Apparent excitation temperature in laser-induced plasmas

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Abstract. This work has shown the existence, for the purpose of experiments of laser-induced plasma spectroscopy, of an apparent (population-averaged) excitation temperature that determines with good approximation the Boltzmann population distribution for each ionisation species. In experiments in which the line intensity (integrated along the line-of-sight) is measured, the values of the apparent temperature obtained for neutral atoms and ions are different. To investigate the population-averaging process, a plasma generated with a Ni-Fe-Al alloy in air at atmospheric pressure has been characterized with complete spatial resolution, determining the local values of the electronic temperature and the relative number densities of Fe neutral atoms and ions. From the distributions of plasma parameters, synthesized distributions of intensities integrated along the line of sight have been obtained for Fe I and Fe II lines, showing good agreement with the experimental distributions. Synthesized Boltzmann plots of neutral atoms and ions, constructed with the spatially-integrated synthesized intensities, have shown linear behaviors, providing the apparent temperatures for neutral atoms (9890 K) and ions (11400 K). The synthesized Boltmann plots are also in good agreement with experimental Boltzmann plots obtained in independent spatially-integrated measurements of the plasma emission, carried out with a fiber optics cable.

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1. Introduction

The characterization of laser-induced plasmas is a subject of great interest, relevant to the laser-induced breakdown spectroscopy (LIBS) technique. A detailed knowledge of the plasma parameters (temperature, electron density and atom density), and the theory and approximations that relate these parameters to the plasma emission are of great interest in order to improve the applications of LIBS. In a recent work [1], we have investigated the spatial characterization of a laser-induced plasma generated with a Fe-Ni alloy in air at atmospheric pressure. In this work, the local values of the plasma parameters were deduced from the intensities of Fe I and Fe II spectral lines measured with spatial resolution. The procedure used included the deconvolution of the spectra to deduce the emissivities from the intensities, which are integrated along the line-of-sight. The results obtained were compatible with the existence of a single electronic temperature that determines both the excitation equilibrium through the Boltzmann equation and the
ionisation equilibrium, given by the Saha equation. These results support the assumption of local thermodynamic equilibrium (LTE) for the conditions of plasma generation and detection of emission used in the experiment. However, this work also showed that, if Boltzmann plots are obtained from spatially-integrated measurements of the intensity, two different values of temperature are obtained for neutral atoms and for ions. Also, in spatially-integrated measurements, the ionisation temperature deduced from the Saha-Boltzmann plot was different from the excitation temperatures obtained from Boltzmann plots. Other groups have also found in experiments with laser-induced plasmas these differences between the excitation temperatures obtained with neutral atoms and ions [2] or between the excitation and ionisation temperatures [3-5]. An explanation to this behaviour [6, 7] is that the temperature determined from the spatially-integrated intensities is an apparent excitation temperature, population-average of the local electronic temperature. As the spatial distributions of the level populations are different for neutral atom and ion lines, the apparent temperatures obtained for the two ionisation species must be different. The purpose of this work is to carry out an experiment, based in the spatially-resolved characterization of the plasma, to confirm this explanation, and demonstrate the existence of the apparent excitation temperatures.

2. Experimental

The experimental system was similar to that used in previous works [1, 8], so it will only be described briefly. To generate the plasma, a Nd:YAG laser (wavelength 1064 nm, pulse energy 100 mJ, pulse width 4.5 ns, repetition rate 20 Hz) was focused with a lens of 128-mm focal length, the lens-to-sample distance being 120 mm. The laser beam was aligned horizontally at right angles to the sample surface. The sample was a home-made Ni90Fe5Al5 alloy and the plasma was generated in air at atmospheric pressure. An achromatic optical system formed by a flat and a concave mirror were used to form a 1:1 image of the plasma onto the entrance slit of an imaging spectrometer (focal length 0.5 m, grating of 3600 lines/mm), provided with an intensified CCD detector (1024x256 pixels, intensifier diameter 18 mm). The CCD pixels were grouped in rows. In this way, spatially-resolved spectra along a slice of the plasma parallel to the sample surface were detected simultaneously by the CCD rows. The spatial resolution in the perpendicular direction was achieved varying the distance of this slice to the sample by displacing the sample and the focusing lens the same distance, so that the focusing conditions were maintained. It was necessary to use four spectral regions of the CCD detector to cover the spectral range of the Fe lines selected for temperature determination. An additional spectral region, containing the line 538.34 nm Fe I, that shows a considerable Stark broadening and shifting, was used to determine the electron density. To measure this weak line with enough signal-to-noise ratio, a sample with Fe concentration increased to 50 % was used. Special care was taken to ensure reproducible conditions between the measurements. In previous works [1, 8], the sample was rotated between measurements, and various spectra obtained at fresh regions of the surface were averaged. In the present work, a different approach was used: the sample was continuously rotated during the measurements, so that a circular crater with lower depth was formed. With this procedure, the dispersion of the measurements was notably reduced. For spatially-integrated measurements, a different system for light collection was used, based in a fiber optics cable and the same spectrometer. The spectral efficiency of both systems was measured using a calibrated tungsten lamp.

