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Views and Criticism

Local Thermodynamic Equilibrium in Laser-Induced Breakdown Spectroscopy: Beyond the McWhirter criterion

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ABSTRACT

In the Laser-Induced Breakdown Spectroscopy (LIBS) technique, the existence of Local Thermodynamic Equilibrium (LTE) is the essential requisite for meaningful application of theoretical Boltzmann–Maxwell and Saha–Eggert expressions that relate fundamental plasma parameters and concentration of analyte species. The most popular criterion reported in the literature dealing with plasma diagnostics, and usually invoked as a proof of the existence of LTE in the plasma, is the McWhirter criterion [R.W.P. McWhirter, in: Eds. R.H. Huddlestone, S.L. Leonard, Plasma Diagnostic Techniques, Academic Press, New York, 1965, pp. 201–264]. However, as pointed out in several papers, this criterion is known to be a *necessary* but not a *sufficient* condition to insure LTE. The considerations reported here are meant to briefly review the theoretical analysis underlying the concept of thermodynamic equilibrium and the derivation of the McWhirter criterion, and to critically discuss its application to a *transient* and *non-homogeneous* plasma, like that created by a laser pulse on solid targets. Specific examples are given of theoretical expressions involving relaxation times and diffusion coefficients, as well as a discussion of different experimental approaches involving space and time-resolved measurements that could be used to complement a positive result of the calculation of the minimum electron number density required for LTE using the McWhirter formula. It is argued that these approaches will allow a more complete assessment of the existence of LTE and therefore permit a better quantitative result. It is suggested that the *mere use* of the McWhirter criterion to assess the existence of LTE in laser-induced plasmas should be discontinued.

1. Introduction

In the last years, Laser-Induced Breakdown Spectroscopy (LIBS) has gained an increasing popularity as an analytical technique, mainly because of its unique attributes of requiring no sample preparation and of its stand-off detection capability [1]. A detailed description of the plasma, interesting both for modeling and analytical purposes, requires a careful knowledge of the distribution of the population of the different atomic and ionic electronic levels as well as of the free electrons. In a general case, this is attainable through a full kinetic description, in which all processes occurring in the plasma, i.e., ionization by collisions, photoionization, radiative and three-body recombination, collisional excitation/de-excitation processes, radiative decay, photoexcitation and Bremsstrahlung processes, are taken into consideration, together with their appropriate reaction rates. The difficulty of carrying out such a task in an inhomogeneous and time-varying multi-element plasma, makes a thermodynamic approach more attractive where a knowledge of a few parameters, such as the electron/excitation/ionization temperatures and the electron number density, allows us to describe the system through the Saha–Eggert relation and the Boltzmann/Maxwell distributions [2,3]. The use of these relations is only possible and meaningful if Local Thermodynamic Equilibrium (LTE) conditions exist. For this reason, papers dealing with the subject assume LTE in laser-induced plasmas, while only a few investigate the correctness of this assumption. Under the above assumption, the plasma can be completely described by only three parameters, i.e., temperature, electron number density and total number density of species. The validity of LTE is even more important when one uses the Calibration-Free (CF) LIBS procedure, which was introduced [4] to circumvent matrix effects which degrade the accuracy of the results obtained using conventional calibration curves. In the CF-LIBS procedure, the values of temperature and electron number density of the plasma, directly calculated from the acquired spectra, allow one to obtain the full chemical composition of the plasma (and consequently of the sample, if we assume that the ablation process is representative of the sample) by observing at least one emission line from each element present in the sample. Implicitly, this is possible because the existence of LTE allows one to derive, from the population of the upper level of the observed transition, the total distribution of populations in all the electronic levels of the species of the element

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considered. It is then clear that any departure from LTE will affect the accuracy of the final results and make the procedure either unusable or semi-quantitative, at best [5].

In view of the above considerations, it is clearly desirable to have at one's disposal a simple criterion (or a set of criteria) to be used in practical cases to assess the validity of the LTE assumption case by case, without necessarily resorting to a complex collisional-radiative (CR) model [6]. The most popular criterion used in the literature is the so-called McWhirter criterion [7], which defines the minimum electron number density which needs to be present in the plasma in order to warrant the existence of LTE. The McWhirter criterion, as well as other similar ones [8–10], which are all revised and refined versions of that originally introduced by Griem [11], are all obtained by requiring that the collisional depopulation rates for all electronic levels of the atom be at least ten times larger than the radiative depopulation rate. In this way, it is established that collisional processes prevail over radiative processes and deviations from LTE are negligible.

As clearly noted in the original publication [7], the McWhirter criterion was derived for *homogenous and stationary* plasmas, thus only determining a necessary but not sufficient condition when dealing with other types of plasmas that do not respond to these requisites, as is certainly the case of laser-induced plasmas (LIP). Due to the extensive literature on this topic, it is not our purpose here to refer to any specific publication, but rather to point out some general remarks generated from an overview of the literature. A random survey of the publications dealing with the existence of LTE conditions in LIBS reveals three general ways of reporting the McWhirter criterion and drawing conclusions from its application. In the first case, it is concluded that, if the electron number density calculated according to McWhirter is lower than that experimentally measured (usually from Stark broadening), LTE conditions are warranted. In a second case, a cautionary statement is added to the above conclusion, i.e., after stating that that the criterion is satisfied and therefore LTE is warranted, the reader is warned that the criterion is a necessary but not sufficient condition for the existence of LTE. In the third case, in addition to pointing out that the criterion is only necessary but not sufficient, other considerations and experiments are presented to further support the existence of LTE.

As a general observation, it appears that the number of papers belonging to the first case above is larger than that of the papers belonging to the second and third cases. It is therefore worth recalling that, in the case of time-dependent and inhomogeneous plasmas, two other conditions should be verified [8,11]. First, to account for the transient behavior of the plasma, the temporal variation of thermodynamic parameters should be small over the times characterizing the establishment of excitation and ionization equilibrium. Second, the variation length of temperature and electron number density in the plasma should be larger than the distance travelled by a particle by diffusion during the time of relaxation to equilibrium. While the McWhirter criterion can be quickly tested by knowing the plasma temperature and electron number density, the other two conditions are much more difficult to test experimentally, since they require information about the temporal evolution and the spatial distribution of those parameters. Understandably, this is the reason why only the McWhirter criterion is reported in the majority of papers.

The importance of the topic does not need to be stressed further. In fact, we feel it deserves more discussion and debate. Therefore, the considerations presented here are intended to serve the following purposes: (i) to summarize the criteria that need to be fulfilled in LIBS plasmas for the validity of LTE approximation; (ii) to propose some theoretical relations that could be used, to a first approximation, to complement the application of the McWhirter criterion, and finally (iii) to apply the above relations to selected cases taken from the available literature, and to discuss experimental approaches, already used or of potential use, that are complementary to the determination of the electron number density.

We will then emphasize what should be, in our opinion, a meaningful use of the McWhirter criterion in LIBS. The considerations discussed below mainly rely on basic plasma work published in the early 1960s and 1970s [6–13]. It is felt that such a critical discussion can be, in fact, very useful for both practical and modeling purposes in LIBS.

It is perhaps worth pointing out that the terms *thermal* and *thermodynamic* are often used interchangeably when referring to TE and LTE. Moreover, we will also use the terms *levels* and *states* interchangeably, although this is strictly not correct.

