Achievement of local thermodynamic equilibrium for
ns laser-induced plasmas on aluminium sample at
different wavelengths

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Abstract. The Collisional-Radiative model CoRaM-Al is elaborated and implemented in a 0D numerical approach in the purpose of describing the formation of the plasma resulting from the interaction between a $\tau = 4$ ns Nd:YAG laser pulse and an aluminium sample in vacuum. The influence of the four harmonics at 266, 355, 532 and 1064 nm on the behavior of the nascent plasma is studied. In each case, the fluence is set equal to the threshold above which a phase explosion takes place (fluence of 7.7, 7.4, 6.8, 5.1 J cm$^{-2}$ in order of increasing wavelength). The model takes into account free electrons and excited states of Al, Al$^+$, Al$^{2+}$ and Al$^{3+}$. Both groups of particles are characterized by their translation temperature in thermal non-equilibrium. Besides, each population density is assumed to be in chemical non-equilibrium and to behave freely through the involved seven elementary processes (electron impact induced excitation and ionization, elastic collisions, multiphoton ionization, inverse laser Bremsstrahlung, direct thermal Bremsstrahlung and spontaneous emission). Atoms passing from the sample to the gas are described by considering classical vaporization phenomena (governed by the Hertz-Knudsen law) so that the surface temperature is limited to values less than the critical point ($T_c = 6700$ K). The relative role of the elementary processes is discussed and the time-evolution of the excitation of the species is analyzed for the four considered wavelengths. This study allows to determine the different excitation temperatures as well as their evolution in time. Thus the conditions required for the achievement of the Local Thermodynamic Equilibrium can be precisely described.

1. Introduction

Large intentions are dedicated to the laser-matter interaction since the development of the technology of the ultra-short laser sources. The plasma results from the absorption of the laser light by the ejected matter. This so-formed plasma radiates lines which can lead through spectroscopic analysis to the identification of the components of the sample: the derived diagnostic method is called LIBS (Laser Induced Breakdown Spectroscopy) [1]. During the last years, different calibration free procedures have been elaborated [2] which has led to the considerable improvement of the LIBS technique. However, the Local Thermodynamic Equilibrium seems to be systematically assumed in the purpose of deriving the elementary composition of the sample [3, 4]. This hypothesis is still largely discussed [5] and conditions to obtain LTE have to be clearly understood to estimate its validity. Indeed, the laser-induced plasmas are characterized by strong radiative losses and by high expansion velocities. As a
result, these plasmas can be in strong non-equilibrium and this non-equilibrium state can last several hundreds of nanosecond after the laser-sample interaction.

Two important consequences can be deduced in the case of a thermodynamic non-equilibrium plasma:

- the equation of state is not valid and considering neutrals and ions excited states as independent species is mandatory,
- the different states number densities do not fulfill the Boltzmann distribution. As a consequence, optical emission spectroscopy experiments do not allow the determination of the ground state number density.

Accordingly, a Collisional-Radiative (CR) model is an appropriate tool to show how the plasma reaches equilibrium. In particular, the time required to reach thermodynamic equilibrium can be obtained.

The present communication put forward the description of the model and the balance equations used. Then, results for the four wavelengths (266, 355, 532 and 1064 nm) are given and discussed.

2. Description of the model

The work reported in the present paper is focused on the ignition process of the plasma in case of irradiance weak enough to avoid any phase explosion, which means that the highest temperature of the target surface is the critical temperature. For aluminium, the critical temperature has been estimated to $T_c = 6700$ K [6]. However, the irradiance has to be sufficiently high to ignite the plasma. As a consequence, two thresholds of the laser fluence can be observed. The first one corresponds to the minimum value leading to the breakdown. For aluminium, this threshold ($F_0 \approx 1$ J cm$^{-2}$) weakly depends on the laser wavelength [7, 8]. The second threshold, $F_1$ corresponds to the observation of an explosion phase and the surface temperature reaches $T_c$. This threshold depends on the laser wavelength as summarized by table 1.

This explosion phase is also characterized by the formation of droplets [13]. Between $F_0$ and $F_1$, the interface melts first, then evaporates and the produced vapor ionizes. The formed plasma radiates and its spectra can be analyzed.