3. Results and discussion

3.1. Saha-Boltzmann plots for the determination of the local temperature and number densities of neutral atoms and ions

The first step in this work has been the characterization of the laser-induced plasma with complete spatial resolution. To determine the plasma parameters starting from the spatially-resolved spectra, we have used the same theoretical framework described in a previous work [1], which was based in the book of Griem
[9], so only the main equations will be given here. The determination of the local electronic temperature is based in the measurement of the emissivity \( \varepsilon_{ji}^z \) (Wm\(^{-3}\)) for various iron lines of each species \( z \) (\( z = 0 \) for neutral atoms, \( z = 1 \) for ions). In order to obtain the local emissivity at each position in the laser-induced plasma from the measured intensity, which is integrated along the line-of-sight, a deconvolution process described in a previous work of our group [10] has been used. Then, the linear relation

\[
\ln \left( \frac{\varepsilon_{ji}^z \lambda_{ji}}{A_{ji} \sigma_j^z} \right)^* = -\frac{1}{kT} E_j^* + \ln \left( \frac{h c N_j^0}{Q^z(T)} \right)
\]

(1a)

which results from the Boltzmann and Saha equilibrium equations [1, 11] and whose graphical representation is known as the Saha-Boltzmann plot, allows to deduce the local electronic temperature \( T \) (K) from the slope of its linear fitting. In this equation, \( A_{ji} \) is the transition probability (s\(^{-1}\)), \( \lambda_{ji} \) is the transition wavelength (m), \( E_j^* \) and \( g_j^* \) are the energy (eV) and degeneracy (adimensional) of the upper level, \( N_j^z \) is the number density (m\(^{-3}\)) of the species (\( N_j^0 \) for neutral atoms, \( N_j^1 \) for ions), \( Q^z(T) \) is the partition function of the species, \( h \) is the Planck’s constant (J s), \( c \) is the speed of light (ms\(^{-1}\)), and \( k \) is the Boltzmann’s constant (eV K\(^{-1}\)). The asterisks indicate that the magnitudes are modified as follows: the left-hand side of the equation (the ordinate of the Saha-Boltzmann plot) includes the subtraction of a correction term that depends on the temperature and the electron density \( N_e \)

\[
\ln \left( \frac{\varepsilon_{ji}^z \lambda_{ji}}{A_{ji} \sigma_j^z} \right)^* = \ln \left( \frac{\varepsilon_{ji}^z \lambda_{ji}}{A_{ji} \sigma_j^z} \right) - B^z(T, N_e)
\]

(1b)

where

\[
B^z(T, N_e) = z \ln \left[ 2 \left( \frac{m k}{2 \pi e h^2} \right)^{3/2} \frac{T^{3/2}}{N_e} \right]
\]

(1c)

Also, the upper level energies (the abscissas of the Saha-Boltzmann plot) have been modified by adding to them the ionization energy of the lower ionization stages, that is, the energy scale begins in the ground state of the neutral atom. For the \( z \) ions, the correction is

\[
E_j^* = E_j^z + \sum_{k=0}^{z-1} \left( E_{j0}^k - \Delta E_{j0}^k \right)
\]

(1d)

where \( E_{j0}^k \) is the ionization energy of species \( k \) for isolated systems (eV) and \( \Delta E_{j0}^k \) is the correction of this quantity for interactions in the plasma. These modifications have only effect for ion lines (\( z \geq 1 \)) and are introduced in equation 1a in order to include the data of the different ionization stages in the Saha-Boltzmann plot.

The validity of the Saha-Boltzmann plot to obtain the local electronic temperature depends on the validity of the excitation (Boltzmann) and ionisation (Saha) equilibrium equations, which are satisfied in a plasma in local thermodynamic equilibrium (LTE). In the previous work [1], where the laser-induced plasmas were generated and detected in similar conditions, the hypothesis of the existence of LTE was supported by the experimental verification that, in local measurements, the values for the temperature deduced from Boltzmann plots obtained with neutral atom and ion emission lines were coincident among them within the experimental error, and also coincide with the temperature deduced from the Saha-Boltzmann plot. In the present work, the determination of the local temperature has been carried out using the Saha-Boltzmann plot, which provides more accurate results than the Boltzmann plot, due to the higher
spread in the values of the energy levels of the neutral atom and ion emission lines involved. The Fe lines selected to obtain the plots were the same as those of the previous work [1], where they are listed with their spectroscopic data. In this work, the lines were checked to be optically thin for a laser induced plasma generated in the same conditions. To this aim, the self-absorption of the lines was estimated by measuring intensity vs. concentration curves and making use of the curve-of-growth theory described in previous works [12, 13]. The decrease of the line intensities due to self-absorption was found to be always lower than 10 %, resulting in a relative error of the temperature lower than 2 %. The distribution of the electron density in the plasma, which has to be introduced in equation 1c, was obtained from the Stark shifting of the 538.34 nm Fe I line, following the procedure described in [14]. A typical Saha-Boltzmann plot is shown in figure 1, where the high correlation of the linear fitting ($R^2 = 0.9997$) can be appreciated. Similar plots have been obtained at all the points in the plasma having significant emission, providing the distribution of the temperature in the plasma.