2. General overview of equilibrium relations and associated definitions

2.1. Thermodynamic equilibrium (TE)

When a plasma is in thermodynamic equilibrium (TE), the whole system, composed by electrons, atoms, ions and radiation, can be fully described by statistical mechanics, where the equilibrium distributions are characterized by the same temperature [3]. In this case, the Electron Energy Distribution Function (EEDF) has a Maxwellian form defined by the temperature of the system. The relative population of excited levels in an atom/ion, i.e., the Atomic State Distribution Function (ASDF), is described by the Boltzmann distribution [14,15]

$$N_n = N\frac{g_n \exp(-E_n / kT)}{Z(T)} \tag{1}$$

where N_n (cm^{-3}), E_n (erg) and g_n (dimensionless) are the population, the energy and the degeneracy of quantum level n, N (cm^{-3}) is the number density of the species involved, k (erg °K^{-1}) is the Boltzmann constant, T (°K) and $Z(T)$ (dimensionless) are the temperature and the partition function of the atomic level system at such temperature.

Under TE, the population of different ionization stages, i.e., neutral (N_{I}) and singly ionized (N_{II}) under typical LIBS conditions, is described by the Saha–Eggert equation [3,15]

$$\frac{n_e N_{\mathrm{II}}}{N_{\mathrm{I}}} = 2\frac{Z_{\mathrm{II}}(T)}{Z_{\mathrm{I}}(T)}\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2}\exp\left(-\frac{E_\infty - \Delta E}{kT}\right) \tag{2}$$

where n_e (cm^{-3}) is the electron number density, m_e (g) is the mass of the electron, E_∞ (erg) and ΔE (erg) are the first ionization energy for an isolated system and the correction of this quantity for the interactions in the plasma, and $\hbar = (h/2\pi)$.

Finally, the photon energy is described by the Planck function at temperature T, where the spectral energy density in vacuum (erg cm^{-3} Hz^{-1}), for a single polarization, is given by [15]

$$W(\nu) = \frac{8\pi h\nu^3}{c^3}\left(e^{h\nu/kT} - 1\right)^{-1} \tag{3}$$

where h (erg s) is the Planck constant and c (cm s^{-1}) is the speed of light.

Under TE, each process is balanced by its inverse process, which is known as the *principle of detailed balancing* [2]. When this principle is broken, a departure from TE is observed, and a different equilibrium can settle, reflecting strongly in the ASDF. A sort of hierarchy of the departure stage from TE exists, due to the different rates of processes involved [3,16].

2.2. Local Thermodynamic Equilibrium (LTE)

In laser-induced plasmas, as well as in most laboratory plasmas, the radiative energy is decoupled from the other forms of energy, since radiative equilibrium requires the plasma to be optically thick at all frequencies (black body). When photons escape from the plasma, their energy distribution deviates from the Planck function and this inevitably affects also the balances involving electrons, atoms and ions [16]. However, if the energy lost by radiation is smaller than that involved in the other processes involving material species, the Saha–Boltzmann and Maxwell distributions are still a valid description of the system and a new equilibrium, namely LTE, is settled. In this case,

$$T_{\mathrm{exc}} = T_{\mathrm{e}} = T_{\mathrm{H}} \neq T_{\nu} \tag{4}$$

where T_{exc} is the excitation temperature characterizing the ASDF, T_{e} and T_{H} are the temperatures of electrons and heavy particles, i.e. atoms and ions, and T_{ν} is the temperature describing the photon distribution. The escape of photons is associated with spatial gradients in the plasma and to time-dependent regimes, so that for LTE to be established, the variations in space and time should be small (see below); in this case, plasmas are called *quasi-stationary* and defined by local values of temperature and electron density [15,17].

A further degree of departure from TE occurs when electrons and heavy particles are decoupled and their velocity distributions are characterized by different temperatures ($T_{\mathrm{e}} \neq T_{\mathrm{H}}$). In such 2 T-plasmas, the ADSF results from the competition between interaction with atoms and electrons. However, in LIBS plasmas, where the ionization degree is sufficiently high, this competition is dominated by the electrons, i.e. $T_{\mathrm{exc}} \sim T_{\mathrm{e}}$, and just a small perturbation (usually negligible) can be expected from the different temperatures of electrons and heavy particles. Such plasmas, where the processes are dominated by collisions with electrons, are usually named Electron Excitation Kinetic (EEK) plasmas [3].

Successive departures from TE are observed when the conditions for LTE break down, i.e., when spatial gradients and temporal variations are strong, and when radiative processes cannot be neglected. While in the first case the only way to describe the system is through a space-resolved CR model also including a description of the expansion dynamics, the second case can still be partly described by the above equilibrium distributions (see Section 2.3) [3,14,18].

Finally, phenomena such as enhanced transport of charged particles in and out of the plasma, an effect that is particularly important in the case of plasmas of small dimensions, can lead to different dynamics of the inelastic processes involved in the system, causing departures from Boltzmann and Saha equilibria [3,19]. In LIBS, this occurs when the initial conditions of the system, immediately after breakdown, are far from equilibrium and the ionization/recombination routes are characterized by "improper" balances [19]. Such phenomena are often neglected in the treatment of LTE in LIBS, but can lead to non-negligible deviation from LTE, affecting significantly the atomic state distribution functions.

2.3. Partial Local Thermodynamic Equilibrium (pLTE)

In an EEK plasma, whenever spatial gradients and temporal variations are small, LTE is reached when excitation and de-excitation rates between levels are dominated by inelastic collisions with electrons, rather than by radiative processes. In other words, for all the excited levels m, the rate of collision-induced transitions from level m to bound levels higher than m is much higher than the radiative decay rate to the level m [11], i.e.

$$e + A(m) \leftrightarrow e + A(n) \tag{5}$$

$$N_m \sum_{j>m} X_{mj} \gg \sum_{j>m} N_j A_{jm} \tag{6a}$$

This is equivalent to say that

$$N_j \sum_{j>m} X_{jm} \gg \sum_{j>m} N_j A_{jm} \tag{6b}$$

since the collisional rates involving the populations N_m and N_n and the coefficients X_{mj} and X_{jm} are related to each other by the expression [7]

$$\begin{aligned} N_j X_{jm} &= N_m X_{mj} \\ \frac{X_{jm}}{X_{mj}} &= \frac{N_m}{N_j} = \frac{\omega_m}{\omega_j} \exp\left(\frac{\Delta E_{jm}}{kT}\right) \end{aligned} \tag{6c}$$

where ω_j and ω_m are the statistical weights of levels j and m, respectively and ΔE_{jm} is the difference between levels j and m.

A simplification of Eq. (6a) can be made by approximating the summations with the most important term in both sides, i.e., the contribution to and from the next higher level $n = m + 1$, i.e.

$$N_m X_{mn} \gg N_n A_{nm} \tag{7}$$

For the summation on the left hand side of Eq. (6a), this is justified, since collisional cross sections rapidly decrease with an increase of the quantum number, as will be shown below, while in the case of the summation on the right hand side of Eq. (6a), the simplification is valid because the population of the excited levels strongly decreases with increasing values of the quantum levels.

