Temporal description of aluminum laser-induced plasmas by means of a collisional-radiative model

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Abstract. A 0D numerical approach including a Collisional-Radiative model is elaborated in the purpose of describing the behavior of the nascent plasma resulting from the interaction between a laser pulse \((\lambda = 532 \text{ nm}, \tau = 4 \text{ ns and } F = 6.5 \text{ J cm}^{-2})\) with an aluminum sample. The species considered are Al, Al\(^{+}\), Al\(^{2+}\) and Al\(^{3+}\) on their different excited states and free electrons. Both groups of particles are characterized by their translation temperature in thermal non-equilibrium state. Besides, each population density is assumed to be in chemical non-equilibrium and behaves freely through the seven involved elementary processes (electron impact induced excitation and ionization, elastic collisions, multi-photon ionization, inverse laser Bremsstrahlung, direct electron Bremsstrahlung and spontaneous emission). Atoms passing from sample to gas phase are described by considering classical vaporization phenomena so that the surface temperature is limited to values less than the critical point. The relative role of the elementary processes is discussed and the time-evolution of the excitation of the species is analyzed.

1. Introduction
The emergence of lasers at the beginning of the 1960’s provided the ability to diagnose solid samples by the LIBS (Laser-Induced Breakdown Spectroscopy) technique which consists in analyzing the spectra emitted by the plasma induced by interaction between a nanosecond laser pulse and a sample [1]. According to the level of the laser fluence \(F\), two thresholds can be observed. The first one corresponds to the minimum value to observe the breakdown \((F_0 \approx 1 \text{ J cm}^{-2} \text{ for aluminum [2]})\) and the second one corresponds to the observation of an explosion phase where the surface temperature reaches at least the critical point \((F_1 \approx 7 \text{ J cm}^{-2} \text{ [3]})\). This explosion phase is also characterized by formation of droplets [4]. Between \(F_0\) and \(F_1\), the interface melts first, then evaporates and the vapor produced is ionized. The plasma formed radiates and its spectra can be analyzed.

The underlined laser-matter interaction is far from being completely understood even when \(F \in [F_0, F_1]\). 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 [5]. The present contribution reports the elaboration of a two-temperatures Collisional-Radiative (CR) model devoted to the verification of these assumptions in the case of a laser pulse \((\lambda = 532 \text{ nm}, \tau = 4 \text{ ns and } F = 6.5 \text{ J cm}^{-2})\) impinging an aluminum sample [6]. This CR model takes into account the seven main elementary processes (electron impact induced excitation and ionization, elastic collisions, multi-photon ionization, inverse
laser Bremsstrahlung, direct electron Bremsstrahlung and spontaneous emission) influencing the number density of the 106 states of Al, Al\(^+\), Al\(^{2+}\) and Al\(^{3+}\) considered.

2. Al excited states, assumptions and processes

The test-case studied corresponds to the classical interaction between a nanosecond Nd:YAG laser pulse assumed of the Gaussian type on an aluminum sample. Equations modeling the heating (melting, then vaporization) of the sample are not solved. The surface temperature is assumed to follow such a Gaussian evolution in time with a maximum \(T_{\text{max}}\) less than the critical temperature \(T_c = 6700\) K [7]. Moreover, the atom flux density \(\varphi_A\) emerging from the interface is assumed to follow the Hertz-Knudsen law with a saturated vapor pressure given at \(T_s\) [8]. These atoms form the Knudsen layer whose characteristics allow a free expansion of the vapor according to a velocity close to the thermal heavies mean velocity [9].

In order to avoid wasteful calculations, the number of aluminum 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 part in table 1.

**Table 1.** Some of the aluminum states considered in the present CR model. No ”0” figures the species ground state. \(E\) is the energy, \(g\) is the statistical weight and \(\ell\) is the angular momentum quantum number.

| Species  | \(i\) | \(E\) (eV) | Core config. | \(g\) | \(\ell\) | Species  | \(i\) | \(E\) (eV) | Core config. | \(g\) | \(\ell\) |
|----------|------|-----------|-------------|------|-------|----------|------|-----------|-------------|------|-------|
| Al(Z=0)  | 0    | 0.0000    | 3s\(^2\)    | 2    | 1     | Al\(^{+}\)(Z=1) | 0    | 05.986    | 3s            | 1    | 0     |
|          | 2    | 0.143     | 3s\(^2\)    | 2    | 0     |            |      | 21.578    | 3s            | 12   | 1     |
|          | 6    | 0.827     | 3s\(^2\)    | 10   | 2     |            |      | 24.669    | 3s            | 14   | 3     |
|          | 12   | 0.600     | 3s\(^2\)    | 38   | 4     |            |      | 16.584    | 3p            | 5    | 1     |
|          | 18   | 0.963     | 3s\(^2\)    | 150  | 2     |            |      | 24.649    | 3p            | 15   | 2     |
|          | 19   | 0.608     | 3s 3p \(^3\)P  | 12   | 1     | Al\(^{2+}\)(Z=2) | 0   | 24.815    | 2p\(^6\)      | 2    | 0     |
|          | 26   | 0.772     | 3s 3p \(^3\)P  | 6    | 1     |            |      | 45.971    | 2p\(^6\)      | 2    | 0     |
|          | 32   | 0.636     | 3s 3p \(^3\)P  | 16   | 1     |            |      | 49.782    | 2p\(^6\)      | 10   | 2     |
|          | 36   | 0.019     | 3s 3p \(^3\)P  | 16   | 1     |            |      | 50.757    | 2p\(^6\)      | 64   | 5     |
|          | 41   | 0.481     | 3s 3p \(^3\)P  | 24   | 1     |            |      | 51.750    | 2p\(^6\)      | 54   | 5     |
|          | 42   | 0.369     | 3s 3p \(^1\)P   | 16   | 1     | Al\(^{3+}\)(Z=3) | 0   | 53.263    | 2p\(^3\)      | 1    | 1     |

