Polydiagnostics performed on high-tech plasmas

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Abstract. The large effluxes generated by high-tech plasmas force plasmas to non-equilibrium conditions. This implies that plasma features are decoupled from each other and that therefore different methods have to be used quasi-simultaneously to characterize the plasma. Even more insight in plasmas and methods is obtained if polydiagnostics is applied to a series of plasma conditions that gradually differ in equilibrium departure. After discussing methods of passive and active spectroscopy, we apply polydiagnostics on an argon plasma operated in open air. By introducing H₂ and reducing the power we approach conditions of cool atmospheric plasmas (CAPs). It is seen that especially the passive methods for the electron temperature determination are very sensitive to the degree of equilibrium departure suggesting that active spectroscopy is preferable. However, one should realize that lasers can easily heat cool plasmas. This is due to the fact that the ionization degree of (semi-) CAPs is small.

Key words: polydiagnostics • high-tech plasmas • passive methods • active methods

Introduction

The increasing success of high-tech plasma applications is based on the fact that plasmas produce large effluxes of photons and radicals. These are directed to application zones where they are used for the treatment of surfaces or volumes [12, 16]. However, generating large effluxes drives the plasma to non-equilibrium conditions; since transport will disturb the plasma balances of forward and corresponding backward processes [21]. The larger the effluxes are the larger the equilibrium-departure will be and the more the laws of classical statistical mechanics, ruled by the Boltzmann exponent \(\exp(-E/k_B T)\), will lose validity.

A method often found to characterize non-equilibrium plasma conditions is to employ several new temperature-types. So, one can find expressions like \(T_e > T_{\text{ion}} > T_{\text{ex}} > T_{\text{rot}} > T_{\text{tot}}\) showing that the electron temperature is larger than the temperature associated to ionization, excitation, vibration and rotation. One might wonder what the use of such a chain of inequalities is. Even if the temperature-values are given we remain with the question of the factual meaning of entities like \(T_e\) or \(T_{\text{tot}}\). A thermodynamic meaning in the sense of representing the mean energy of a certain particle-type is and can seldom be given. Nevertheless,

\[\text{with high-tech we refer to modern plasmas, i.e. plasmas used in the most advanced technology currently available.}\]
this temperature inequality chain clearly shows that various plasma properties are decoupled; that is to say more or less independent of each other.

A more precise characterization of high-tech plasmas demands, apart from temperatures values, also the determination of the flux and number densities of active species. The best way to do that is by employing several different experimental techniques quasi-simultaneously. This polydiagnostic approach is needed since the departure from equilibrium makes different plasma aspects more independent, while the determination of independent plasma parameters in general asks for different techniques. Another reason is, that working on the edge of validity regimes, demands for a cross validation of different methods. Especially experimental methods based on equilibrium assumptions (like Boltzmann plots) will lose validity.

In this study we deal with passive and active spectroscopic methods and we will discuss how they perform as a function of equilibrium departure. Passive spectroscopy, also known as optical emission spectroscopy (OES), has the advantage that only the light produced by the plasma is analysed. So, in contrast to, for instance, electrical probe measurements the method is non-intrusive. The experiments are easy to perform but the interpretation of line and continuum radiation in terms of the main plasma properties is far from simple. Moreover, since OES methods are based on line-of-sight observations, we need inversion methods to get space resolved information.

The laser scatter techniques of Thomson (TS), Rayleigh (Rys) and Raman scattering (RnS), so-called active spectroscopic techniques, allow the simultaneous determination of the electron density $n_e$, electron temperature $T_e$ and gas temperature $T_{\text{gas}}$. These methods, based on the scattering of laser photons by free and bound electrons, can be considered as direct techniques; meaning that the interpretation of signals created by TS, RnS and RyS does not depend (much) on the state of equilibrium-departure. Another advantage is that laser scattering techniques give plasma quantities with high spatial and temporal resolution. However, laser techniques are experimentally demanding and expensive. Moreover, care should be taken with the laser power; laser-plasma heating or even worse, laser-plasma creation, must be avoided.