The cross section of inelastic collisions $m \to n$ (with $m<n$, see Eq. (5)), in the case of an optically allowed transition, can be expressed by the Bethe–Born approximation [20], as modified by Van Regenmorter [21], as follows:

$$\sigma_{mn} = \frac{2\pi^2}{\sqrt{3}} \frac{f_{mn} \bar{g} e^4}{\frac{1}{2} m_{\mathrm{e}} v_{\mathrm{i}}^2 \Delta E_{nm}} \tag{8}$$

where f_{mn} (dimensionless) is the absorption oscillator strength of the transition, ΔE_{nm} (erg) the energy difference between levels n and m, e the electron charge (statC), ν_{i} (cm s^{-1}) is the incident velocity of the electron and $\bar{g}$ (dimensionless) is an effective Gaunt factor determined empirically and tabulated in Ref [21,22]. The rate of excitation/de-excitation by collision can be calculated by averaging the cross section over the Maxwellian-distributed electron kinetic energies and obtaining [10]

$$X_{mn} = n_{\mathrm{e}} \langle \sigma_{mn} v \rangle = 4\pi \frac{f_{mn} e^4 n_{\mathrm{e}} \langle \bar{g} \rangle}{\Delta E_{nm}} \left(\frac{2\pi}{3mkT}\right)^{1/2} \exp(-\Delta E_{nm} / kT) \tag{9}$$

The values of $\langle \bar{g} \rangle$ for neutral atoms and positive ions are reported in Fig. 1.

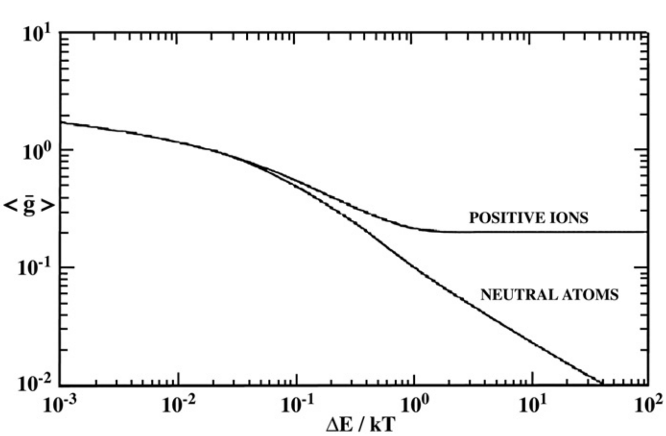

Fig. 1. Effective Gaunt factor $\langle \bar{g} \rangle$ averaged over the EEDF for neutral atoms and positive ions as a function of $\Delta E/kT$.
The figure has been taken from Ref. [21] (reproduced with permission of the American Astronomical Society).

Since the rate is inversely proportional to ΔE_{nm} ($\Delta E_{nm} \ll kT$), the excitation/de-excitation by electron impact is more efficient between highly excited levels, where ΔE_{nm} decreases. On the other hand, the radiative decay rate, A_{nm} related to the absorption oscillator strength f_{mn} by the relation [14],

$$A_{nm} = \frac{8\pi^2 e^2 \Delta E_{nm}^2}{h^2 m_e c^3} \frac{g_n}{g_m} f_{mn} \tag{10}$$

increases with ΔE_{nm}, so that de-excitation by radiative decay is weaker for highly excited levels. It is then clear that, for a fixed n_e, the LTE condition expressed in Eq. (7), can be fulfilled by high-energy excited levels and not by low-energy levels. If a level n' exists for which the two rates are the same, then the plasma is in partial LTE (pLTE), where the levels $n>n'$ and the free electrons are in equilibrium with each other, while the levels $n<n'$ are not. In this case, the ASDF is divided in two parts: the upper side containing the high-energy levels $n>n'$, which are easily thermalized, follow a Boltzmann distribution at the temperature $T_{exc}=T_e$ and are related to the ion population by the Saha relation, and the bottom side, where the energy gap with the continuum is too large, and the associated levels do not follow the Saha–Boltzmann distributions. It is obvious that for plasmas in pLTE, the experimental determination of T_{exc} by using a Boltzmann plot obtained by considering all the spectral lines will result in T_{exc} values being different from T_e.

3. Criteria for assessing the validity of LTE

Understandably, the criteria to be considered when assessing LTE conditions vary according to the temporal and spatial characteristics of the plasma under consideration. The three broad categories considered here are representative of plasmas that can be described as *stationary and homogeneous*, *transient and homogeneous* and finally *transient and inhomogeneous*. Each of these cases will be discussed separately. For each case, theoretical expressions, taken directly or derived from the existing literature, will be given for the pertinent physical parameters associated with each case. Moreover, the calculated values of these parameters will be compared with directly available literature values or with values derived from experimentally published data.

3.1. Case of a stationary and homogenous plasma

This case does not consider the problems related to spatial gradients and time-variation of the plasma. Here, LTE conditions can be tested following a criterion, derived in slightly different formulations by many authors [8–11], which is usually referred to as the McWhirter criterion [7]. This criterion is obtained by requiring that the left hand side term in Eq. (7), expressed as the number of downward transitions per unit time and per unit volume due to collisions, is at least ten times larger than the right hand side term, i.e.,

$$N_n X_{nm} > 10 N_n A_{nm} \tag{11}$$

In a semi-classical treatment of the cross sections for inelastic collisions, by using the relations given in Eqs. (6c) and (10), the McWhirter criterion is expressed by the relation:

$$n_e(\text{cm}^{-3}) > 1.6 \cdot 10^{12} T^{1/2} (\Delta E_{nm})^3 \tag{12}$$

where T and ΔE_{nm} are expressed in K and eV, respectively.

Note that the same expression (apart from the units of m^{-3} instead of cm^{-3}) is reported in Thorne's book [23]. A more precise calculation, accounting for appropriate quantum-mechanical corrections with the introduction of the Gaunt factor, can be calculated from Eqs. (8) and (9) according to the formulation of Hey [10], and expressed by the relation:

$$n_e > \frac{2.55 \cdot 10^{11}}{\langle \overline{g} \rangle} T^{1/2} (\Delta E_{nm})^3 \tag{13}$$

In order to assure that the plasma is in LTE, the conditions expressed by Eq. (12) or (13) must hold for the largest ΔE_{nm} gap between *adjacent* levels. In fact, if the couple of adjacent levels m,n and n,p are in thermal equilibrium, the same holds for the non adjacent m,p levels. Since ΔE_{nm} decreases with increasing values of the level quantum number, the ground level and the first excited level, corresponding to the first resonance transition, are usually considered. In the presence of low-lying metastable states, care should be exercised (see below).

It is worth noting that, in LIBS plasmas, the fulfilment of Eqs. (12) and (13) cannot be sufficient for assessing the validity of LTE, even in the approximation of a stationary and homogenous plasma, because of the extremely high ionization degree of the plasma after the breakdown, which causes an unbalance between the ionization and recombination processes, the latter prevailing. Therefore, in this case, within the dominance of electron collision excitation and de-excitation mechanisms over radiative decay, it is important to check the equilibrium within different inelastic processes leading to the Boltzmann and Saha balances.

A parameter describing the closeness to equilibrium of the various collisional processes, which can be determined experimentally, is the so-called b_i factor [6,17,24], defined as the ratio of the atomic population of a level i, N_i, determined by the atomic state distribution, over the same quantity calculated by the Saha equation, N_i^S, i.e.,

$$b_i = N_i / N_i^S \tag{14}$$

The above relation is based upon the intrinsic cooperation of Saha and Boltzmann processes: in other words, in LTE conditions, one relation implies the other. If $b_i=1$, LTE is verified. $b_i>1$ suggests either an ionizing character for the plasma or the failure of the optically thin system assumption, while if $b_i<1$, the plasma has a recombination character or a non-negligible radiative decay contribution. Therefore, the value of the b_i factor represents a *direct* measurement of the deviation from LTE conditions. However, this factor is not easily calculated by optical emission measurements, as it requires the knowledge of the ion ground state population N_0^+ [14].