The laser-matter interaction described above is far from being fully understood even with $F \in [F_0, F_1]$. In particular, the mechanism leading to an excitation equilibrium is not well known. This question is crucial because the treatment of LIBS signals is generally based on equilibrium assumptions [14]. The present contribution reports the elaboration of a two-temperatures CR model devoted to the verification of these assumptions in the case of a laser pulse impinging an aluminium sample [12]. The plume expansion is controlled mainly by the laser energy, while the spot diameter weakly influences the plasma development [15]. So, in our model, the spot diameter is fixed at $d = 1$ mm and the pulse energy is calculated by the equation $E = \pi d^2 F/4$.

| $\lambda$ (nm) | $F_1$ (J cm$^{-2}$) | Ref.          |
|--------------|---------------------|---------------|
| 1064         | 5.1                 | [7], [9], [10]|
| 532          | 6.8                 | [7], [11]     |
| 355          | 7.4                 | [12]          |
| 266          | 7.7                 | [12]          |
where the fluence is wavelength-dependent. The pulse time is fixed at $\tau = 4$ ns. This CR model takes into account the seven main elementary processes (electron impact-induced excitation and ionization, elastic collisions, multiphoton ionization, inverse laser Bremsstrahlung, direct electron Bremsstrahlung and spontaneous emission) influencing the number density of the 107 states of Al, Al$^+$, Al$^{2+}$ and Al$^{3+}$ considered in the model.

The studied test-case corresponds to the classical interaction between a nanosecond Nd:YAG laser pulse assumed of the Gaussian type and an aluminium sample. The conservation equations governing the heating (melting, then vaporization) of the sample are not solved. The surface temperature $T_s$ is assumed to follow in time a similar Gaussian evolution with a maximum $T_{\text{max}}$ less than the critical temperature $T_c = 6700$ K [6]. Moreover, the atoms flux density $\varphi_A$ emerging from the interface is assumed to follow the Hertz-Knudsen law with a saturated vapor pressure given at $T_s$ [16]. These atoms form the Knudsen layer whose characteristics allow a free expansion of the vapor according to a velocity close to the thermal mean velocity [17].

In order to avoid wasteful calculations, the number of aluminium excited states is reduced with respect to the actual states. Levels of close energy are grouped according to their core configuration. The resulting energy spectrum contains finally 106 fictitious levels which are listed in [18].

The dynamics of these states results from the following elementary processes which are completely detailed in [12].

(i) **Multiphoton ionization (MPI).** The vapor produced by the heated sample can be ionized by multiphoton ionization. This process is taken into account under the form proposed by Müsing et al. [19]

$$\sigma_{MPI}^{(k)} = \frac{\sigma_1 \nu}{(k-1)! (h\nu^2)^k}$$

where $\sigma_1$ is calculated by the form given by Zel’dovich and Raizer [20]

$$\sigma_1 = \frac{64 \pi^4 e^{10} m_e}{3\sqrt{3} (4\pi\epsilon_0)^3 h^5 c \nu^3} \frac{E_{ioni}^{5/2}}{E_{ioni}^{Z} (E_{ioni}^{H})^2}.$$  \hspace{1cm} (2)

In equation (2), the different values of $\sigma_1$ and $\sigma_{MPI}^{(k)}$ are calculated for the four wavelengths considered in table 1. Table 2 summarizes the characteristics of the multiphoton ionization process (3) considering only ground states.

$$Al_0 + k h\nu \xrightarrow{\sigma_{MPI}^{(k)}} Al_0^+ + e^-$$  \hspace{1cm} (3)

| $\lambda$ (nm) | $E_{ph}$ (eV) | $k$ | $k h\nu - E_{ioni}$ (eV) | $\sigma_1$ (m$^2$) | $\sigma_{MPI}^{(k)}$ (m$^{2k}$ W$^{-k}$ s$^{-1}$) |
|----------------|---------------|-----|--------------------------|------------------|--------------------------|
| 1064.48        | 1.17          | 6   | 1.00                     | $2.44 \times 10^{-19}$ | $2.35 \times 10^{-24}$ |
| 532.24         | 2.33          | 3   | 1.00                     | $3.05 \times 10^{-20}$ | $8.59 \times 10^{-34}$ |
| 355.83         | 3.49          | 2   | 1.00                     | $9.04 \times 10^{-21}$ | $3.08 \times 10^{-19}$ |
| 266.12         | 4.66          | 2   | 3.33                     | $3.81 \times 10^{-21}$ | $2.31 \times 10^{-20}$ |
The residual energy transferred to electron is also calculated in the fourth column of table 2. We can notice the same value (1 eV) in case of 1064, 532 and 355 nm. As a consequence, the electron temperature will reach 7750 K at maximum through multiphoton ionization effect only.

