Characterization of a high-pressure hydrogen microwave plasma torch using the method of dBR

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Abstract. A hydrogen plasma flame produced by an axial injection torch powered at the microwave frequency of 2.45 GHz is studied using the method of disturbed Bilateral Relations (dBR). The application of this method which relates the influence of equilibrium disturbing, as produced by transport, to equilibrium restoring processes, reveals that the most dominant excitation balance is the Excitation Saturation Balance. Moreover, a global discharge model leads to an electron density of \( n_e = 4.10^{20} \text{m}^{-3} \) and an electron temperature of \( T_e = 0.86 \text{ eV} \). The gas temperature was estimated to be \( T_h = 0.3 \text{ eV} \). The values of \( n_e \) and \( T_e \) were found to be in good agreement with the value obtained with the modified Boltzmann-plot and the crossing method of Stark broadening. The dBR method points out that the first level in partial local Saha equilibrium will be the level with principal quantum number \( p = 10 \) which is in fair agreement with experimental results.

1. Introduction

The Torche à Injection Axiale [1] (TIA, the axial injection torch) is a device designed for the production of plasmas by microwaves at atmospheric pressure. It was found to be robust against the change in gases and apart from the noble gases, Ar or He, it can also be operated with admixtures of molecular gases such as CO\(_2\), O\(_2\) and N\(_2\) [2] in noble gases. Depending on the experimental conditions, such as the shape of the nozzle, it is even possible to drive the TIA on pure molecular gases.

In [3] the new challenge was described to operate the TIA device as a hydrogen discharge. In that setting very rigorous precautions were needed since the hydrogen plasma can react explosively when it comes into contact with the oxygen in the open air. Therefore the plasma was shielded with an outer flow of He.

From the Balmer series we were able to construct a substantial part of the Atomic State Distribution Function ASDF [3]. This was found to be largely out of Saha-Boltzmann equilibrium and ruled by the Excitation Saturation Balance (ESB). This is an improper balance\(^a\) that is often found for plasma (regions) that are strongly ionising. An important part of the ionisation flow is step-wise in nature and the population of an excited state (mainly) originates from the (electron induced) excitation

\(^a\) An improper balance is a balance for which the forward and backward processes are not each others reverse process in the sense of detailed balancing.
of the adjacent lower level while the depopulation (predominantly) leads to the production of the adjacent higher level.

This stepwise excitation flow in the active plasma zone is needed to generate electron-ion (e-i) pairs and to support the efflux of electron-ion (e-i) pairs from this zone to outer plasma regions. This paper is devoted to a further characterization of this microwave induced hydrogen plasma for which we will use the method of disturbed Bilateral Relation. This dBR method, explained in [4,5], aims to find good estimates for the basic plasma properties: like the electron density \( n_e \), the electron temperature \( T_e \), the gas temperature \( T_b \) and the degree of equilibrium departure. The latter is important information since it tells us whether and in which way the ASDF (the occupation of excited levels as a function of excitation energy or effective principal quantum number) can be used to find information of the plasma properties. Thus the method of dBR can serve as a guide for the interpretation of results from diagnostics.

An important parameter for the determination of the degree of equilibrium departure is the Saha-normalized overpopulation

\[
\delta b(p) \equiv b(p) - 1, \quad \text{where} \quad b(p) \equiv \frac{n(p)}{n^S(p)}
\]

equals the density \( n(p) \) of an excited level \( p \) divided by the value \( n^S(p) \) as predicted by the Saha formula. The latter is given by

\[
\eta^S(p) = \frac{n(p)}{g(p)} = \frac{(n_e/2)(n_+/g_+)}{[h^3/(2\pi mkT_e)^{3/2}]} \exp \left( \frac{I_p}{kT_e} \right)
\]

in which \( \eta^S(p) = n(p)/g(p) \) is the number density of an atomic state, that is the number density \( n(p) \) of a level ‘\( p \)’ divided by the statistical weight \( g(p) \); \( n_e \) and \( g_+ \) are the number density and the statistical weight of the ion ground-level respectively. In the case of Hydrogen we have \( g_+(H) = 1 \). The symbol \( I_p \) refers to the ionization potential of the level in question. Levels for which the density obeys equation (2) are said to be in partial Local Saha Equilibrium (pLSE) [6].