A similar relation can be obtained by comparing two ratios. The first is the ratio of the relative population of atomic species in the excited level i with that of ions in the excited level j (belonging to the same atomic system) as obtained by the experimental Boltzmann distribution. The second is the ratio obtained using the Saha–Boltzmann equation at the excitation temperature of the ionic state distribution function and the electron number density obtained by an independent measurement. This comparison is expressed by the relation:

$$\frac{N_i^B}{N_j^{+B}} = \frac{N_i^S}{N_j^{+S}} \tag{15}$$

The above equality clearly shows that, in LTE conditions, the Boltzmann relation and the Saha equation can be mutually applied to the observed system. Any deviation from the equality expressed by Eq. (15) can be adopted as a realistic estimation of the deviations from LTE due to an unbalance of the collisional processes involved.

If the criterion reported in Eqs. (12) and (13) (McWhirter/Hey) is verified and the plasma can be considered optically thin, then Eq. (15) can be verified in a simpler way by comparing the electron number density directly measured with the Stark effect with the corresponding value obtained using the Saha equation. In this way, the comparison of the electron number density calculated in three different ways, i.e., from

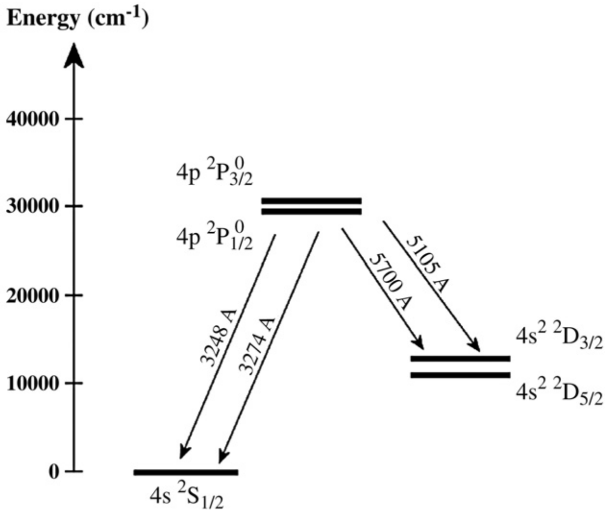

Fig. 2. Partial Grotrian diagram of Cu I.

the McWhirter expression (Eqs. (12) and (13)), the use of Saha equation and the measurement of the Stark broadening of a suitable transition, provides a reliable way for assessing LTE .

3.1.1. Effect of self-absorption

The hypothesis made in deriving the McWhirter/Hey criteria (see Eqs. (12) and (13) is that the plasma is optically thin. This hypothesis requires some discussion. As stated above, the criterion is calculated for optically thin plasmas, i.e., for negligible self-absorption. In this case, if the electron number density is insufficient, the ground level is slightly overpopulated with respect to the populations predicted by LTE. However, in many practical cases, the strong self-absorption of the resonance transition tends to lower the population of the ground state and to re-equilibrate it toward the LTE population. In this case, the effective radiative population rate of the ground state is reduced by a factor of the order of the ratio of the actual intensity of the first resonance line to the corresponding intensity that the line would have if self absorption was absent [14]. This leads to a corresponding reduction of the electron number density needed for LTE by the same factor. Detailed calculations show that in the case of strong self-absorption of the first resonance line, often occurring in typical LIBS experiments, the electron number density needed for assuring LTE, as derived from the McWhirter criterion, can easily be relaxed by about an order of magnitude [8,11,24].

3.1.2. Influence of low-lying metastable states

Another hypothesis made in deriving Eqs. (12) and (13) is that, between the energy levels considered, radiative decay is allowed. In fact, the collisional cross section reported in Eq. (8) refers to an optically allowed transition, where levels m and n possess an electric dipole matrix element [10]. However, in many cases (e.g., Fe I–II, Cu I–II, O I–II, N I–II, Ni I–II, etc.), metastable states, i.e., states that weakly decay radiatively to the ground state through forbidden (magnetic dipole or electric quadrupole coupling) or through intercombination transitions (spin-orbit coupling), exist between the ground level and the first optically allowed level. As an example, we consider the Grotrian diagram of Cu I shown in Fig. 2, where the number of levels indicated is limited to low-energy levels [25]. The levels $4s^2\,^2D_{3/2}$ and $4s^2\,^2D_{5/2}$ are metastable and therefore not coupled to the ground state $4s\,^2S_{1/2}$ through a dipole transition.

In this case, the Bethe–Born approximation, valid for long range dipole interaction, fails and similar approximate and generalized formulas are not available [10]. This is unfortunate because it would be a mistake to assume, on the basis of the relative oscillator strength, that the rates of collisional excitation between the ground state ($4s\,^2S_{1/2}$) and the metastable states ($4s^2\,^2D_{3/2}/4s^2\,^2D_{5/2}$) are negligible. On the other hand, as in most similar cases, the rate of collisional dipole excitation from the ground state to the optically allowed doublet levels ($4p\,^2P^0_{1/2}/4p\,^2P^0_{3/2}$) is very high, so that cascading is the dominant process responsible for the population of the $4s^2\,^2D_{3/2}/4s^2\,^2D_{5/2}$ levels. In essence, the approximation used to simplify Eq. (6a) into Eq. (7) is no longer valid, since the larger term in the summations of Eq. (6a) is that relating the ground level to the first optically allowed level. For this reason, to a first approximation, in the case of low-lying metastable states, the first resonance transition (corresponding for Cu I to the transition $4s\,^2S_{1/2}\rightarrow 4p\,^2P^0_{1/2}/4p\,^2P^0_{3/2}$) should be considered in the McWhirter criterion to assess the validity of the LTE hypothesis. In many practical cases, this leads to a higher value of ΔE_{nm} (see Table 1 for a listing of ΔE_{nm} values to be used for some elements). A method for obtaining more accurate estimates of the minimum electron number density necessary for LTE, which takes into account metastable states, has been presented by Hey [10], where corrections due to step-wise excitation *via* adjacent metastable levels are considered. In the case of Cu I, this would correspond to the ladder $4s\,^2S_{1/2}\rightarrow 4s^2\,^2D_{3/2}/4s^2\,^2D_{5/2}\rightarrow 4p\,^2P^0_{1/2}/4p\,^2P^0_{3/2}$ (see Fig. 2).

Table 1
ΔE values to be inserted in the McWhirter criterion for neutral and single ionized species of the element of interest. The values have been determined by considering the first resonance transition, neglecting forbidden and intercombination lines. The notations used for describing configurations and spectroscopic terms of excited and ground levels are the standard ones used in NIST database *.