The dynamics of these states results from the following elementary processes:

(i) multi-photon ionization (MPI). The vapor produced by the sample heating can be ionized by multi-photon ionization. This process is taken into account under the form proposed by Müsing et al. [10].

(ii) inverse Bremsstrahlung (IB). Inverse Bremsstrahlung phenomenon can heat electron gas during the laser pulse: its contribution is accounted for [11].

(iii) electron-induced excitation (EE) and ionization (EI). The increase of electron temperature \(T_e\) and density \(n_e\) promotes electron-induced excitation and ionization. The forms proposed by Drawin [12] for the cross sections (depending on the angular momentum quantum number \(\ell\), see table 1) are used.
(iv) elastic collisions (EC). Owing to the increase of $T_e$ 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. [13] is adopted for their contribution.

(v) spontaneous emission (SE). The increase of the excited states population density promotes spontaneous emission. The related probabilities obtained from the NIST database [14] are used and corrected by an escape factor resulting from the optical thickness of the plasma. Escape factors are calculated assuming a Stark line broadening.

(vi) electron thermal Bremsstrahlung (BE). The direct Bremsstrahlung [15] is also accounted for owing to its experimental observation at early time [16].

3. CR model and balance equations

The previous elementary processes are involved in the collisional-radiative term of the classical balance equation [17] where the atom flux resulting from the vaporization is taken into account. The electrons and heavies energy balance equations are coupled with the previous ones. We do not reproduce here any details (cf. [6]), but we obtain finally the following equations:

$$\frac{dT_e}{dt} = \frac{2}{3 k_B n_e} \left( P_e + \frac{\varphi_e(t)}{\Delta(t)} \right) - \frac{T_e}{n_e} \frac{dn_e}{dt}$$

$$\frac{dT_A}{dt} = \frac{2}{3 k_B \sum_{Z,i} [Al_{Z,i}^2]} \left[ P_A + \frac{\varphi_A(t)}{\Delta(t)} - \sum_{Z,i} \left( 3 \frac{k_B T_A + E_{Z,i}}{2} \right) \frac{d[Ai_{Z,i}^{2+}]}{dt} \right]$$

In these equations, $\varphi_e(t)$ is the electron flux density emerging from the surface, $\Delta(t)$ is the instantaneous thickness of the plasma layer, and $P_A$ and $P_e$ are the source terms involving the elementary processes listed in section 2.

4. Results

Two typical values for $T_{max}$ (3000 and 4000 K) are adopted. The resulting time-evolutions for $T_A$ and $T_e$ are displayed on figure 1. We observe two consecutive phases: the first one which corresponds to the plasma formation is followed by a second phase where the plasma recombines. The transition between both phases takes place when the laser flux is maximum. At long time, the thermal equilibrium is reached: $T_A$ and $T_e$ are equal when $t = \tau_{eq} \approx 1 \mu s$ with $T_{max} = 4000$ K and when $t = \tau_{eq} \approx 20 \mu s$ with $T_{max} = 3000$ K.

Figures 2a and 2b display the evolution in time of the elementary processes contributions to $dT_e/dt$ (figure 2a) and $dT_A/dt$ (figure 2b) in equations 1 and 2 when $T_{max} = 3000$ K.

We can notice the preponderant influence of the multi-photon ionization phenomena on $T_e$ during the plasma formation. The increase of $T_e$ is often ascribed to inverse Bremsstrahlung: we can see that IB phenomena play a minor role. Except MPI phenomena, the radiative processes can be considered as almost negligible: in particular, the contribution of electron thermal Bremsstrahlung is rather weak. Among the collisional contributions listed above, only superelastic electron-induced collisions and elastic collisions play a role: the first type of collisions promotes energy gain to the electron gas whereas the second type induces electron energy losses. Both types are almost counterbalanced: the $T_e$ decrease is slow.