We will compare the results of passive methods with each other and with those of the active group. The disagreement between the method-results can in many cases be attributed to the state of equilibrium departure. In this way polydiagnostics not only gives insight into the methods but also into the plasma. Special attention will be paid to discharges in open air and we will investigate how the experimental cross-validation will change as a function of power density and molecular loading. For low power densities, we will enter the regime of cool atmospheric plasmas (CAPs). These plasmas are popular nowadays because they are easy to operate. However, as we will show; they are not easy to characterize. The low power density and associated low electron densities will drive diagnostics to (and over) the edge of validity regimes. The low gas temperature (the plasma is "cool") will introduce molecule-like processes like van der Waals broadening and excimer formation. Moreover, the electron-atom (ea) interaction during laser scatter techniques will obscure the results of TS.

Experimental setup and techniques

The setup

Figure 1 gives a sketch of the setup used in our study showing diagnostics gathered around an atmospheric surface-wave induced plasma (SIP). This plasma, a semi-CAP, was studied in [14] were we changed the power density and introduced molecules in order to reach CAP conditions. This polydiagnostic setup is constructed in such a way that other techniques can be added while the plasma source can be replaced easily by

![Fig. 1. Schematic view of the setup showing the plasma source (here an atmospheric suratron), the laser, the active detection branch (TGS), and the passive detection branch (spectrometer). Note that the passive and active branches are not used simultaneously.](image-url)
other plasma sources. For instance, in order to investigate how far plasma features depend on air entrainment or pressure we perform the measurements on another plasma source like a low-pressure SIP.

Passive spectroscopy

In this study, the OES methods consist of the measurement of line-broadening of the Hα line and absolute intensity measurements (AIM). The latter can be divided into absolute continuum and line intensity. In both cases the radiation is collected by a monochromator, while the intensities were calibrated using a tungsten ribbon lamp. For a more precise description of the methods, we refer to [5, 11].

Active spectroscopy

For the laser scattering techniques frequency doubled Nd:YAG lasers were used. The laser photons are (partially) scattered on either bound or free electrons, which creates respectively Rayleigh- and Thomson-scattered photons. The RyS along with a false stray light created by the scattering of the laser beam on nearby solid surfaces can be filtered out. For this purpose, we use a triple grating spectrograph (TGS) in which the combination of the two first gratings together with an intermediate mask forms a notch filter for the spectral range of 552 ± 0.2 nm. Only the spectrally broader signals of TS and RnS can pass this filter [18]. After the subsequent dispersion by the third grating, the photons are collected by an intensified-CCD camera (Andor iStar743). For more details, see, for instance, [14, 15, 22].

In TS the number of scattered photons is directly proportional to \( n_e \); the calibration is obtained via RnS. On the other hand the Doppler broadening of the scattered photons gives an insight in the electron energy distribution, and therewith \( T_e \). By removing the mask in the notch filter, we can use the same detection system to determine RyS. Ergo, the system can get quasi simultaneously \( n_e, T_e \) and \( T_{gas} \). To unravel the RnS scattering on entrained air molecules from TS on electrons a fitting procedure needs to be employed. For this method, we refer to [22].

Experimental methods; features and pitfalls

Passive spectroscopy

Absolute line intensity (ALI) measurements

Figure 2 shows part of the argon atomic state distribution function (ASDF) of the semi-CAP described in Ref. [14]. It is constructed by combining the results of ALI measurements performed on several transitions together with the ground state density \( n_1 \) determined via the ideal gas law \( p = n_r k_u T_e \). In the same study we found \( n_1 \)-values in the range of \( 10^{12} \) m\(^{-3}\). For such reasonable high \( n_1 \)-values, one can neglect the impact of radiation-escape on the ASDF. The electron-induced processes are frequent enough to compensate for the corresponding radiation-transport losses. This dominance of e-collision over radiative decay is often regarded as a justification to assume the presence of local thermodynamic equilibrium (LTE). However, the plasma being small in size will generate large effuxes of ei-pairs; and these will affect the ASDF inducing a variable shape. So, although e-collisions are dominant over radiative decay the plasma can be far from LTE in the sense that the ASDF strongly deviates from the equilibrium shape as prescribed by the Saha-Boltzmann equation.

