserwatorium Astronomiczne na Suhorze, Uniwersytet Pedagogiczny, Krakow, Poland*
[4] *LP3, Aix-Marseille University/CNRS, , Marseille, France*
[5] *"Gheorghe Asachi" Technical University of Iași, Faculty of Electrical Engineering*

We investigate the laser generated plasma in argon using Thomson scattering (TS) and optical emission spectroscopy (OES) techniques. The experiment is performed with two nanosecond Nd:YAG lasers: one generates the plasma while the second one probes the formed spark. The main objective of this work is to study the local thermodynamic equilibrium (LTE) in argon plasma using these two methods. First, LTE is studied by comparing temperature and electron density measured by OES with parameters found using Thomson scattering technique. Secondly, the rate of the collisional to radiative processes (the McWhirter criterion) was investigated. Our results show satisfactory agreement between electron densities obtained with these two methods, while we find very big discrepancy between electron temperature determined from the TS spectra and the excitation temperature from OES data. Also the Mc Whirter criterion is not fulfilled for Ar II during the first microsecond of plasma life as it is indicated by plasma parameters obtained with TS method

1. Introduction

Laser-induced plasma (LIP) which was first reported in 1963 by Maker *et al* [1], has achieved a great interest as a source of spectroscopic data. LIP has also many applications like X-ray sources for lithography, plasma igniters, pulsed laser deposition or it has become very popular analytical technique. The latter is mainly due to its applicability to different kinds of samples, no sample preparation or in-situ and remote sensing capability. However, despite many theoretical and experimental works and significant advances in instrumentation over the last decade, the performance of the LIBS method is not considerably better. The sensitivity still remains moderate, the quantitative results are subject to large uncertainties and the matrix effects strongly affect the signal. The quantitative elemental analysis by LIBS requires a thorough knowledge of atom, ion and electron number densities and their temperatures. These parameters are commonly deduced in indirect way from the optical emission spectra assuming plasma in local thermodynamic equilibrium (LTE).

The electron number density N_e^{OES} is usually determined from the Stark width of some reference emission lines while electron temperature T_{ex}^{OES} is obtained from emission data applying either Boltzmann or Saha-Boltzmann equations. The use of Stark widths is difficult because of the limited number of lines with Stark data of satisfactory accuracy with respect to both their electron density and temperature dependencies. Also the use of Boltzmann and Saha-Boltzmann equations is only possible if plasma is at least in the partial local thermodynamic equilibrium.

Therefore, LTE assumptions are not already fullfield in the plasma, inducing errors in calculated parameters. In order, to validate OES methode, LTE was first studied by comparing electron density and température measured with TS (N_e^{TS}, T_e^{TS}), wich are free from equilibrium assumption, to those obtained by OES (N_e^{OES}, T_{ex}^{OES}). Moreover, the Mc Whirter criterion was calculated by the two methods.

2. Experimental setup

The experiment was carried out in a vacuum chamber, purged and filled with argon and equipped with six optical view ports. Two frequency-doubled Q-switched Nd:YAG lasers operating at 10 Hz repetition rates were used to generate the plasma and to probe the plasma plume in TS experiments. The durations of laser pulses were 4.5 ns and 6 ns, respectively. The laser beams were arranged orthogonally and were focused using anti-reflection coated plano-convex lenses with focal lengths of 100 mm (fluency of 1.8 kJ/cm^2) for generating laser and 500 mm (fluency of 10 J/cm^2) for the probe one. The emission and the TS spectra were recorded using an intensified charge coupled device (ICCD) matrix detector mounted on a spectrometer.