Note that the density ratio of two levels \( p \) and \( q \) in pLSE (and both belonging to the same atomic system) is given by the well-known Boltzmann relation

\[
\frac{\eta^S(p)}{\eta^S(q)} = \exp \left( \frac{I_p - I_q}{kT_e} \right)
\]

The Boltzmann exponent is often used as a diagnostic tool. By plotting, in a so-called Boltzmann plot, \( \ln \eta^S(p) \) versus the ionization energy \( I_p \), we get a slope that equals \( 1/kT_e \). However, if the observational part of the ASDF is ruled by the ESB, this method will give erroneous results.

From studies [6] it is known that in that case the ASDF can be described by the power-law

\[
\delta b(p) \propto I^{\alpha/2}
\]

with the \( \alpha \)-value in the interval \( 5<\alpha<6.5 \)

Thus, if \( \delta b(p) >> 1 \) we get for the level occupation \( \eta = \eta^S I^{\alpha/2} \) which implies (cf equation (2)) that \( \eta \propto I^{\alpha/2} \exp \left( I/kT_e \right) \). If this function is plotted in a Boltzmann plot; i.e. \( \ln \eta \) versus \( I \), we find a variable slope temperature that tends towards \( T_{slope} \propto 2I/\alpha \). Thus, approaching the continuum \( (I = 0) \) the ASDF will decrease steeply.

In order to isolate the Boltzmann exponent one should multiply the measured \( \eta \)-value with \( I^{-\alpha/2} \) and plot the resulting \( \ln(\eta I^{-\alpha/2}) \) versus \( I \). Since the value of \( \alpha \) is not known a priori we have to apply a fitting procedure that gives values for both \( T_e \) and \( \alpha \). This so-called modified Boltzmann plot method was used in [3] and the results were found to be in reasonable agreement with those of other techniques.

2. Experimental
**Experimental settings**

The plasma is launched by coupling microwave energy at 2.45 GHz with a power of 600 and 1000 W in a flow of hydrogen gas. The plasma is created in the open atmosphere with implies that the pressure equals $10^5 \text{ Pa}$. The plasma shape is cylindrical with a height of $3 \text{ cm}$ and a diameter of about $2 \text{ mm}$. This leads to volume of $V = 9.5 \times 10^{-8} \text{ m}^3$. In the case of 1000 W, to which we confine ourselves in this study, we thus find an average power density of $\varepsilon = 1.1 \times 10^{10} \text{ W/m}^3$. Based on Thomson scattering measurements on a TIA in Ar [4] we estimate that the gradient length of the electron density equals $A_e = 0.1 \text{ mm}$.

In contrast to the TIA plasma operated in Ar, it was found that the hydrogen plasma is very close to the nozzle and that much heat was produced and transferred to the wave-launching device. The nozzle was eroding quickly which points towards a temperature of 1000 K. The fact that no molecular radiation could be observed in the bulk plasma suggests that the heavy particle temperature in plasma equals at least 3500 K (0.3 eV). Much higher values are not likely due to large heat conductivity of hydrogen.

**Experimental results**

Most of the observations were done in a zone located at 1 mm above the nozzle. There the electron density was measured to be in the order of $10^{20} \text{ m}^{-3}$ and the electron temperature 9500 K. These values were found using the Stark crossings method [7]; which apart from $n_e$ also gives $T_e$. This value of $T_e$ was found to be in good agreement with the value found with the modified Boltzmann method [3].

3. **Global discharge model**

In this section we use the insight and formulas developed in [5, 8] to find estimate values of plasma properties $T_e$ and $n_e$. This method is usually based on the system of three balance equations; the electron particle balance, the electron energy balance and the heavy particle energy balance. The input of this model is formed by the (radial) size $A$ of the plasma, the power density $\varepsilon$ and the pressure $p$. However, the heavy particle energy balance as given in [5, 8] is based on the assumption that the heat transport of the heavy particles is dominated by heat conduction. This assumption is questionable for this case-study since convection and dissociation are expected to be important as well. Therefore we will confine ourselves to the system of two balance equations: the electron particle and energy balance. The temperature of the heavy particles is assumed to be $T_h = 0.3 \text{ eV}$.