	Element	Configurations	Terms	ΔE_I (eV)	Configurations	Terms	ΔE_{II} (eV)
		Neutral atoms			Ions		
Metals	Cu	$3d^{10}4s–3d^{10}4p$	$^2S–^2P^0$	3.8	$3d^{10}–3d^9(^2D)4p$	$^1S–^1P^0$	9.1
	Al	$3s^23p–3s^24s$	$^2P^0–^2S$	3.1	$2p^63s^2–3s3p$	$^1S–^1P^0$	7.4
	Fe	$3p^63d^64s^2–3p^63d^6(^5D)4s4p(^3P^0)$	$a^5D–z^5D^0$	3.2	$3d^6(^5D)4s–3d^6(^5D)4p$	$a^6D–z^6D^0$	4.8
	Mn	$3d^54s^2–3d^5(^6S)4s4p(^3P^0)$	$a^6S–z^6P^0$	3.1	$3d^5(^6S)4s–3d^5(^6S)4p$	$a^7S–z^7P^0$	4.8
	Ni	$3d^8(^3F)4s^2–3d^9(^2D)4p$	$^3F–^3F^0$	3.6	$3p^63d^9–3p^63d^8(^3F)4p$	$^2D–^2F^0$	7.1
	Zn	$3d^{10}4s^2–3d^{10}4s4p$	$^1S–^1P^0$	5.8	$3d^{10}4s–3d^{10}4p$	$^2S–^2P^0$	6.0
	Mg	$2p^63s^2–3s3p$	$^1S–^1P^0$	4.3	$2p^63s–2p^63p$	$^2S–^2P^0$	4.4
Non-metals	O	$2s^22p^4–2s^22p^3(^4S^0)3s$	$^3P–^3S^0$	9.5	$2s^22p^3–2s2p^4$	$^4S^0–^4P$	14.9
	N	$2s^22p^3–2s^22p^2(^3P)3s$	$^4S^0–^4P$	10.3	$2s^22p^2–2s2p^3$	$^3P–^3D^0$	11.4
	H	$1s–2p$	$^2S–^2P^0$	10.2			
	C	$2s^22p^2–2s^22p(^2P^0)3s$	$^3P–^3P^0$	7.5	$2s^22p–2s2p^2$	$^2P^0–^2D$	9.3
	Si	$3s^23p^2–3s^23p4s$	$^3P–^3P^0$	4.9	$3s^23p–3s3p^2$	$^2P^0–^2D$	6.9
	Cl	$3s^23p^5–3s^23p^4(^3P)4s$	$^2P^0–^2P$	9.2	$3s^23p^4–3s3p^5$	$^3P–^3P^0$	11.6
	S	$3s^23p^4–3s^23p^3(^4S^0)4s$	$^3P–^3S^0$	6.9	$3s^23p^3–3s3p^4$	$^4S^0–^4P$	9.8

(physics.nist.gov/Phys.Ref Data?ASD/Html.ref.html).

3.1.3. Considerations

In order to understand the limits imposed to the LTE approximation in typical LIBS plasmas, we can consider the results shown in Ref. [26], where the distribution of the temperature and electron number density along the spatial profile are calculated for a laser-induced iron plasma at different time windows and operating pressures (Fig. 3).

By taking $\Delta E \approx 4.77$ eV, corresponding to the first transition of the resonance series for ionized iron, the threshold value of the electron number density given by the criterion is $\sim 8 \cdot 10^{15}$–$1.8 \cdot 10^{16}$ cm^{-3}, depending on the plasma region considered. It can be easily seen that, at 1000 mbar, the criterion is fulfilled at 0.5–1 μs in all the measured plasma regions, while at longer times it is verified only in the core of the plasma and not in the outer regions. On the other hand, in the case of plasmas induced at 10 mbar, the criterion is fulfilled only in the 0.5–1 μs time window, while it is not verified at later times. These results suggest that for *metal plasmas* at ambient pressure, the McWhirter criterion is usually fulfilled, except occasionally in the outer regions of the plasma. On the contrary, particular care should be taken in cases of plasma induced at lower gas pressure, since the fast expansion of the plume induces a strong decrease of electron number density, leading to the failure of the criterion.

The situation is different in the case of *non-metal plasmas*, such as those obtained from soil samples, where elements like oxygen, nitrogen or carbon are the main components, since the ΔE values to be used in the McWhirter criterion are significantly higher than for metals (see Table 1). In this case, by taking the corresponding ΔE from the resonance transitions of ion species and a temperature of 1 eV, the calculated threshold values of the electron number density for oxygen, nitrogen or carbon plasmas are $5.7 \cdot 10^{17}$ cm^{-3}, $2.6 \cdot 10^{17}$ cm^{-3} and $1.4 \cdot 10^{17}$ cm^{-3}, which in many cases can be higher than the actual values found in the plasma. This observation suggests that particular attention should be taken in a CF-LIBS analysis of samples such as soils, where the non-metal elements could depart from the LTE condition, in particular at later observation times. As will be shown in the following sections, the departure of non-metals from LTE can also be attributed to the longer relaxation times needed to reach equilibrium and to the larger values of their diffusion coefficients.

When the McWhirter criterion is not fulfilled, meaning that LTE cannot exist, a pLTE can still be satisfied in the plasma, which however involves only the excited levels that are Boltzmann-distributed at the temperature $T_{exc} = T_e$. In this case, the temperature calculation through the Boltzmann plot method leads to large errors, as pointed out and shown in Ref. [24].

The equality described by Eq. (15) can also be verified for excited levels in pLTE. In this specific case, the study of the population distribution function for a large number of different levels allows an estimation of the decoupling levels. It is obvious that Eq. (15) will never be verified for ionic and atomic distributions of excited levels with significant difference in the excitation temperature.

3.2. Case of homogenous and transient plasma

Even if the criteria described in Section 3.1 for LTE plasmas have been successfully checked, in the case of LIP any general assumption should be taken with caution as a consequence of the transient nature of the system. In fact, if the evolution of the plasma is too fast, the electrons and the atoms could not have time to reach thermodynamic equilibrium.

However, if the variation of the plasma thermodynamic parameters (mainly n_e) is sufficiently slow, the plasma evolves through quasi-equilibrium near-LTE states and Eqs. (1) and (2) can be safely applied. This happens when the McWhirter criterion is fulfilled (necessary but not sufficient condition) *and* when the relaxation time τ_{rel} of the plasma, i.e., the time needed for the establishment of excitation