The shape of the ASDF shown in Fig. 2, with its variable slope, is typical of ionizing plasmas. These are plasmas, or active plasma zones, in which the continuous loss of ei-pairs demands for (step-wise) ionization processes in order to guarantee a (quasi) steady plasma operation. Other examples of ionizing plasmas are those formed under low pressure conditions [5, 8]; the corresponding ASDF differs in absolute value, but has more or less the same shape. By means of an analytic collisional radiative model (CRM) based on hydrogen-like cross sections for \( e \)-induced transitions one can show that the ASDF slope at the location \( p \) in excitation space mainly depends on the ionization potential \( I_p \) of that location [19, 20].

\[
k_u T_{slope} \approx I_p / 3
\]

Although the ladder-climbing stepwise ionization is driven by electron collisions we see that the temperature in the above equation has no thermodynamic meaning; it does not depend on the mean electron energy.

In Fig. 2 we indeed see that the slope changes drastically, the more we approach the continuum the steeper...
the slope will be. This results from the fact that the flux in excitation space, preparing the creation of ei-pairs, is spread out over a diverging density of states\(^8\) whereas the cross section for excitation increases\(^8\) drastically.

In [1, 7] we presented a CRM dedicated to Ar with an analytical H-like top and a numerical bottom. In [5, 11] this CRM is employed to deduce the electron temperature \(T_e\) from the lower part of the ASDF. It basically is a two-step approach. In the first step the density per statistical weight \(n(3) = n(3)/g(3)\) of the \(4\)\(p\) levels, by short level “3”, and the \(\eta\) value of the ground state, level “1”, delivered by the pressure \(p = n_k T_{gas}\) are used to compute the temperature \(T_{13}\). In the second step we employ a CRM to convert \(T_{13}\) into \(T_e\).

We stress the fact that the density of the ground state cannot be obtained by OES; its absolute value is deduced from the pressure. Therefore, we have to determine the density of \(n(3)\) in absolute way as well; the method of relative intensities does not lead to useful results.

In the conversion of \(T_{13}\) into \(T_e\), where the CRM is employed, we need a value of \(n_e\). This can be obtained from the absolute continuum intensity (ACI) measurements; see next section.

It should be mentioned that the use of CRMs for the determination of plasma parameters can be done in different ways, see, e.g. [10]. In [25] methods are given to get information on the structure of the electron energy distribution function EEDF.

**Absolute continuum intensity (ACI) measurements**

The above shows that temperatures derived from slopes of distribution functions or intensity ratios should be handled with care. This also holds for the classical method of \(T_e\)-determination using line/continuum ratios. This method can be used for plasmas in, or close to LTE. However, in ionizing plasma in which the density of the ions is pressed down, whereas the bottom part of the ASDF is pushed up (see Fig. 2) we can no longer expect reliable \(T_e\)-values. On the other hand we might expect the influence of the continuum generated in electron-atom (ea) interactions. This will be studied below.

The local source of continuum radiation is determined by the spectral emission coefficient \(j\_s(\lambda)\) that can be obtained experimentally from the spectral intensity \(I\_s(\lambda)\) and the size \(D\) of the plasma along the line of sight. The size \(D\) can be obtained by estimation or by means of an Abel inversion procedure. Theoretically, \(j\_s(\lambda)\) is composed of three contributions:

\[
(2) \quad j\_s(\lambda) = j\_s\^e\_b(\lambda) + j\_s\^e\_f(\lambda) + j\_s\^e\_n(\lambda)
\]

Here \(j\_s\^e\_b(\lambda)\) represents the radiation generated during electron-ion (ei) recombination, \(j\_s\^e\_f(\lambda)\) the free-free ei bremsstrahlung and \(j\_s\^e\_n(\lambda)\) the free-free radiation created by ea-interactions. The two ei contributions can be taken together [9] as

\[
(3) \quad j\_s\^e\(\lambda\) = j\_s\^e\_b(\lambda) + j\_s\^e\_f(\lambda) = j\_s\^e(\lambda) = n\_e^2 f(\lambda, T_e)
\]

where we assumed that \(n\_ion = n\_e\) and introduced \(f(\lambda, T_e)\). Defining \(g(\lambda, T_e)\) such that

\[
(4) \quad j\_s\^e\_n(\lambda) = n\_e n\_i g(\lambda, T_e)
\]

we get, combining Eqs. (3) and (4) for the electron density the expression

\[
(5) \quad n\_e = n\_e g(2 f\_e)^{-1} \cdot \{1 + 4 j\_s\^e\(\lambda\) / (n\_e g\_e)^2\}^{1/2} - 1
\]

where \(j\_s\^e\(\lambda\) = I\_s(\lambda)/D\) is the measured value of the emission coefficient.