*The particle balances for the electrons*, which in a simplified form equates the electron production to the diffuse efflux of electron-ion (e-i) pair leads to an expression for the electron temperature

\[
n_{e_i}K_{\text{ion}}(T_e) = n_eD_a\hat{n}_a^{-2}
\]

so that

\[
K_{\text{ion}}(T_e) = \hat{D}_a/(\hat{n}_a n_e A^2)
\]

where according to [5]

\[
\hat{D}_a = D_a \hat{n}_a = 2/(3 \hat{\sigma}_{\text{iu}}) (kT_h/\pi M)^{1/2} (1 + T_e/T_h) = 5.521 \times 10^3 (\hat{\sigma}_{\text{iu}} A^{1/2})^{-1} F(T_e, T_h)
\]

with $\hat{\sigma}_{\text{iu}}$ the ion-atom cross section for momentum transfer in $10^{-20} \text{ m}^2$, $A$ the ion mass number ( for H, $A = 1$) and $F(T_e, T_h) = \hat{T}_h^{-1/2}(1 + T_e/T_h)$. We recall that $\hat{D}_a$ is the $D_a$ value for $n_a = 10^{20} \text{ m}^{-3}$.

Taking for the ion-atom cross section $\sigma_{\text{iu}} = 3.5 \times 10^{-18} \text{ m}^2$ from [9] ($\hat{\sigma}_{\text{iu}} = 350$), $\hat{T}_h = 0.3$ and $T_e/T_h = 2$, so that $F(T_e, T_h) = 1.64$, we find $\hat{D}_a = 25.9 \text{ m}^2/\text{s}$.
The rate $K_{\text{ion}}(T_e)$ is effective ionization rate. Apart from the direct process $I \rightarrow +$ it also accounts for the contribution of step-wise processes $I \rightarrow 2 \rightarrow 3 \rightarrow 4$ etc. It can be written as [5]

$$K_{\text{ion}} = C_i (H) [8kT_e/(\pi a)]^{1/2} [4\pi a^2] (R/I*)^2 \exp (-I^*/kT_e) \tag{7}$$

Or numerically

$$K_{\text{ion}} = k_i C_i(H) (R/I*)^2 \hat{T}_e^{0.5} \exp (-I^*/kT_e) \quad \text{with} \quad k_i = 2.35 \times 10^{14} \text{ m}^3\text{s}^{-1}\text{eV}^{-0.5} \tag{8}$$

where $\hat{T}_e$ is the electron temperature in eV while the symbol $I^*$ stands for the effective ionization potential. By adjusting equation (7) to the results found in [10] we find $I^* = 10.2 \text{ eV}$ (so that $R/I^* = 1.33$) and $C_i(H)=0.258$. Inserting equations (6) and (8) into equation (5) gives

$$854.0 \hat{T}_e^{5.0} = -\epsilon \ln\frac{\hat{T}_e}{\hat{T}_h}$$

where $\hat{n}_1 = (2 \times 10^4)$, and $\hat{D}_a(0.1)$ are the neutral ground state number density and the diffusion length in units of $10^{20} \text{ m}^{-3}$ and mm. Inserting these values together with $C_i(H)=0.258$ and $\hat{D}_a = 25.9 \text{ m}^2\text{s}^{-1}$ into equation (9) gives a $T_e$-value of 0.86 eV. This is in good agreement with the experimental results.

The energy balance for the electrons in simplified form reads (cf. [5])

$$\epsilon = n_e n_1 K_{\text{heat}} (kT_e - kT_h) + n_e n_1 K_{\text{crea}} (I + 3/2 kT_e) \tag{10}$$

showing that power density $\epsilon = P/V_{\text{act}}$ ($P$ is the power and $V_{\text{act}}$ the volume of the active plasma zone) is divided over two channels; the heat channel and the plasma creation channel.