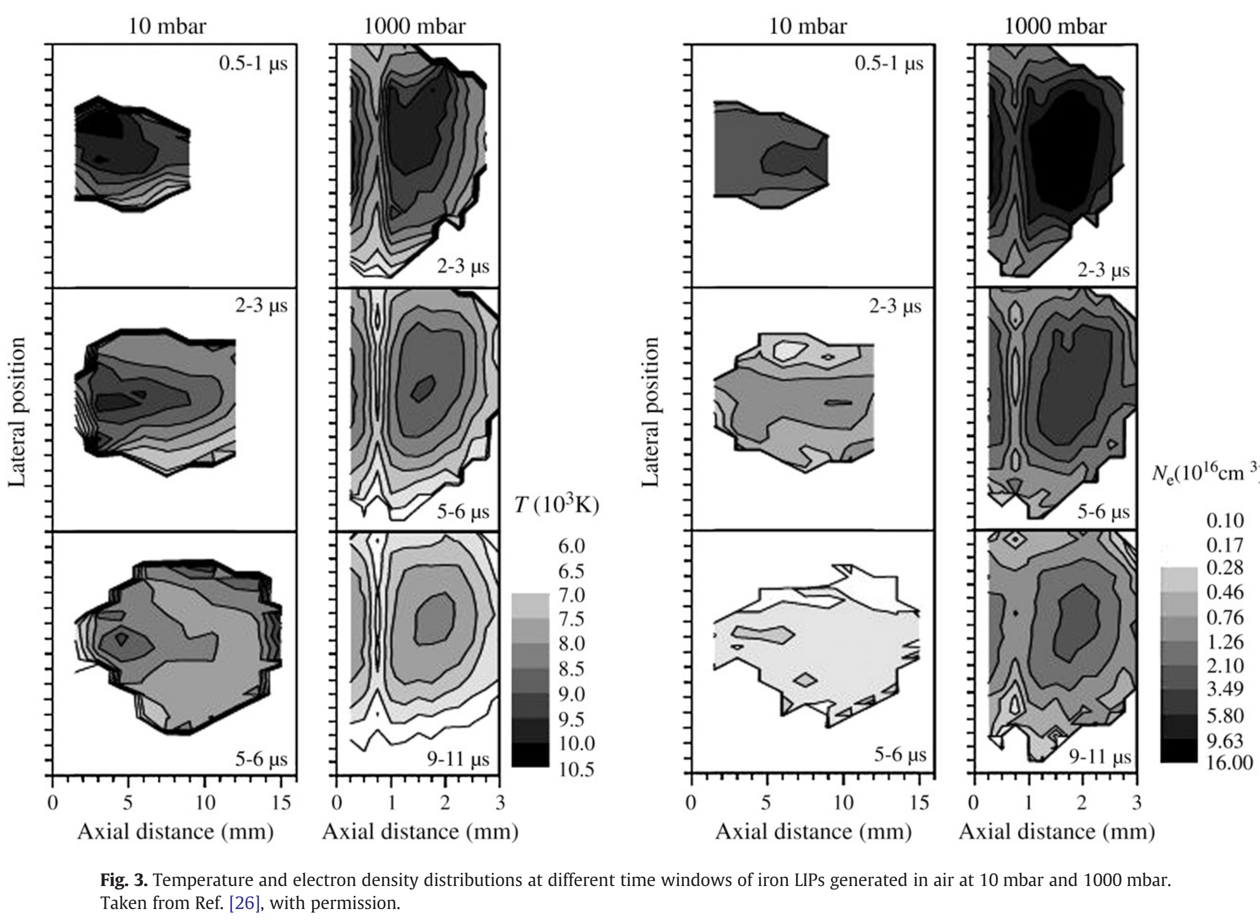

Fig. 3. Temperature and electron density distributions at different time windows of iron LIPs generated in air at 10 mbar and 1000 mbar. Taken from Ref. [26], with permission.

and ionization equilibria, is much shorter than the time of variation of thermodynamic parameters, i.e., when the following relations hold true:

$$\frac{T(t+\tau_{\mathrm{rel}})-T(t)}{T(t)}<<1 \quad \frac{n_{\mathrm{e}}(t+\tau_{\mathrm{rel}})-n_{\mathrm{e}}(t)}{n_{\mathrm{e}}(t)}<<1 \tag{16}$$

In other words, the rates associated with the elementary processes must be higher than the variation rate of thermodynamic parameters. Eqs. (16) constitute the *second criterion* to be satisfied for the validity of LTE approximation in a time-varying plasma.

Looking in more detail at the transient nature of a LIP, the evolution can be roughly subdivided into three steps [27]: *breakdown*, *expansion* and *confinement*. During ns-ablation, when target breakdown is obtained and the material is ejected, the laser pulse is still on, heating the free electrons to temperatures of the order of a few tens of thousands Kelvin, depending on the laser photon energy.

In this stage, the ionization degree is close to unity as a consequence of the kinetic mechanisms involved in the breakdown process and of the extremely high number density of the ejected atomic gas (around 10^{22}–10^{23} cm^{-3} according to the density of the investigated sample).

When the laser pulse has ended, the ionization degree is found to be much higher than the corresponding equilibrium value at the observed electron temperature, as estimated by the Saha equation [28–31]. This condition will characterize the LIP features for the rest of its expansion. To get closer to the equilibrium conditions described by the Saha equation, the LIP system destroys charged particles by means of recombination mechanisms in order to reduce the degree of ionization. The same mechanisms cause a drop in the electron kinetic temperature due to expansion cooling, because the electrons lost in the recombination processes are mainly those with lower energy.

During the phase of plasma expansion, despite the cooling due to collisions with cold ambient gas atoms, the variation of particle number density and gas temperature is predominantly produced by the physical expansion of the high pressure ablated material in the surrounding environment [17]. In this case, Eq. (16) reduces to a comparison of the thermodynamic relaxation time with the expansion rate of the plume. By considering Fig. 4, rearranged from Ref. [27], where the expansion of a Ti-LIP is reported in different experimental conditions (single and double pulse operation at different pressures), the following observations can be made. In the case of single pulse LIBS, we can clearly observe that the LIP initially expands quickly until it reaches a certain volume with a radius of approximately 1–1.5 mm.

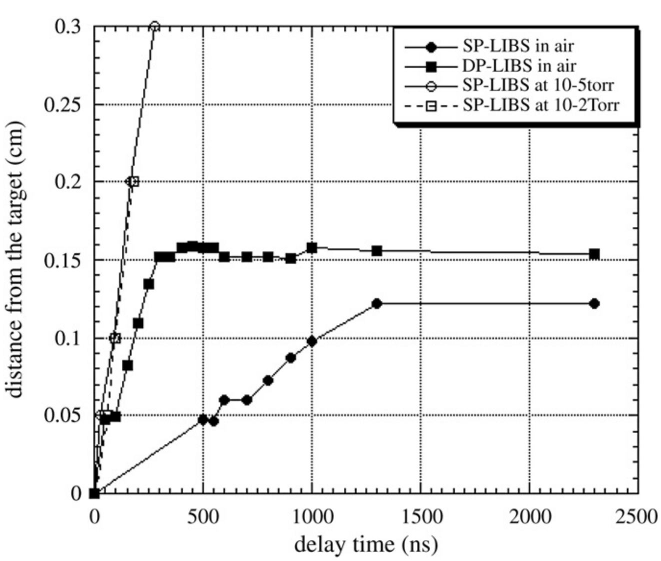

Fig. 4. Expansion profile of the maxima of the spatial distribution of Ti II (344.42 nm) during SP- (fluence = 3.5 J cm^{-2}) and DP-LIBS (1st laser fluence = 3.5 J cm^{-2}; 2nd laser fluence = 3.5 J cm; inter-pulse delay = 5 µs) on a titanium target. Also shown are the results obtained in air at low pressure.
Rearranged from Ref. [27].

In this case, for any measurements obtained with a detection delay-time shorter than 1.3 µs, the validity of LTE conditions should be considered with caution. As a matter of fact, during the initial expansion stage, all the processes with an associated time longer than microseconds could not reach equilibrium as a consequence of the fast change of plasma particle number density and temperature. As an example, we can consider the three-body recombination time as a function of the electron number density [28]. Assuming an average rate constant of the order of 10^{-30} cm^6 s^{-1} and a typical electron number density value of 10^{17}–10^{18} cm^{-3}, we obtain a recombination time comparable or higher than that previously estimated for the expansion time. This issue dramatically arises when the background pressure is in the sub-Torr range and a net difference in the atomic and ionic distribution can be observed during the entire expansion.

Furthermore, by looking at Fig. 4, even at ambient pressure, one can see that the evolution is different in the case of double pulse, where a more rapid expansion of the plume occurs in a shorter time duration, of the order of some hundreds of ns.

After the first stage of expansion, the plasma front stops while the shock wave continues moving in the ambient gas. At this stage, the volume occupied by the plume keeps the same approximate dimension for several microseconds. In this period, the variation rate of the thermodynamic parameters is mainly due to the plasma cooling effect, resulting from collisions with cold atoms in the ambient gas. This rate is markedly lower than that in the expansion phase, so that Eq. (16) is more easily satisfied. In this phase, the variation of the electron number density is governed by the equation

$$\frac{dn_{\mathrm{e}}}{dt} = N_{\mathrm{a}}n_{\mathrm{e}}K_{\mathrm{ion}}-\alpha_{\mathrm{rec}}n_{\mathrm{e}}^3 \tag{17}$$

where N_{a} is the number density of atoms and K_{ion} and α_{rec} are the ionization and recombination rates. Under complete LTE, because of the principle of detailed balance, $\mathrm{d}n_{\mathrm{e}}/\mathrm{d}t = 0$. When $\mathrm{d}n_{\mathrm{e}}\mathrm{d}t > 0$, the ionization process prevails over the recombination process and the plasma is ionizing. On the contrary, when $\mathrm{d}n_{\mathrm{e}}\mathrm{d}t < 0$, the recombination process prevails and the plasma is recombining. LIBS plasmas in the confinement phase are in the latter condition, where the plasma is recombining, but can evolve through quasi-equilibrium near-LTE states if Eq. (16) is verified.