![Figure 1. Saha-Boltzmann plot obtained at the axial position $z = 1.75 \text{ mm}$ and radial position $r = 0 \text{ mm}$. The value of the local temperature deduced from the linear fitting is indicated.](image)

The approach used in the present work to obtain the relative number densities of neutral atoms and ions was different from that used previously [10]. Instead of deducing the number density of neutral atoms $N^0$ from the emissivity of a single line and the temperature, it has been obtained from the intercept of the Saha-Boltzmann plot (see equation 1a). Then, the number density of ions $N^I$ is deduced by the application of the Saha equation [9]. This procedure provides more accurate values of the number densities, as the emissivities of several spectral lines participate in the determination. The relative error of the number density obtained with this method equals the absolute error of the intercept, which in the present experiment had a typical value of 10 %. A similar approach was used previously by Ciucci et al. [15], but in their case, the intercept of the Boltzmann plot, instead of the Saha-Boltzmann plot, was used to deduce the concentration of the emitting atomic species in the sample. In the present work, the distributions of the relative number densities of Fe neutral atoms and ions in the laser-induced plasma have been obtained using this method. The distributions of plasma parameters (temperature and number densities) obtained here were very similar to those reported in the previous article [1] for a similar laser-induced plasma generated with a Fe-Ni alloy.

3.2. Convolution of the emissivities to obtain the synthesized distributions of intensity

Once the distributions of temperature and number densities of neutral atoms and ions had been obtained, the next step consisted in showing that these distributions describe the plasma with enough accuracy to be able to synthesize the intensity distribution for any spectral line. Two iron emission lines with very different upper level energies, one of the neutral atom and another from the ion have been selected to
check the method, which was based in retracing the steps given to deduce the plasma parameters. Firstly, for each line, the distribution of emissivity has been obtained from the distributions of temperature and number density, using the equation 

\[ \varepsilon_{ji} = \frac{hc}{\lambda_{ji}} A_{ji}^z \frac{N^z}{Q^z(T)} g_{ji}^z \exp \left( -\frac{E_j^z}{kT} \right) \]  

(2)

Secondly, the deconvolution procedure has been reversed in order to obtain synthesized distributions of intensities, integrated along the line-of-sight. The convolution of the emissivities carried out for this purpose is simply a part of the deconvolution algorithm described in [10]. In figure 2, the synthesized distributions of the intensities of neutral atom and ion Fe emission lines are shown, together with the experimental distributions. It has to be mentioned that, as described in [10], due to the lack of complete symmetry of the experimental intensity distributions with respect to the laser beam, it was necessary to carry out a symmetrization process of the intensity profiles previous to the application of the deconvolution procedure. As can be seen in the figure, the intensity distributions synthesized starting from the plasma parameters describe well the shape of the experimental distributions, which are different for neutral atoms and ions, and also the quantitative values of the intensity.

3.3. Apparent excitation temperature for neutral atoms and ions

The Boltzmann plot method, commonly used to determine the excitation temperature in laser-induced plasmas, is based in the linearization of equation 2 through the calculation of its natural logarithm. However, in most cases, the characterization is carried out using experimental systems in which all (or at least a part) of the emission from the plasma is collected, for example by a fiber optics cable or a spectrometer slit. Moreover, in most experiments, the magnitude that is measured is the line intensity, integrated along the line-of-sight, instead of the emissivity, and the Boltzmann plot relation is