In the heat channel kinetic energy is transferred from the electrons to the heavy particles (by means of elastic collisions) whereas the plasma creation channel conducts the energy flow associated with excitation and ionization (thus inelastic) processes. The rate of heat exchange is given by

$$K_{\text{heat}} = 3 (m/\lambda) K_{\text{mom}}$$

with $K_{\text{mom}} = \sigma_{\text{eh}} [8kT_e/(\pi a)]^{1/2} \tag{11}$

the rate for momentum transfer between electrons and heavy particles for which we assume that it can be approximated by the product of the (average) electron-atom cross section and the thermal velocity of the electrons. The rate of inelastic collisions $K_{\text{crea}}$ can in this case-study be replaced by $K_{\text{ion}}$ (cf. equation (7)).

The power density corresponding to the creation branch can be estimated using equation (8) which together with a $n_e$-value of $5 \times 10^{20} \text{ m}^{-3}$, $n_1 = 2 \times 10^{24}$ and $T_e = 0.86 \text{ eV}$ gives a power density of $\epsilon_{\text{crea}} = 3 \times 10^8 \text{ Wm}^{-3}$, which is less than 3% of the power density of the energy coupling. So that we have to conclude that the heat channel is dominant. Thus the electron density can be found via

$$n_e = \epsilon [n_1 K_{\text{heat}} (kT_e - kT_h)]^{1/4} \tag{11}$$

Inserting the values $\epsilon = 1.1 \times 10^{10} \text{ Wm}^{-3}$, $T_e = 0.86 \text{ eV}$, $T_h = 0.3 \text{ eV}$ and $K_{\text{heat}} = 2.66 \times 10^{16} \text{ m}^3\text{s}^{-1}$ we find a $n_e$-value of about $3.6 \times 10^{20} \text{ m}^{-3}$. To calculate $K_{\text{heat}}$ we took the $\sigma_{\text{eh}}$-value from [11]. Note that the rate
coefficient for momentum transfer is based on the assumption that electron atom (e-H) collisions dominate. If the molecules are involved this can increase the \( K_{\text{heat}} \). This will lead to lower \( n_e \)-values.

**Concluding:** based on the experimental settings and the assumption that the heavy particle temperature equals \( T_h = 0.3 \) eV we have found with the global model the following plasma parameters \( n_e = 3.6 \times 10^{20} \) m\(^{-3}\) and \( T_e = 0.86 \) eV.

4. **The state of equilibrium departure**

With the values of the plasma parameters found in the previous section we can determine the values of the equilibrium-departure parameters. First of all we will estimate the influence of the escape of radiation. For this we use equation (9) of [5] which gives the number of radiative decay processes per collisional lifetime

\[
[V_{\text{rot}}, \tau_{\text{rot}}]^B(p) = \frac{A^*(p)}{n_e K(p)} = 10^{23} \frac{\hat{T}_e}{(\hat{T}_e + 2)} \frac{0.5}{p^9 n_e^{-1} Z^2}
\]  

where \( A^*(p) \) and \( n_e K(p) \) are respectively the total probability of radiative and collisional depopulation, \( \hat{T}_e \) is the electron temperature in eV, \( Z \) the charge number of the core (for Hydrogen \( Z = 1 \)) and \( p \) the (effective) quantum number given by

\[
p = Z(Ry/I_p)^{1/2}
\]

The level \( p_{cr} \) on the boundary between the radiative and collisional part of the ASDF is defined as the level for which \( (\nu \tau) \) equals unity; thus \( [V_{\text{rot}}, \tau_{\text{rot}}]^B(p_{cr}) = 1 \).

Inserting \( n_e = 3.6 \times 10^{20} \) m\(^{-3}\) and \( \hat{T}_e = 0.86 \) we find that \( p_{cr} = 2.1 \). Using equation (12) for \( p = 3 \) we find that \( [V_{\text{rot}}, \tau_{\text{rot}}]^B(p = 3) = 0.04 \) so that we may assume that the levels \( p \geq 3 \) are in ESB. However, as the Lyman radiation is absorbed substantially, reducing the effective radiative decay probability of level \( p = 2 \), we can conclude that the whole system is fully collisional; thus, the escape of radiation will not affect the ASDF.