The cross sections for ei-interactions are, in general, much larger than those for ea-interactions. This implies that \(f\_e >> g\_e\) and suggests that ea radiation can be neglected. However, for the plasmas under study the low ionization factor \(\alpha = n\_i/n\_e\) will favour ea-over ei-continuum. A critical ionization degree for 532 nm is given by the expression

\[
(6) \quad \alpha\_cont = g/f \approx 0.012 T_e^{-0.027} T_e^{2} + 0.023 T_e^{-0.007}
\]

for the \(T_e\) range 0.6 < \(T_e\) < 3 eV. For \(\alpha < \alpha\_cont\), the ea interactions will rule the continuum. This is opposite to what is found in classical, that is LTE-like plasmas, such as arcs, shock tubes or astrophysical plasmas.

The values of \(f\_s(\lambda, T_e)\) and \(g(\lambda, T_e)\) depending on \(T_e\) have to be determined via ALI (section ‘Absolute line intensity’). For the expressions of \(f\_s(\lambda, T_e)\) and \(g(\lambda, T_e)\) and their \(T_e\) dependence, we refer to [9].

The AIM-method in which ALI and ACI are treated in an iterative way giving \(n\_e\) and \(T_e\) was described and applied to a TIA plasma in [11]. In [8] it was used for plasmas created by a coaxial wave-guide. This AIM method can be applied to other plasma sources as well. If the plasmas are created in a different gas, e.g. He instead of Ar, one must change the functions \(f\_s(\lambda, T_e)\) and \(g(\lambda, T_e)\) and their \(T_e\) dependence, we refer to [9].

**Line broadening methods**

The AIM method presented above gives values of the basic plasma parameters \(n\_e\) and \(T_e\) with the advantage that the method is non-intrusive. One of the disadvantages is that absolute measurements have to be performed, meaning that the plasma radiation has to be calibrated with a standard light source. Most experimentalists find this cumbersome and prefer to work with relative instead of absolute intensities. However, this comes with the price that the plasma characterization loses validity.

If plasma parameters can be determined by line-shapes instead of intensities one can skip the calibration procedure. A well-known example is the Stark broadening of the H\(\alpha\) line. It provides a reliable method to determine \(n\_e\) since the broadening, \(\Delta\_L\), is (almost) independent of other plasma parameters such as \(T_e\). Other lines of the Balmer series, for instance H\(\alpha\), are
known to depend not only on \(n_e\) but also on \(T_e\); in short \(\Delta\lambda = \Delta\lambda(n_e, T_e)\). This means that a measured \(\Delta\lambda\)-value represents a curve in \((n_e, T_e)\) space. By measuring the broadening of two Balmer lines, for instance \(\Delta\lambda_1\) and \(\Delta\lambda_2\), we get two curves in \((n_e, T_e)\) space and the intersection determines a pair of \(n_e\)- and \(T_e\)-values.

This Stark intersection method (SIM) was successfully applied to argon plasmas created by the TIA [17]. However, the method fails for cooler plasmas. One of the reasons is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening. What remains valid for a large range of conditions is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening. What remains valid for a large range of conditions is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening. What remains valid for a large range of conditions is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening. What remains valid for a large range of conditions is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening. What remains valid for a large range of conditions is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening. What remains valid for a large range of conditions is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening. What remains valid for a large range of conditions is that in CAPs the (atom) density is extra high. This favours van der Waals broadening that might compete with, or even dominate over Stark broadening.
stochastic motions, thus heat, if electrons collide during these oscillations. The amount of heat generated in this way depends on the laser energy \( E \), the cross section \( \sigma \) of the laser beam and the rate of the electron collisions with heavy particles. The formulas for laser heating given in the literature are almost exclusively based on ei-collisions. However, in CAPs where the neutral density is high, we find that ea-interactions are much more important. Compared to the classical ei-induced heating we get an enhancement of \( (n_e k_{ea})/(n_a k_{ei}) \), where \( k_{ea}/k_{ei} \) stands for the rate coefficient for momentum transfer from electrons to atoms (ions). For CAPs, this factor \( (n_e k_{ea})/(n_a k_{ei}) \) can easily amount to \( 10^2 \). From this, we can obtain a critical ionization degree below which the ea induced heating is more important than the ei contribution [2].