The evolution of $T_A$ follows a different dynamics. Figure 2b shows the preponderance of the energy flux from the sample surface until the recombination starts. MPI phenomena do not play a noticeable role. This is common to all radiative phenomena: in particular, spontaneous emission is negligible. At long time, the elementary processes play on $T_A$ a reverse role with respect to the case of $T_e$. When the laser pulse ends, the interface is no longer acting on the
plasma. Electrons and heavies are alone: this situation leads to their mutual interaction and to thermal equilibrium owing to elastic collisions.

The characteristic time scale \( \tau_{eq} \) required to reach thermal equilibrium is shortened when \( T_{max} \) is higher. This is due to the higher levels of population obtained under these conditions. Figure 3 illustrates the influence of \( T_{max} \) on these levels. It is interesting to note that the maximum number density obtained for Al ground state with \( T_{max} = 3000 \, \text{K} \) is of \( 10^{23} \, \text{m}^{-3} \) approximately whereas this density reaches \( 10^{25} \, \text{m}^{-3} \) with \( T_{max} = 4000 \, \text{K} \). This strong increase of the plasma density when \( T_{max} \) is higher leads to the elastic collisions frequency increase and to an important reduction of \( \tau_{eq} \).

Moreover, figure 3 shows the absence of temporal symmetry between the production of the plasma and its recombination. The plasma is indeed formed during the increase of the laser flux
in few nanoseconds, whereas its recombination lasts some microseconds.

Figure 3 gives also an insight into the behavior of $n_e$ when $T_{max}$ increases. The maximum electron density is concomitant with the maximum laser flux. When $T_{max} = 3000$ K, this maximum corresponds to $n_e \approx 10^{22}$ m$^{-3}$ whereas $n_e \approx 10^{23}$ m$^{-3}$ with $T_{max} = 4000$ K. In both cases, the plasma ionization degree remains smaller than 10%. However, additional calculations performed with higher values of $T_{max}$ put forward the rapid increase of the ionization degree with the interface maximum temperature: the plasma can even be totally ionized.

It is worth to further analyze the elementary processes contribution. Figures 4a and 4b display their time-dependent influence on the Al and Al$^+$ ground states number density respectively. The time scales non symmetry between the plasma creation and relaxation is again observed. Besides, figure 4a illustrates the fundamental role played by vaporization from the sample. The atoms reaching the gas phase are then ionized through MPI phenomena. The end of the laser pulse induces the relaxation of the excited states: this relaxation plays a preponderant role in the Al ground state dynamics. Three-body recombination does not play a significant role and spontaneous emission remains a minor process owing to the escape factors weak value.

The Al$^+$ ground state behaves of course in a different way. The vaporization from the surface is not the main source of Al$^+$ ions: this role is in this case played by multi-photon ionization from the Al ground state. The electron-induced processes do not play a significant role, except after the end of the laser pulse. When $t \gg \tau$, the electron excitation of Al$^+$ decreases and the contribution of electron-induced ionization is negative: the plasma is recombining. All the time, spontaneous emission is totally negligible in the present case.

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 Boltzmann plots from our results at different delay times. Figures 5 and 6 illustrate the results obtained for Al and Al$^+$ respectively. The situation remains far from excitation equilibrium from early time until the laser pulse end. This is the result of the steep ionization of the gas under laser flux and of the interface vaporization. After, electron-induced collisions become sufficiently efficient for ensuring excitation equilibrium: the Boltzmann plot displays a characteristic linear distribution. Long after the pulse, we can note a weak decrease of the number densities well coupled to each other. In the same time, the depopulation of the Al$^+$ excited states is stronger owing to the plasma recombination (see figure 6). Even for Al$^+$, the
linear distribution is obvious. However, we have to comment cautiously these results owing to the large ranges over which they are shown: a seemingly linear form does not mean that equilibrium is necessarily reached. The excitation temperature $T_{exc}$ defined over a set $\Sigma$ of well coupled excited states \[17\] such that:

$$T_{exc}(Al^{Z+}) = -\frac{1}{k_B} \frac{d\ln([Al_i^{Z+}]/g_i)}{dE_i}\Sigma$$

allows a largely better estimate of the excitation state. Calculations show that $T_{exc}$ is approximately equal to $T_e$ for $t \geq 0.1 \mu s$: as a result, the excited states can be then considered in equilibrium with electrons.

5. Conclusion
The behavior of a plasma produced by a nanosecond laser pulse on an aluminum sample is modeled by using a 0D approach involving a Collisional-Radiative (CR) model. 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 in time independently of the laser flux.

The results put forward the fundamental role played by vaporization from the interface and multi-photon ionization in the formation of the plasma. Even if the electron parameters reach high levels, the influence of free electrons on this formation is rather weak in our conditions. The electron temperature depends weakly on inverse Bremsstrahlung phenomena. When the laser pulse ends, the relaxation of the plasma takes place until equilibrium mainly through electron-induced processes.

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