COLLISIONAL-RADIATIVE MODEL (CRM) TO DESCRIBE LASER ALUMINUM PLASMA

By

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Thesis

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TITLE: COLLISIONAL-RADIATIVE MODEL (CRM) TO DESCRIBE LASER ALUMINUM PLASMA

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Using the quasi-steady-state approximation, a collisional-radiative model (CRM) is developed for laser induced aluminum plasma to calculate the population density distribution of different aluminum energy levels, we also have investigated the effect of electron density, plasma temperature and escape factor on the departure of local thermodynamic equilibrium (LTE). To quantify the departure from the statistical equilibrium Saha decrement has been calculated for each level, we found that the higher energy levels show more statistical equilibrium behavior than the lower levels at the same conditions of electron density and temperature.

By calculating Saha decrement at different electron densities we found that LTE conditions were satisfied at higher values of electron densities ($10^{10}\text{ cm}^{-3}$), and higher values of electron densities will be required to maintain the equilibrium at higher values of escape factor.

In this model we considered collisional and radiative elementary processes affecting the population and depopulation of the aluminum 28 energy levels, taking into account electron collisional processes only, while atom-atom collisional processes have been neglected.

We have developed generic software to solve the model equations and analyze the generated data using java programing language; the developed software can be configured to model similar plasma systems other than aluminum plasma.
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## CONTENTS

### CHAPTER (1)

### INTRODUCTION

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>INTRODUCTION</td>
<td>11</td>
</tr>
<tr>
<td>1.1.1</td>
<td>Collisional-Radiative Model</td>
<td>14</td>
</tr>
<tr>
<td>1.1.2</td>
<td>Aluminum Industrial Application</td>
<td>15</td>
</tr>
<tr>
<td>1.1.3</td>
<td>Local Thermodynamic Equilibrium</td>
<td>17</td>
</tr>
<tr>
<td>1.1.4</td>
<td>Saha Decrement</td>
<td>18</td>
</tr>
<tr>
<td>1.1.5</td>
<td>Model Assumption</td>
<td>18</td>
</tr>
<tr>
<td>1.2</td>
<td>COLLISIONAL RADIATIVE PROCESSES</td>
<td>20</td>
</tr>
<tr>
<td>1.2.1</td>
<td>Electron Collision Reactions</td>
<td>20</td>
</tr>
<tr>
<td>1.2.1.1</td>
<td>Electron Excitation Reaction</td>
<td>21</td>
</tr>
<tr>
<td>1.2.1.2</td>
<td>Electron De-Excitation Reaction</td>
<td>22</td>
</tr>
<tr>
<td>1.2.1.3</td>
<td>Electron Ionization Reaction</td>
<td>22</td>
</tr>
<tr>
<td>1.2.1.4</td>
<td>Three-Body Recombination Reaction</td>
<td>23</td>
</tr>
<tr>
<td>1.2.2</td>
<td>Radiative Reactions</td>
<td>23</td>
</tr>
<tr>
<td>1.2.2.1</td>
<td>Photoexcitation Reaction</td>
<td>24</td>
</tr>
<tr>
<td>1.2.2.2</td>
<td>Radiative Decay Reaction</td>
<td>25</td>
</tr>
<tr>
<td>1.2.2.3</td>
<td>Photoionization Reaction</td>
<td>25</td>
</tr>
<tr>
<td>1.2.2.4</td>
<td>Photo Recombination Reaction</td>
<td>26</td>
</tr>
<tr>
<td>1.3</td>
<td>POPULATION DENSITY DISTRIBUTION</td>
<td>26</td>
</tr>
<tr>
<td>1.4</td>
<td>HISTORY OF COLLISIONAL-RADIATIVE MODEL</td>
<td>27</td>
</tr>
<tr>
<td>1.5</td>
<td>AIM OF THE WORK</td>
<td>28</td>
</tr>
</tbody>
</table>
CHAPTER (2)
MODELING WORK

2.1 RATE EQUATION ................................................................. 30
2.2 ELECTRON COLLISION REACTIONS ........................................... 31
  2.2.1 Collisional Excitation Reaction Rate ........................................ 33
    2.2.1.1 Optically Allowed Collisional Excitation ......................... 33
    2.2.1.2 Optically Forbidden Collisional Excitation ..................... 34
  2.2.2 Electron De-excitation Reaction Rate .................................... 36
  2.2.3 Collisional Ionization Reaction Rate .................................... 37
  2.2.4 Three-Body Recombination Reaction Rate ............................. 38
2.3 RADIATIVE REACTIONS ....................................................... 40
  2.3.1 Bound-Bound Transitions .................................................... 40
  2.3.2 Optical Escape Factor .......................................................... 41
  2.3.3 Free-Bound Transitions ....................................................... 42
    2.3.3.1 Radiative Recombination Rate ....................................... 42
2.4 POPULATION NUMBER DENSITY .............................................. 44