\[
(8) \quad \alpha_{crit} = \frac{k_{ea}/k_{ei}}{3.4 \cdot 10^{-3}(T_e^{5/2})(1 + 6.4 T_e + 14.2 T_e^2)}
\]

where \( T_e \) is expressed in eV. This form of Ohmic heating is also known as inverse bremsstrahlung (IB) and the fact that for CAPs the heating due to ea-interactions dominates over that created by ei-interactions and is closely related to the dominance of the ea continuum treated in section 'Absolute line intensity (ALI) measurements'.

The increase of the \( T_e \) due to the laser action can be controlled by tuning the laser power. Calculations and experiments show that for the semi-CAPs under study the laser fluency \( \Phi = \Phi/\Phi_0 \) should not exceed \( 10^5 \) J/m², a value that corresponds to a pulse energy of only 10 mJ focused on a focal area of \( 10^{-3} \) mm². This fluency is small in comparison to what is usually used in LIF, TALIF and TS experiments. So, care must be taken in the interpretation of the corresponding results.

**Polydiagnostic comparison**

The methods treated in classical sections can be used to investigate several types of plasmas. Most insight in the methods and plasmas is obtained if measurements are performed (quasi) simultaneously. In [3] we performed polydiagnostics on an inductively coupled plasma; in [4, 13] such a study is reported for a low pressure SIP. In this section we initially follow [14] in a polydiagnostic study performed on a semi-CAP in which CAP conditions are approached step-by-step. To that end the semi-CAP was subjected to three plasmas conditions A, B, C. In case A the plasma is generated by coupling 74 W to a pure argon flow. In case B and C we applied 88 W and 57 W, respectively to an argon flow at which 0.3% of H₂ was admixed. For all three settings, the plasma was observed at a 1 mm distance from the origin of the torch. The sequence A → B → C is that of approaching CAP conditions; i.e. the gas temperature decreases.

**Polydiagnostics for the \( n_e \) determination**

Figure 4a shows the \( n_e \) results for the three different methods: Thomson scattering (TS), absolute continuum intensity (ACI) measurements and H₂ Stark broadening. The agreement is good; all methods show the same decrease in \( n_e \) while approaching CAP conditions. By approaching CAP conditions even further and performing polydiagnostics at each stage it is possible to extend the \( n_e \) method to \( n_e \)-values below those for which theoretical methods are available. This is the aim of [13].

**Polydiagnostics for the \( T_e \) determination**

Figure 4b, giving the results of the \( T_e \)-values obtained with TS and ALI, shows a reasonable agreement for A and B, but a disagreement for case C. Approaching CAP conditions apparently induces an increase in \( T_e(TS) \), whereas \( T_e(ALI) \) remains more or less constant. A subsequent study [23] on the same semi-CAP shows that the \( T_e(TS) \) also increases for increasing \( z \)-values; i.e. distances to the launcher. Since one of the reasons for the discrepancy \( T_e(TS) > T_e(ALI) \) might lay in a possible destruction of excited Ar levels by (entrained) molecules we studied pure Ar plasmas; thus isolated from the environment. To that end argon SIPs were used operating at lower pressures in the range of 6–20 mbar. The TS and ALI measurements were done as a function of axial positions. In comparing the results of three studies: 1) the semi-CAP at the fixed \( z \)-value following A → B → C, 2) the semi-CAP for different \( z \)-values and 3) intermediate pressure SIPs for different axial positions we found the same trend: the \( T_e(TS) \) increases if the ionization ratio \( \alpha = n_i/n_e \) decreases; whereas \( T_e(ALI) \) remains more or less constant.