(ii) Inverse Bremsstrahlung (IB). Inverse Bremsstrahlung phenomenon heats the electron gas during the laser pulse. The electron-ion [20] and electron-neutral [21] inverse Bremsstrahlung are accounted for.

(iii) Thermal Bremsstrahlung (TB). Thermal Bremsstrahlung corresponds to the emission of photons at wavelengths different from the laser one by electrons in interaction with heavy particles. A continuum is then emitted at early times. Its contribution is accounted for [20, 22, 23, 24].

(iv) Electron-induced excitation (EE) and ionization (EI). The increase in electron temperature \( T_e \) and density \( n_e \) promotes electron-induced excitation and ionization. The forms proposed by Drawin [25] for the cross sections (depending on the angular momentum quantum number \( \ell \)) are used.

(v) Elastic collisions (EC). Owing to the increase in \( T_e \) by MPI and IB processes, thermal non equilibrium between heavies (with the temperature \( T_A \)) and electrons occurs. The resulting elastic collisions play a role and the form given by Decoster et al. [26] is adopted for their contribution.

(vi) Spontaneous emission (SE). The increase in the excited states population density promotes spontaneous emission. The related probabilities obtained from the NIST database [27] are used and corrected by an escape factor resulting from the optical thickness of the plasma [28]. Escape factors are calculated assuming a Stark line broadening.

All the related data are further described in previous paper [12] and [18].

3. CR model and balance equations

The previous elementary processes are involved in the collisional-radiative source term of the classical balance equation [29] where the atom flux resulting from the vaporization is taken into account. The electrons and heavies energy balance equations are separated but coupled (cf. [18]). Finally, the following equations are obtained

\[
\frac{dT_e}{dt} = \frac{2}{3k_B n_e} \left( P_{ee} + \frac{\varphi_{ee}}{\Delta(t)} \right) - \frac{3}{2} k_B T_e \frac{dn_e}{dt} \tag{4}
\]

\[
\frac{dT_A}{dt} = \frac{2}{3k_B \sum Z,i [Al_i^{2+}]} \left[ P_{eA} + \frac{\varphi_{eA}}{\Delta(t)} - \sum_{Z,i} \left( \frac{3}{2} k_B T_A + E_{Z,i} \right) \frac{d[Al_i^{2+}]}{dt} \right] \tag{5}
\]

\( \varphi_{eA} \) and \( \varphi_{ee} \) are the ablation rate for heavy particles and electrons, respectively. \( \Delta(t) \) is the instantaneous thickness of the plasma layer, and \( P_{eA} \) and \( P_{ee} \) are the source terms involving the elementary processes listed in section 2.

In the upcoming sections, the following terms will be discussed.

- \( \Theta_e(CRP) = \frac{P_{ee}}{3k_B n_e} \), the contribution of the Collisional-Radiative elementary Processes (CRP) to the derivative of \( T_e \),
- \( \Theta_e(\varphi) = \frac{\varphi_{ee}/\Delta(t)}{\frac{3}{2} k_B n_e} \), the contribution of vaporization,
4. Results

4.1. Temperatures

The temporal evolution of $T_A$ and $T_e$ are displayed in Figure 1 for $\lambda = 266$ and 355 nm in Figure 2 for $\lambda = 532$ and 1064 nm. Two trends can be distinguished.

• Before the maximum irradiance, the electron temperature reaches a maximum which corresponds to the residual energy transferred to electron through multiphoton ionization process. The maximum is 8000 K for the 355 and 532 nm case and 26000 K for the 266 nm case. For $\lambda = 1064$ nm there is no increase in $T_e$ and a strong coupling between $T_A$ and $T_e$ is observed.