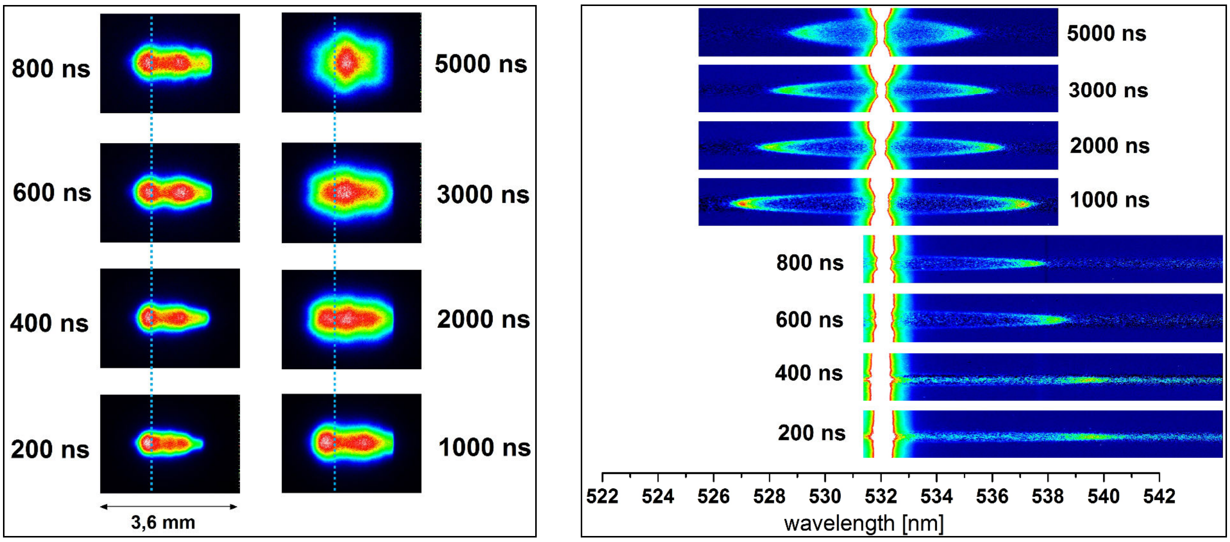

Fig 1: Plasma imaging at the left and TS spectra at the right. Dash blue line corresponds to the position of the probe beam [Generating laser fluency: 1.8 kJ/cm^2; Probe laser fluency: 10 J/cm^2]

3. Results and discussions

Images of plasma and TS spectra as registered by the ICCD camera are shown in Fig 1. For the emission, only spectral ranges with lines of interest are recorded and N_e^{TS} and T_e^{TS} are obtained by fitting Salpeter [2] function to the experimental spectra. The plasma parameters are spatially and temporally resolved and independent of the plasma equilibrium hypothesis. On the other hand, T_{ex}^{OES} and N_e^{OES} are determined from OES measurements. In this case experimental spectra are compared to the spectral radiance of plasma in LTE. The plasma parameters, e.g. N_e^{OES} and T_{ex}^{OES}, are deduced from the best agreement between measured and computed spectra, using iterative procedure as presented in [3]. Calculations take into account the self-absorption of emission lines by dividing the plasma into two zones. That is the hot and dense core and cooler boundary responsible for self-absorption of spectral lines emitted from the core.

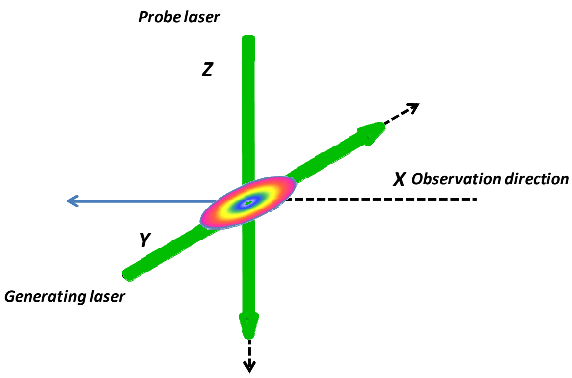

Fig 2: Geometry of the experiment

The temporal evolution of temperature and electron density on the plasma axis ($Y = 0$, $Z = 0$) and in the focal plane of the breakdown pulse is presented in Fig 3. N_e^{OES} decreases from 6.5×10^{17} cm^{-3} at 400 ns to 4.2×10^{16} cm^{-3} at 5 μs after the breakdown pulse. At the same time T_{ex}^{OES} drops from 17900 K to 6700 K. Besides N_e^{TS} decreases from 5.4×10^{17} cm^{-3} at 400 ns to 6×10^{16} cm^{-3} at 5 μs, while T_e^{TS} drops from 58500 K to 16200 K.