In order to check the criterion expressed in Eq. (16), an estimation of the value of the thermodynamic relaxation time is needed. By assuming a sudden departure from the quasi-stationary LTE condition, the time, τ_{rel}, needed by the atomic system to return to LTE is given by the characteristic time of the slowest process, which corresponds to the re-equilibration of the ground state. Following the work of Griem and Drawin [8,11], it is clear that, among all the processes involving the ground state, the rate coefficient for collisional excitation to the first excited level of the resonance series is the slowest one, and can therefore be taken into consideration for a rough estimate of τ_{rel}. By considering Eq. (9), τ_{rel} can be expressed by

$$\tau_{\mathrm{rel}} \approx \frac{1}{n_{\mathrm{e}}\langle\sigma_{12}v\rangle} = \frac{6.3\cdot 10^4}{n_{\mathrm{e}}f_{12}\langle\overline{g}\rangle}\Delta E_{21}(kT)^{1/2}\exp\left(\frac{\Delta E_{21}}{kT}\right) \tag{18}$$

where both ΔE and kT are expressed in eV. The previous estimate is derived for complete ionization of the plasma. In the case of partial ionization, the value of τ_{rel} is obtained by multiplying Eq. (18) by the fraction of ionization of the species considered $N_{\mathrm{II}}/(N_{\mathrm{I}}+N_{\mathrm{II}})$ [8]. A more accurate estimate of τ_{rel} can be found by considering the corrections associated with the other processes involving the ground level and accounting for the self-absorption of the resonance line [8].

Detailed estimates of τ_{rel} can be calculated by means of the time-dependent collisional-radiative models, as introduced by Bates et al. [6]. These quasi-stationary models rely on the fact that the relaxation times of the excited states are much shorter than those of the ground state and of the low-lying (metastable) states, as shown for example in ref. [32]. In this way, the concentration of the excited states adapts instantaneously to the LTE condition, and the CR model reduces to a linear system of equations accounting for the population of the ground state, low-lying states, and electron number density. Detailed quasi-stationary CR models solved for dense plasmas produced at atmospheric pressures are at present missing. Results extrapolated from the works of Cacciatore et al. [33,34], as thoroughly discussed in ref. [17], show that in the case of neutral oxygen, an electron number density higher than 10^{16} cm^{-3} is needed for meeting the criterion of a quasi-stationary plasma, which is in agreement with the approximate results obtained by the use of Eq. (18).

3.2.1. Considerations

Many publications [29–31,35–37] deal with the temporal evolution of LIPs, showing decay times of temperature $T(t)(\mathrm{d}T(t)/\mathrm{d}t)^{-1}$ and electron number densities $n_e(t)(\mathrm{d}n_e(t)/\mathrm{d}t)^{-1}$ in the range 10^{-5}–10^{-6} s at the typical delay times of signal acquisition. Even shorter decay times are found in the first hundreds of ns of plasma lifetime, during the expansion stage of the plume, in agreement with the calculation of the characteristic time of plasma expansion, τ_{exp}. Here, considering that $\tau_{exp} \approx d/v$, where $d \approx 1$ mm is the plasma diameter and $v \approx 10^5$cm/s is the plasma expansion velocity [17,38], a value of $\tau_{exp} \approx 10^{-6}$ s is found.

As discussed in the previous section, in the expansion stage of the plasma life, LTE is critical because the relaxation time τ_{rel} is comparable to, or higher than, the expansion time τ_{exp}. In addition, for ns-LIPs, the ionization degree in this stage is higher than that predicted by the Saha balance. Experimental studies [28–31,35,39], based on a comparison of temperatures measured by the Boltzmann plot of line intensities (T_{exc}) and by the ratio of ions to neutral atoms ($T_e = T_{ion}$) seem to indicate that the criterion is not satisfied at these times. For these reasons, experiments in this range should be avoided or, at least, results obtained in such conditions should be handled with care.

The temporal range of the expansion stage is of the order of µs in typical LIBS conditions but can vary significantly by changing the buffer gas pressure, the laser irradiance or the laser-to-sample distance [38,40,41].

Typical LIBS measurements are performed in the subsequent stage of plasma evolution, i.e. in the confinement phase. Here, calculations made on the basis of Eq. (18) show that the criterion is easily fulfilled by most plasmas obtained with metals. As an example, in the case of neutral copper ($\lambda = 3248/3274$ Å, $\Delta E \approx 3.78$ eV, $f_{12} \approx 1.37$), by taking $n_e = 5 \cdot 10^{16}$ cm^{-3} and $kT = 1$ eV, a value of $\tau_{rel} \sim 3.8 \cdot 10^{-9}$ s can be calculated, which is much lower than typical decay times of T and n_e. However, particular attention should be paid for elements characterized by higher values of ΔE, for which the criterion can be critical or not fulfilled at all. As an example, the relaxation times of oxygen and hydrogen ($\Delta E_{21}^{OI} \approx 9.5$ eV, $f_{21}^{OI} \approx 5.2 \cdot 10^{-2}$; $\Delta E_{21}^{HI} \approx 10.2$ eV, $f_{12}^{HI} \approx 0.14 \cdot 10^{-2}$), calculated in the same conditions as above, are $1.6 \cdot 10^{-4}$ s and $1.2 \cdot 10^{-4}$ s, respectively. These values are much larger than the calculated decay times, i.e., $T(t)(\mathrm{d}T(t)/\mathrm{d}t)^{-1}$ and $n_e(t)(\mathrm{d}n_e(t)/\mathrm{d}t)^{-1}$, which are in the range 10^{-5}–10^{-6} s. In the case of double pulse experiments, the conditions seem more suitable for LTE, since the plume rapidly reaches a quasi-stationary regime due to the confinement by the shock wave produced by the first laser pulse.

As a consequence of this discussion, from an experimental point of view, the LTE assumption would require a detection gate, Δt_g, of the same order of magnitude of τ_{rel}, so that we can replace τ_{rel} with Δt_g in Eq. (16), verifying the quasi-stationary criterion. Unfortunately, in order to obtain a reasonable S/N ratio in the confinement stage, much longer detection gates are necessary. For this reason, when one needs to collect different spectroscopic lines in order to perform a multi-element chemical analysis or to build a Boltzmann plot, it should be verified that, during the entire detection gate, the temporal profiles of the selected emission lines are exactly the same over the entire acquisition time. This can be achieved by selecting lines involving transitions with emission coefficients much larger than the reciprocal of the acquisition gate.