• After the maximum irradiance, increasing the wavelength leads to the same behavior of $T_A$ and $T_e$ for $\lambda = 266$, 355 and 532 nm, whereas their strong increase is observed for $\lambda = 1064$ nm. In this case, $T_A$ and $T_e$ exceed 9000 K after the laser pulse with a maximum at 13,500 K for $T_e$. For the three other cases, $T_A$ and $T_e$ remain lower than 9000 K.

Figure 1. Time-evolution obtained for $T_A$, $T_e$ and $T_S$ (top) and irradiance $\varphi_{\text{las}}$ (bottom) calculated to avoid explosion phase when $\lambda$ evolves between 266 nm (continuous lines) and $\lambda = 355$ nm (dashed lines).

Figure 2. Same as figure 1, but for $\lambda = 532$ nm (continuous lines) and $\lambda = 1064$ nm (dashed lines).
We can analyze these results using $\Theta_e$ and $\Theta_A$. Figures 3, 4, 5 and 6 display the evolution in time of their different contributions for $\lambda = 266$, 355, 532 and 1064 nm, respectively. We can see that evolution of $\Theta_A$ for $\lambda = 1064$ nm, a competition takes place after 10 ns among the processes electron-induced excitation, elastic collisions and spontaneous emission. Whereas in other cases, the cooling is due to elastic collisions with electrons ($T_e < T_A$). However in all cases, for $t \leq 10^{-8}$ s, the evolution mainly results from the evaporation and from the translational energy storage. From a transversal view of the term $\Theta_e$, we can see that multiphoton ionization takes place before inverse Bremsstrahlung. In addition, the role of MPI decreases as $\lambda$ increases, whereas the one of IB increases. Table 3 summarizes the maximum of $\Theta_e(MPI)$ and $\Theta_e(IB)$ and the corresponding time. We can see that the heating of the electron gas is due to multiphoton ionization at the pulse onset in the UV range, and to inverse Bremsstrahlung in the IR range after the maximum irradiance. Besides, figures 3, 4, 5 and 6 point out that the electron gas cooling is mainly due to excitation under electron impact (EE) for $t > 10^{-8}$ s. We can also notice that, for $t > 2 \times 10^{-8}$ s, elastic collisions (EC) play a significant role on the evolution of $T_e$. These collisions lead to the thermal equilibrium observed for $t \approx 10^{-7}$ s.
4.2. Population densities

Figures 7 and 8 display the evolution in time of the number densities of electrons and of main atomic and ionic excited states for \( \lambda = 266, 355, 532 \) and 1064 nm. Starting from very small values due to the evaporation of the sample at its melting point, the number densities strongly increase over ten orders of magnitude until \( t \approx 10^{-8} \) s. At this time, the critical temperature is reached for the sample. The total number density is then of \( 2.5 \times 10^{26} \text{ m}^{-3} \). In the subsequent part of the evolution, the amplitude of the variations is much lower. The cases at \( \lambda = 266, 355 \) and 532 nm are very close. Despite a slight delay in ionization for \( \lambda = 532 \) nm with respect to the cases at \( \lambda = 266 \) and 355 nm, the electron number density approximately reaches \( 2 \times 10^{24} \text{ m}^{-3} \) for \( \lambda = 266 \) nm and \( 4 \times 10^{24} \text{ m}^{-3} \) for \( \lambda = 355 \) and 532 nm at the end of the pulse. The ionization degree is then slightly lower than 0.02. On the other hand, electron number density is higher by one order of magnitude (\( 4 \times 10^{25} \text{ m}^{-3} \)) at the end of the pulse at \( \lambda = 1064 \) nm. This is due to the increase in \( T_e \). Electrons then have enough energy to ionize atoms, as illustrated by figure 6. They are also responsible for the production of \( \text{Al}^{2+} \) and \( \text{Al}^{3+} \), the density of which reaches \( 10^{21} \text{ m}^{-3} \) and \( 10^{12} \text{ m}^{-3} \) at \( t \approx 1.3 \times 10^{-8} \) s, respectively. The \( \text{Al}^{2+} \) and \( \text{Al}^{3+} \) densities are totally negligible for the other wavelength cases. Globally, the densities increase with time except for the case at \( \lambda = 1064 \) nm where we can notice an evolution of the first excited states population density of Al after the maximum irradiance due to recombination of ions.