![Fig. 4](image_url)

For the three conditions A, B, and C we show left \( n_e \) obtained by the three different methods given in the legenda; and right \( T_e \) delivered by two methods.
The understanding of this trend in which \( \alpha \) again plays a key role can best be studied by applying the electron particle balance (EPB) to the findings in experiment 3. This EPB reading

\[
(9) \quad n_e n_i k_{\text{ion}}(T_e) = -\nabla (D_{\text{amb}} \nabla n_e) = D_{\text{amb}} n_e R^{n-2}
\]

states that the diffusive efflux of ei-pairs has to be delivered by effective ionization. Here \( k_{\text{ion}}(T_e) \) stands for the effective ionization rate coefficient, while \( D_{\text{amb}} \) is the ambipolar diffusion coefficient. In the last equation-member we replaced the double action of the \( \nabla \) operator by \( R^{n-2} \), that is the square of the effective discharge radius. The EPB sets a strict demand for \( T_e \), due to the strong dependence of \( k_{\text{ion}}(T_e) \) on \( T_e \) and it is clear that steeper gradients (small \( R^{n-2} \)-values) and higher diffusion coefficients demand for higher \( T_e \)-values; these are needed for the higher ei-pair creation demands to sustain larger effluxes.

In conditions of relatively high \( \alpha \)-values we found good agreements between the \( T_e \)-values measured by ALI and TS [4] and the \( T_e \) demanded by EPB based on a Maxwellian \( k_{\text{ion}} \) hereafter shortly by the Maxwellian-electron balance (ePB). However, for low \( \alpha \)-values a discrepancy is found between the Maxwellian EPB and ALI on the one hand and TS on the other hand.

This dependence on \( \alpha \) points towards the study reported [20] where it was found that \( \alpha \) plays an important role in the criterion for the presence of Maxwell equilibrium. This equilibrium is present provided that

\[
(10) \quad \alpha >> \alpha_{\text{crit}}^{\text{max}} \quad \text{with} \quad \alpha_{\text{crit}}^{\text{max}} = C(S) (2 \ln \alpha_e)^{-1} (k_{a} T_e/E_{12})^{-1}
\]

In the case of argon we have \( C(\text{Ar}) = 0.3 \) and \( E_{12} = 12 \) eV. Inserting for the Coulomb logarithm \( \ln \alpha_e = 7 \) and \( k_{a} = 1.2 \) eV we find that \( \alpha_{\text{crit}}^{\text{max}} = 2 \times 10^{-4} \). Inspecting Fig. 4 where we find for condition C typically \( n_e = 2.5 \times 10^{20} \text{m}^{-3} \), whereas \( T_e = 1400 \text{K} \) and \( \alpha = n_i T_e/k_{\text{ion}} \) = 1 bar gives a gas density \( n_i = 5 \times 10^{24} \text{m}^{-3} \) so that \( \alpha = 5 \times 10^{-5} \). Thus the criterion given in Eq. (10) is not fulfilled, meaning that departures from a Maxwell EEDF can be expected. The Coulomb collisions between electrons are not able to compete with the loss of high energy electrons as demanded by a Maxwellian rate. This leads to an EEDF with a broken tail.

The statements given above that EPB puts a demand on \( T_e \) need some refinement: for a Maxwellian EEDF the EPB dictates the \( T_e \) value, such that large ei effuxes demand for high \( T_e \) values; however, for a non-Maxwellian EEDF with a broken tail an even higher \( T_e \) (better: mean energy) is demanded since a tail-depleted EEDF needs a higher mean energy to generate the same ei-pairs creation. Since \( T_{\text{e}} \) (TS) probes the bulk (the mean energy) it will go up.

The fact \( T_{\text{e}}(\text{ALI}) \) does not change (much) for decreasing \( \alpha \)-values suggests that \( T_{\text{e}}(\text{ALI}) \) probes the effux; i.e. it is directly connected to the last member of Eq. (9) which does not change if we increase the axial position. The radius and diffusion coefficient remain unaltered. So, \( T_{\text{e}}(\text{ALI}) \) probes the creation of ei-pairs and can best be denoted by the creation temperature.