The decays of temperatures and densities with time were fitted with power laws. We found N_e^{TS} to fall off as $t^{-(0.91 \pm 0.06)}$ when T_e^{TS} follows two different power laws: quickly as $t^{-(0.77\pm0.028)}$ during the first microsecond, and then as $t^{-(0.37\pm0,026)}$. On the other hand N_e^{OES} and T_{ex}^{OES} evolve respectively as $t^{-(1.01 \pm 0.05)}$ and $t^{-(0.39 \pm 0.022)}$.

As shown in Fig 3, N_e^{OES} and N_e^{TS} are comparable within the uncertainty limits. However, at each moment T_e^{TS} largely exceeds T_{ex}^{OES}, sometimes more than by a factor of 2. Parameters from TS are comparable to the results of Mendys *et al* [4]. In fact, the temperature varies from 50700 K to 16000 K and electron density from 4.3 to 0.7×10^{17} cm^{-3}, respectively 400 ns and 5 μs. As mentioned previously in the paper T_e^{TS} varies from 68000 K to 16100 K and N_e^{TS} from 5.4×10^{17} to 0.6×10^{17} cm^{-3}.

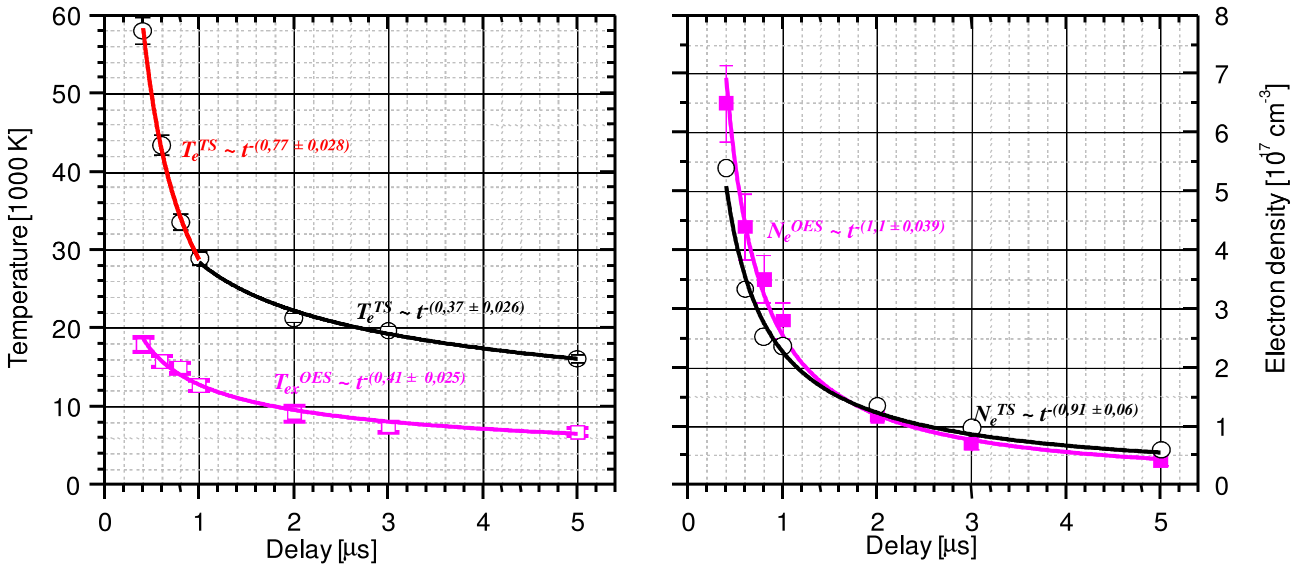

Fig 3 : Temporal evolution of electron density and electrons and excitation temperatures on the plasma axis
[$Y = 0$, $Z = 0$; Generating laser fluency : 1.8 kJ/cm^2; Probe laser fluency : 10 J/cm^2]

Liu *et al* [5] investigating aluminium plasma also with TS and OES, as well observed a large discrepancy between electron and excitation temperatures found with the two methods. Under their experimental conditions they found T_e^{TS} to fall from 100000 K at 400 ns to 15000 K at 2500 ns while at the same time T_{ex}^{OES} varies from 10000 K to 7500 K. Similar observation were made by Farah-Sougueh [6] in aluminium plasma. In this study big discrepancy is observed at shorter delay times while at longer time the temperatures seem to converge (discrepancy between T_e^{TS} and T_{ex}^{OES} was about 32000 K at 800 ns when it was only about 1100 K at 2500 ns).