Figure 2. Synthesized (left) and experimental (right) distributions of the intensity of a neutral atom and an ion emission lines. All the distributions are drawn in the same scale of arbitrary units. Wavelengths are expressed in nanometers.
It has to be remarked that the local magnitudes (electronic temperature and number density) in equation 2 are only related to the line emissivity. Therefore, the constant term in equation 3 is not related to the local value of the number density, and the temperature is not the local electronic temperature. Then, the question arises why a linear relation like equation 3 is obtained in many works where spatially-integrated measurements are carried out. The answer was already given by Boumans [6] and, for laser-induced plasmas, by Radziemski et al. [7]. These authors described that, for inhomogeneous sources, the temperature resulting from spatially-integrated measurements is a population-averaged temperature, a parameter that describes the source but is not identical with the local temperature. We have called this parameter apparent temperature $T_a$, a name that emphasizes the fact that it is not the true electronic temperature. This idea has remarkable consequences because, as will be seen below and was already reported in a previous work [1], due to the different location of the population distributions of neutral atoms and ions, different apparent temperatures are obtained for the two species. In the present work we have tried to increase the insight into the concept of apparent temperature. To this aim, we have proceeded as follows. Starting from the spatially-resolved plasma parameters (temperature and number densities), we have obtained the synthesized distributions of intensity, as described in 3.2, for a set of neutral atom and ion Fe emission lines. From the distributions, synthesized integrated intensities, that include the emission from the whole plasma, have been obtained for all the lines, and a Boltzmann plot for each species has been constructed. As the calculation procedure includes the use of equation 2 to obtain the emissivities, it is clear that in this process the population-averaging of the temperature in the plasma is carried out, so the temperature values deduced from the slopes of the synthesized Boltzmann plots are the apparent temperatures for each species. Figure 3 shows in solid circles the synthesized Boltzmann plots obtained for neutral atom and ion emission lines. The very high correlation of these plots to linear fittings ($R^2>0.9999$) shows that, for a broad range of upper level energies, the use of Boltzmann plots in integrated measurements of intensity is experimentally valid with high approximation, despite the fact that, as mentioned previously, it is not justified from the theoretical point of view. From this figure, the usefulness of the concept of apparent temperature to describe the level excitation in laser-induced plasmas is also deduced. As expected, the apparent excitation temperature obtained for ions (11400 K), which are populated in the average in a hotter region of the plasma, is higher than that of neutral atoms (9890 K).

In order to provide additional evidence of the validity of the distribution of plasma parameters obtained in the present work and of the existence of the apparent excitation temperatures, we have also carried out independent measurements of the spatially-integrated intensities of the neutral atom and ion emission lines. In this case, the emission from the whole laser-induced plasma has been collected by a fibre optics cable placed at right angles to the laser beam direction. The experimental intensities have been used to obtain Boltzmann plots, one for each species, that are shown as open circles in figure 3. In order to compare the synthesized and experimental plots, the experimental data have been displaced along the $y$-axis by multiplying the intensities by the same factor. It has to be remarked that this factor is unique because both the experimental system and the calculation carried out in the present work provide the line intensities in the same relative scale for all the emission lines, including those of the neutral atom and the ion. As can be seen in figure 3, the line intensities synthesized from the spatially-resolved plasma parameters lead to a Boltzmann plot that is in good agreement with that obtained from the experimental integrated intensities. The apparent excitation temperatures deduced from the experimental Boltzmann plots are $9600 \pm 160$ K for neutral atoms and $11900 \pm 250$ for ions, where the errors have been estimated as the standard deviation $\sigma$ of the slope of the linear fittings. These values are different among them and almost coincide within the errors with the synthesized apparent temperatures, the coincidence being
complete if a 2\(\sigma\) criterion is taken for the errors of the experimental temperatures. The good agreement of the experimental and synthesized Boltzmann plots of figure 3 supports the validity of the model used, the accuracy of the spatially-resolved plasma parameters obtained and the existence and usefulness of the apparent temperatures.

![Figure 3. Synthesized (solid circles) and experimental (open circles) Boltzmann plots corresponding to the spatially-integrated emission from the plasma. The apparent (population-averaged) excitation temperatures for neutral atoms and ions deduced from the linear fittings are indicated.](image)

4. Conclusions
In this work we have tried to understand the population-averaging process that is involved in spatially-integrated measurements of the temperature of inhomogeneous sources like laser induced plasmas. To this aim, the spatially-resolved characterization of a laser induced plasma has been carried out, obtaining the local values of the parameters (temperature and number densities of neutral atoms and ions) which determine the emissivity of any spectral line at each point within the plasma. By the convolution of the emissivity values, synthesized distributions of the line intensities, integrated along the line-of-sight, have been obtained, which are in good agreement with the experimental distributions. Finally, for a set of neutral atom and ion spectral lines, the total intensity emitted by the laser-induced plasma has been synthesized starting from the spatially-resolved parameters. Using the synthesized intensities, Boltzmann plots with high correlation linear fittings have been obtained for neutral atoms and ions, which are in good agreement with experimental plots measured with spatial integration of the plasma. These plots demonstrate the existence of an apparent excitation temperature, different for neutral atoms and ions, resulting from the population-average of the local electronic temperature in the plasma. The results of the present work may explain the different values of temperature obtained in spatially-integrated measurements when using neutral atom and ion lines. The name apparent temperature is in fact more suitable for these different results of spatially-integrated measurements, the word temperature being only strictly applicable to local measurements.

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