### Table 3. Time of the maximum of \( \Theta_e(MPI) \) and \( \Theta_e(IB) \) and related values for \( \lambda = 355, 532 \) and 1064 nm.

| \( \lambda \) (nm) | Multiphoton ionization | Inverse Bremsstrahlung |
|-------------------|------------------------|------------------------|
|                   | \( t_{\text{max}} \) (ns) | \( \Theta_e(MPI) \) (K s\(^{-1}\)) | \( t_{\text{max}} \) (ns) | \( \Theta_e(IB) \) (K s\(^{-1}\)) |
| 266               | 7.2                    | \( 3.9 \times 10^{14} \) | 10.7 | \( 2.8 \times 10^{13} \) |
| 355               | 7.2                    | \( 1.2 \times 10^{14} \) | 10.7 | \( 4.9 \times 10^{13} \) |
| 532               | 6.9                    | \( 6.5 \times 10^{13} \) | 10.7 | \( 9.3 \times 10^{13} \) |
| 1064              | 9.8                    | \( 1.4 \times 10^{12} \) | 11.0 | \( 3.7 \times 10^{14} \) |
Figure 9. Temporal evolution of the excitation temperatures $T_{\text{Al}(6-19)}$, $T_{\text{Al}^+ (66-79)}$, $T_{\text{Al}^{2+} (99-106)}$ and of the ionization temperatures $T_{i(\text{Al})}$ and $T_{i(\text{Al}^+)}$ calculated with Eqs.(6) and (7) for a laser pulse at $\lambda = 266 \text{ nm}$.

Figure 10. Same as figure 9, but for $\lambda = 355 \text{ nm}$.

Figure 11. Same as figure 9, but for $\lambda = 532 \text{ nm}$.

Figure 12. Same as figure 9, but for $\lambda = 1064 \text{ nm}$.

4.3. Excitation and ionization temperatures

This model allows to calculate in time the different excitation temperature and ionization temperature. Therefore, the departure of the plasma from chemical equilibrium can be estimated. The excitation temperature $T_{X(i_{\text{min}}-i_{\text{max}})}$ for the species $X$ is calculated by

$$T_{X(i_{\text{min}}-i_{\text{max}})} = - \frac{1}{k_B} \left[ \frac{d}{dE_i} \left( \ln \frac{N_i}{g_i} \right) \right]_{sl_{i_{\text{min}} < i < i_{\text{max}}}}$$

where $sl$ means that the derivative is the slope of the least squares line over the excited states interval $i_{\text{min}} < i < i_{\text{max}}$. $E_i$ and $g_i$ are the excitation energy and the statistical weight of the level $i$. The ionization temperature $T_{i(\text{Al}(Z+))}$ is calculated by
The behavior of a plasma produced on an aluminium sample by either one of the Nd:YAG harmonics laser source in nanosecond regime is modeled by using a 0D approach involving the Collisonal-Radiative (CR) model CoRaM-Al. Free electrons and heavy species temperatures are assumed different. About hundred excited states of Al, Al$^+$, Al$^{2+}$ and Al$^{3+}$ are considered. These species are assumed to behave freely through seven different collisional and radiative elementary processes. A simplified approach is adopted: the interface temperature evolves like the laser irradiance and the target surface temperature reaches the critical temperature, therefore the maximum level avoiding the explosion phase.

5. Conclusion

The behavior of a plasma produced on an aluminium sample by either one of the Nd:YAG harmonics laser source in nanosecond regime is modeled by using a 0D approach involving the Collisonal-Radiative (CR) model CoRaM-Al. Free electrons and heavy species temperatures are assumed different. About hundred excited states of Al, Al$^+$, Al$^{2+}$ and Al$^{3+}$ are considered. These species are assumed to behave freely through seven different collisional and radiative elementary processes. A simplified approach is adopted: the interface temperature evolves like the laser irradiance and the target surface temperature reaches the critical temperature, therefore the maximum level avoiding the explosion phase.