This might suggest that the ASDF will follow the Saha-Boltzmann law equation. (2) and that its slope can be used to determine the electron temperature. However, as explained in [5] there can be other transport processes disturbing the ASDF such as the escape of e-i pairs. Therefore we will compute the ground state overpopulation \( \delta b_1 \) using the following expression ([5])

\[
\delta b(1) = [V, \pi]^F(1) = 1.30 \times 10^7 C_{b} \hat{D}_a \left( \hat{n}_a^n \hat{n}_e^2 \hat{\Lambda}_e \right)^{1/2} \hat{T}_e^{3/2} \exp(-I_2^*/kT_e),
\]

where \( I_2^* = I^* - I_1 \) and \( C_{b}(S) = (2g_e/g_i) C_{d}(S)^{-1} (I^*/R)^j \) while \( \hat{n}_a, \hat{n}_e, \hat{\Lambda}_e \) is given in mm. Inserting \( C_{b}(H) = 0.258, \hat{D}_a = 25.9, \hat{n}_e = 3.6, \hat{n}_h = 2 \times 10^4, \hat{\Lambda}_e = 0.1 \) and \( \hat{T}_e \exp(-I_2^*/kT_e) = 0.8 \) gives a values of \( \delta b_1 = 2.3 \times 10^5 \). The atomic ground state is thus highly overpopulated with respect to Saha, which implies that the atomic H system is largely ionising. This overpopulation will propagate to higher levels and gives shape to the ESB part of the ASDF. During its propagation the Saha-overpopulation will decrease in a way given by the equation [5]

\[
\delta b(p) = [V, \pi]^F(p) = 1.20 \times 10^7 \hat{D}_a \left( \hat{n}_e^2 \hat{\Lambda}_e \hat{n}_h \right)^{1/2} \hat{T}_e \exp(-I_{p+1}/kT_e)
\]
The boundary between ESB and the pLSE part of the system is defined as the level \(p_{ES}\) for which \(\delta b(p) = 1\). Inserting the values \(\hat{D}_a = 25.9\), \(\hat{n}_e = 3.6\), \(\hat{n}_h = 2 \times 10^4\) and \(\hat{\Lambda}_e = 0.1\) we find that \(p_{ES} = 6.8\). So that up level to about \(p = 7\) the ESB is firmly present. The level first level in full pLSE is defined as the level for which \(\delta b(p) = 0.1\). Using equation (15) we find that the first level in pLSE is \(p = 10\).

In [3] we presented the measured ASDF and found that the ESB is firmly present up till \(p = 9\), which suggests that the departure form equilibrium is larger than what is calculated here. This might be a consequence of the fact that, in reality, apart from diffusion also convection removes e-i pairs out of the plasma which will extend the ESB to higher energy levels. The precise influence of convection is a subject for further study.

5. Conclusion and recommendations
The global discharge model formed by the electron particles and energy balance give values of the electron density and temperature that are in reasonable agreement with experimental results. If these are used in the equations from the equilibrium departure we find that the ASDF is not influenced by the escape of radiation and that the ESB extends towards the level \(p = 7\). This implies that most of the observable lines are emitted by the ESB part of the H-system. Therefore it is not allowed to treat the ASDF in a Boltzmann-Saha plot as if it were an equilibrium function. However, results of the modified Boltzmann plot are expected to be valid. This latter was done in [3] and the value of \(T_e\) found in this way was in agreement with the Stark crossing method and the value calculated in this study.

It is recommended to investigate in the future the role of convection and to construct the modified Boltzmann plot in absolute form. The latter will provide, apart from the electron temperature, an independent value of the electron density. To that end we need absolute line intensity measurements.

Acknowledgments
This work was supported by the Bulgarian National Fund for Scientific Research under Grant F-1401/2004 and by the Fund for Research of Sofia University under Grant 124/2005. One of the authors (E. I.) would like to thank the University of Eindhoven, the Netherlands for the possibility to work there for several months.

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