As there is very big difference between electron temperature (T_e^{TS}) and excitation temperature (T_{ex}^{OES}), we can conclude that no LIP at LTE exists.

However, the using of powerful laser as a probe to generate the TS spectra may induce heating of the plasma. So T_e^{TS} can be overestimated. Dzierzega et al [7] but also Mendys [4] quantified this heating respectively on an argon thermal discharge and argon laser induced plasma, concluding that heating effect can be neglected for low probe laser fluencies. In our case the fluency was about 10 J/cm^2, excluding heating of the plasma by the probe laser.

LTE was also verified by the well known Mc Whirter criterion which imposes a minimal electron density in the plasma indicating that the electrons collisions dominate radiative processes and it is written as:

$$Ne^W > \frac{2.55\times10^{11}\, T_e^{1/2}}{<g>} (\Delta E_{nm})^3 \quad [\mathrm{cm}^{-3}] \qquad (1)$$

where g is the Gaunt factor and T_e and ΔE_{nm} expressed in K and eV, are respectively the temperature and the largest energy gap between adjacent levels. The latter corresponds to the gap between the ground and the first excited level.

Fig 4 shows the minimal electron density imposed by Mc Whirter criterion for Ar I and Ar II calculated according to both TS and OES data In the case of TS data, the criterion is fullfield neither for Ar I nor for Ar II. In case of OES results: Ar I the criterion is not satisfied for Ar I almost at all moments while for Ar II it is fulfilled during the first microsecond of plasma life. Merk *et al* [8] who studied LTE via Mc Whirter criterion using OES, came to same conclusions than ours. In fact they observed that criterion was fullfield in the first microsecond for the single ionized argon.

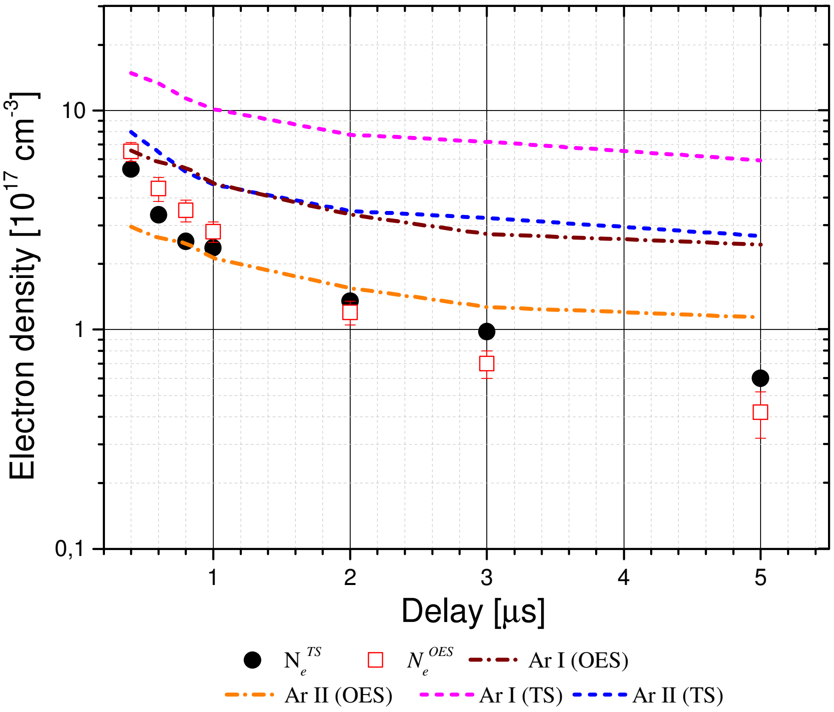

Fig 4: Mc Whirter criterion for Ar I and Ar II using TS and OES
[$Y = 0$, $Z = 0$; Generating laser fluency : 1.8 kJ/cm^2; Probe laser fluency : 10 J/cm^2]

4. Conclusion

In this work Thomson scattering and optical emission spectroscopy were applied to quantify temporally and spatially resolved electron number density and temperature in laser induced spark in argon at atmospheric pressure. We found a fairly good agreement between electron densities determined with these two methods while a large discrepancy is found for temperatures. Moreover, we found our plasma to be out of LTE.

5. References

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