The relation with the line intensity of the 4p level can be understood better by realizing that the ionization is mainly stepwise with the level block 4p as important intermediate station. Therefore, the 4p radiation, and thus \( T_{\text{10}} \), probes the ionization flux in excitation space and thus the ei-pair creation. So, concluding \( T_{\text{e}}(\text{TS}) = T_{\text{bulk}} \) and \( T_{\text{e}}(\text{ALI}) = T_{\text{creation}} \): in high \( \alpha \)-values, under Maxwell equilibrium, these temperatures are the same. Low \( \alpha \)-values force \( T_{\text{bulk}} \) upward, whereas \( T_{\text{creation}} \) remains (almost) the same.

**Approaching CAP conditions more closely**

In Ref. [14] we could reach semi-CAP conditions with central gas temperatures of around 1400 K. This is relatively low, but still too high for soft surface treatment such as wound healing. On the contrary, by personal experience we found that the semi-CAP is more suitable for wound creation than for wound healing: real CAP conditions were not reached. Nevertheless, the trends observed in the study of gradual approach can be extended to predict what happens at further cooling. This will be discussed using the following schematic energy flow

\[ \{\text{EM}\} \rightarrow \{\text{e}\} \rightarrow \{\text{h}\} \rightarrow \{\text{elast}\} \rightarrow \text{radicals} \rightarrow \text{inelastic} \]

showing that electrons heated by the electromagnetic field will use part of their energy in the elastic branch for the heating of heavy particles (\{h\}) and part for the creation of radicals (\{h*\}) in the inelastic branch. If the power density is reduced or if the \{h*\} branch is enhanced due to the introduction of molecules, we can expect that the electron density goes down. This is associated with a reduction of \( T_e \) and thus with an increase of the gas density \( n_e \). This will favour the ea-over the ei-continuum and facilitate laser-plasma heating. Another consequence of the corresponding decrease in \( \alpha \) is a further depletion of the EEDF tail. This means that the \( T_{\text{e}}(\text{TS}) \) (the bulk temperature) must go up. The performance and interpretation of TS will be obscured since a low \( n_e \) implies that we approach (or exceed) the TS detection limit since the weak (low \( n_e \) and broad (high \( T_e \)) signal will be embedded in a large ea continuum. Applying high laser powers is not an option since that will induce laser heating.

So, active spectroscopy on CAPs will be difficult and the solution is to extend polydiagnostics in gradual approach as far as possible. In such a study we need to calibrate OES step-by-step and employ for TS a high rep-rate laser producing low energy pulses of short duration. The former is needed to avoid laser heating the latter since the smaller the measurement-time the less we are hindered by plasma light.

**Summary and conclusions**

The application of emission spectroscopy deducing temperatures from relative intensities, using a Boltzmann plot, does not give insight. More information is obtained if absolute intensities of the line and continuum emission are combined. A better solution is to use laser aided diagnostics, but then we have to avoid laser heating of the plasma. The best is to combine various methods.
and to perform polydiagnostics for a series of plasma conditions for which equilibrium departure is changed gradually.

We started the study by a discussion of the pros and cons of three passive methods. Stark broadening and the absolute intensity measurements (AIM) of the continuum (ACI) and line emission (ALI). After that, we discussed Thomson scattering (TS). Special attention was paid to the nature of the electron temperature as determined by TS and the danger of plasma laser heating. A mechanism that is often overlooked for plasmas with low degree of ionization.

Equipped with the background knowledge of the various methods we performed a gradual polydiagnostic approach study with a semi-CAP moving toward CAP conditions by reducing the power and adding H₂ molecules. Comparing the results approaching CAP conditions gave an insight in the validity of the various methods and in the plasmas in question.

For the case of the electron temperature, the agreement found in the results of TS and ALI on an almost pure argon plasma suggests that ALI provides a reliable method for the Te determination for moderate non-equilibrium conditions. However, when H₂ is introduced and the power is reduced, we see that the agreement between ALI and TS becomes worse. The temperature values obtained by TS are systematically larger than those given by ALI. A comparison with the results obtained on a low pressure surfatron suggests that the most likely reason for this discrepancy is that the tail of the electron energy distribution function (EEDF) gets depleted when the ionization fraction decreases. Theoretical considerations make clear that the ionization ratio α = n_e/n_i is the key parameter and that low α-values create an EEDF with a broken tail. Such a tail-depleted EEDF demands for mechanisms. Pure Appl Chem 74;3:349–358

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