$T_{i(Al^{Z+})} = \frac{E_{i}^{(Z+)}(Al)}{k_B \ln \left[ 2 \frac{g_0^{(Z+)}(Al)}{g_0^{(Z+)}(Al)} \frac{[Al]^{(Z+)}(Al)}{[Al]^{(Z+)}(Al)} \frac{2 \pi m_e k_B T_{i(Al^{Z+})}}{\hbar^2} \right]^{3/2}}$

where $g_0^{(Z+)}$ and $[Al]^{(Z+)}$ are the statistical weight and the density of the ground state of $Al^{(Z+)}$, respectively.

Equation (7) indicates that the ionization temperature is calculated using an iterative procedure. $T_{i(Al)}$ is the temperature of the plasma at equilibrium having the same ratio between number densities of Al and Al$^+$ ground states.

Figure 9, 10, 11 and 12 illustrate the evolution in time of these characteristic temperatures for $\lambda = 266, 355, 532$ and 1064 nm, respectively. $T_A$, $T_e$ and $T_S$ are also displayed in order to facilitate comparisons. In spite of small integration time steps, some curves are noisy. At early times, the population number densities can be very small and strongly vary from a step to an other. Their evolution leads to strong variations of the characteristic temperatures despite the smoothing induced by equations (6) and (7). Despite this noise, couplings occur rapidly in each case. Before the maximum irradiance, the characteristic temperatures clearly depart from $T_e$. After this maximum, the coupling is obvious but takes more time for $T_{Al^{2+}}$ with respect to other excitation temperatures. This coupling results from the very high efficiency of collisions under electron impact.

We have stated that the coupling is obtained if the discrepancy between $T_e$ and $T_X(t_{i_{min}}-t_{i_{max}})$ or $T_{i(Al^{Z+})}$ is lower than 1000 K. The coupling is therefore observed at $t \approx 9.1 \times 10^{-9}$, $t \approx 9.1 \times 10^{-9}$, $9.6 \times 10^{-9}$ and $9.7 \times 10^{-9}$ s for $\lambda = 266, 355, 532$ and 1064 nm, respectively. This slight delay is correlated with the delay of $n_e$. When $n_e$ reaches $10^{23}$ m$^{-3}$, electron number density is high enough to induce the chemical equilibrium of the plasma. Radiative losses and transport phenomena are often responsible for departures from equilibrium [30, 31]. In the present case, despite the significant radiative losses illustrated by figure 6 at $\lambda = 1064$ nm and the sonic expansion of the plasma layer, electron number density is so high that the chemical equilibrium is fulfilled during almost the entire duration of the pulse.

These results extend the conclusions put forward in [18]. In this paper, the maximum temperature of the sample surface was assumed lower than in the present case. Indeed, the maximum temperature was set equal to 3900 K. Data of Alcock et al. [32] give a value of $7 \times 10^6$ Pa for the equilibrium vapor pressure $p_v$, whereas $p_v$ is almost equal to $4 \times 10^8$ Pa at $T_e = 6700$ K. As a result, the plasma density was lower at a value of $10^{25}$ m$^{-3}$ instead of some $10^{26}$ m$^{-3}$ in the present case. This increase in the plasma density leads to a higher collision frequency, to a higher absorption of the laser light and consequently to a higher electron number density. The efficiency of the electron-induced collisions is then higher, which explains the quasi equilibrium of the plasma in the present conditions for $t > 10^{-8}$ s. The plasma is formed by absorption of the laser light during the pulse and not from the direct ejection of electrons from the heated surface.
The results put forward the fundamental role played by vaporization from the interface and by multi-photon ionization in the formation of the plasma at lower wavelengths. The electron temperature depends weakly on inverse Bremsstrahlung phenomena in UV range and strongly depends on inverse Bremsstrahlung at 1064 nm. When the laser pulse ends, the relaxation of the plasma takes place until equilibrium mainly through electron-induced processes and elastic collisions.

We have previously mentioned that LIBS signals analysis is in part based on equilibrium hypotheses: in particular, the excitation is often assumed in equilibrium. The present CR model is a particularly suitable tool to verify the validity of this assumption. We have indeed derive excitation temperature and ionization temperature from our results. In the present conditions, equilibrium is reached rapidly due to the high electron density.

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