3.3. Case of inhomogeneous and transient plasmas

LIPs show spatial gradients of temperature and electron number density which can be significant, especially at their edges. This is mainly due to the dissipation of heat at the plasma edges through conduction and to radiative processes [42]. In the case of strong gradients, the diffusion of atoms and ions can be important and must be considered when assessing LTE. Therefore, for inhomogeneous plasmas, in addition to the criteria reported above, a *third criterion* must be satisfied. This criterion requires that the *diffusion length* of atoms/ions, during a time period of the order of the relaxation time to the equilibrium, is shorter than the *variation length* of temperature and electron number density in the plasma [11,12]. If this condition is not fulfilled, the excitation and ionization states of the atom/ion are not determined by the local values of temperature and electron number density, but rather by the values of such parameters in a different region of the plasma, from which the atom/ion is diffused [11]. The condition for LTE at the position x can be expressed as

$$\frac{T(x) - T(x+\lambda)}{T(x)} \ll 1 \quad \frac{n_e(x) - n_e(x+\lambda)}{n_e(x)} \ll 1 \tag{19}$$

where $\lambda = (D \cdot \tau_{rel})^{1/2}$ is the diffusion length during the relaxation time τ_{rel}. Calculating the diffusion coefficient of atoms and ions in a LIBS plasma is a very complex task, since it requires a knowledge of the cross sections of several collision processes and of the absolute atom and ion number density. However, with the use of some approximation, a rough estimate of the order of magnitude of λ can be achieved. Here, only the diffusion lengths of atoms will be considered, since they are typically larger than those of ions and then impose more restrictive limits for the establishment of LTE. By taking at first a plasma composed of a single-element, the processes affecting the diffusion coefficient for atoms are the elastic collisions with atoms and ions and the resonance charge-exchange collisions with ions ($A + A^+ \rightarrow A^+ + A$). Since the cross section of the first process is typically much lower than that of the latter [8], only the resonance collisions with ions will be considered here. This approximation is valid for ionization degrees higher than ~1%, which is typically the case in LIBS plasmas. For a more accurate determination of the diffusion lengths of atoms and ions, including the correction for elastic collisions, Ref. [8] should be consulted. Within the above hypotheses, and after rearranging the expression shown in Ref. [8], the diffusion coefficient D (cm^{2}s^{-1}) can be expressed as

$$D \approx 3 \cdot 10^{19} \frac{kT}{N_{II} M_A} \tag{20}$$

where kT is expressed in eV, N_{II} is the absolute number density of ions and M_A is the relative mass of the species considered ($M_H = 1$). Finally, by considering Eq. (16) and for $N_{II} = n_e$, the diffusion length λ (cm) can be expressed as

$$\lambda \approx 1.4 \cdot 10^{12} \frac{(kT)^{3/4}}{n_e} \left(\frac{\Delta E}{M_A f_{12} \langle \bar{g} \rangle} \right)^{1/2} \exp\left(\frac{\Delta E}{2kT} \right) \tag{21}$$

where ΔE and kT are expressed in eV. The previous estimate is derived for complete ionization of the plasma. In the case of partial ionization, the value of τ_{rel} is obtained by multiplying Eq. (18) by $[N_{II}/(N_I + N_{II})]^{1/2}$, accounting for the percentage of ionization. In addition to the McWhirter criterion, the condition for the validity of LTE in an inhomogeneous plasma is that *d is at least 10 times larger than* λ, i.e., $d>10\lambda$, where $d \approx T(x)(\mathrm{d}T(x)/\mathrm{d}x)^{-1}$ is the characteristic variation length in the plasma, which can be taken as the plasma diameter or a fraction of it. In the case of a multi-element plasma, the diffusion length λ is generally larger than that expressed in Eq. (21) since a lower amount of ions of the element considered are available for resonance charge-transfer collisions. The situation can be dramatic for trace elements, since in this case such processes become rare and elastic collisions with the main gas atoms/ions become predominant (the asymmetric charge transfer between trace atoms and main gas ions can be neglected because of its extremely small cross section) [8]. In this case, the diffusion length associated with trace element atoms can be 1–2 orders of magnitude larger than that calculated by Eq. (21).

3.3.1. Considerations

Among the three criteria considered for the validity of LTE, the one concerning the non-homogeneity of LIPs is certainly the least studied. The most likely reason is the complexity of calculating the diffusion length of atoms and ions in multi-element plasmas, which explains the small number of papers dealing with their spatial distribution. Despite the scarce attention dedicated to this issue, it is important to stress that the spatial gradients existing in LIPs can sometimes lead to significant departures from LTE. In order to have an indication of the variation length of temperature, we can re-arrange the results shown in Ref [43], where the spatial distribution of temperature in a Fe–Ni plasma is calculated in a 3–3.5 µs time window. The length $d \approx T(r)/(\mathrm{d}T(r)/\mathrm{d}r)^{-1}$ can be calculated and found to be $d \approx 2$ mm at a plasma radius of 1 mm. In this case, the criterion is fulfilled if $\lambda<0.2$ mm. A similar value can be obtained by rearranging the data shown in Ref. [44] for a Cu–Zn target, where a value of $d \approx 1$ mm is obtained at a radius of 0.75 mm, resulting in $\lambda<0.1$ mm for the criterion to be fulfilled.

For the sake of illustration, we will consider here the cases of copper, iron, nickel, oxygen and hydrogen in a plasma characterized by $n_e = 5 \cdot 10^{16}$ cm^{-3} and $kT = 1$ eV. By considering Eq. (21) and the corrections for the ionization percentage, we obtain $\lambda_{\mathrm{Cu\ I}} \approx 1.9 \cdot 10^{-3}$ mm, $\lambda_{\mathrm{Fe\ I}} \approx 1 \cdot 10^{-2}$ mm, $\lambda_{\mathrm{Ni\ I}} \approx 2 \cdot 10^{-2}$ mm, $\lambda_{\mathrm{O\ I}} \approx 0.2$ mm and $\lambda_{\mathrm{H\ I}} \approx 0.7$ mm. It is clear that the criterion is verified for copper, iron and nickel since the values obtained are much lower than the plasma dimensions. On the contrary, it is also clear that the criterion cannot be fulfilled in the cases of hydrogen and oxygen. In addition, if only trace concentrations in the plasma are considered, it can be concluded that the fulfilment of the criterion is also at risk in the case of metal atoms.

4. Conclusive remarks

From the previous discussion, several considerations can be summarized as follows:

(i) The McWhirter criterion is simple to use, once the plasma temperature and the electron number density have been experimentally evaluated. However, this criterion will tell us whether LTE conditions *do not exist*, and not whether LTE conditions *exist*. If the measured electron number density is higher than that calculated with this criterion, the only conclusion that can be drawn is that LTE conditions *may exist*, depending upon the outcome of additional tests, which are necessary to complete the characterization.

(ii) It is important to realize that the checking of LTE criteria may be successful for some elements but may fail for others.

(iii) Unless other calculations or measurements are performed, reporting n_e values calculated with McWhirter's equation as a test of the existence of LTE conditions in LIBS should be discouraged.

(iv) Considering the characteristics of many laser-induced plasmas, the right question should be not whether equilibrium conditions exist, but rather how far we are from equilibrium.

(v) Modeling should include kinetic reactions and considerations.

The examples reported in the various sections referring to stationary homogeneous, inhomogeneous and transient plasmas suggest the experiments that would be needed in order to check the validity of the other criteria regarding the relaxation time and the variation length of the parameters in the plasma, e.g., the achievement of spatially and temporally resolved profiles of temperature, electron number density and atom/ion number density from locally resolved observations of the emission signals on selected atomic/ionic transitions, the measurement of ion/neutral ratios, the experimental evaluation of the *b-parameter*, and the diffusion coefficients of atoms and ions.

Finally, one can note that, in addition to emission measurements, absorption and fluorescence measurements are capable of providing data such as plasma expansion velocity, absolute number density of atoms and ions in selected levels, and relaxation times due to both radiative and collisions processes. Interestingly, it seems inevitable to conclude that the experimental efforts need to be refined as well as (if not more than) the theoretical simulation and modeling efforts.

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