CHAPTER (3)
RESULTS AND DISCUSSIONS

3.1 ALUMINUM ENERGY LEVELS .................................................. 46
3.2 REACTION RATES ................................................................. 47
  3.2.1 Collisional Excitation and De-excitation ............................... 47
  3.2.2 Collisional Ionization and Three-Body Recombination ............. 53
3.2.3 Radiative Recombination ................................................................. 59
3.3 POPULATION DENSITY DISTRIBUTION ......................................... 63
  3.3.1 Saha Decrement ........................................................................ 73
3.4 ESCAPE FACTOR ........................................................................... 77

CONCLUSION ......................................................................................... 79

REFERENCES ....................................................................................... 81

APPENDIX A (LIST OF ABBREVIATIONS) ............................................. 90

APPENDIX B (NILES-CODE) ................................................................. 91

APPENDIX C (OUTPUT DATA) ............................................................... 97

ARABIC SUMMARY .............................................................................. 114
LIST OF FIGURES

Figure 1: Argon/Aluminum de-excitation rate coefficient ......................................................... 49
Figure 2: Electron/Aluminum de-excitation rate coefficient .......................................................... 49
Figure 3: Argon/Aluminum excitation rate coefficient ................................................................. 50
Figure 4: Electron/Aluminum excitation rate coefficient .............................................................. 50
Figure 5: Electron collisional excitation (cm³ s⁻¹) at electron density =1.0E15 cm³ and Temperature (2,000 to 20,000) K for different electronic transitions .............................................. 51
Figure 6: Collisional excitation rate coefficient (cm³ s⁻¹) at high temperature (20,000 to 300,000) K ................................................................................................................................................... 52
Figure 7: Collisional ionization rate coefficient at Nₑ =1.0E15 and temperature range (2,000 to 20,000) K .......................................................................................................................................... 54
Figure 8: Collisional ionization rate coefficient (cm³ s⁻¹) at high temperature (10,000 to 200,000) K .................................................................................................................................................. 55
Figure 9: Effective ionization rate coefficient of each charge state of carbon ............................... 55
Figure 10: Ionization rate coefficient for aluminum energy levels at temperature 6,000K and electron density of 1.0E15 cm⁻³ ................................................................................................................. 56
Figure 11: Three-body recombination rate coefficient (cm⁶ s⁻¹) at temperature (2,000 to 20,000) K for different excited levels ..................................................................................................................... 57
Figure 12: Three-body recombination rate for aluminum energy levels at temperature 6,000K and electron density 1.0E15 cm⁻³ .................................................................................................................. 58
Figure 13: Radiative recombination rate coefficient (cm³ s⁻¹) for different aluminum energy levels at temperature range [10,000 to 90,000 K]. ........................................................................................................ 61
Figure 14: Radiative recombination rate coefficient for aluminum energy levels at temperature 6,000K and electron density 1.0E15 cm⁻³ ...................................................................................................... 62
Figure 15: Population number density calculated by the presented model using NILES-CODE for different electron density temperature =6,000 K (N_e= 1.0E11 to 1.0E15 cm$^{-3}$) .......................... 66
Figure 16: Population number density calculated by the presented model using NILES-CODE for different electron temperature =6,000 to 12,000 K and electron density = 1.0E15 cm$^{-3}$ ........... 67
Figure 17: Population density for aluminum energy levels calculated by the presented model at temperature 6,000 K and Ne 1.0E7 (cm$^{-3}$)........................................................................................................ 69
Figure 18: Population density calculated by Saha law for aluminum energy levels at temperature 6,000 K and Ne 1.0E7 (cm$^{-3}$)........................................................................................................ 70
Figure 19: Population density for aluminum energy levels calculated by the presented model at temperature 6,000 K and Ne 1.0E14 (cm$^{-3}$)........................................................................................................ 71
Figure 20: Population density calculated by Saha law for aluminum energy levels at temperature 6,000 K and Ne 1.0E14 (cm$^{-3}$)........................................................................................................ 72
Figure 21: Saha Decrement for different aluminum levels at Temperature 6,000K and different Electron densities (cm$^{-3}$)........................................................................................................ 74
Figure 22: Saha Decrement for aluminum ground level and level number 25 as a function of electron density N_e. ........................................................................................................ 75
Figure 23: Saha Decrement at different temperatures at electron density =1.0E15 cm$^{-3}$........ 76
Figure 24: Saha Decrement for aluminum ground level as a function of electron density at different values of escape factor ($^\gamma$)........................................................................................................ 78
LIST OF TABLES

Table 1: Aluminum Energy Levels .............................................................................................................. 46
Table 2: Electron Collisional De-Excitation And Excitation Rate Coefficients At Low Temperature .................................................................................................................................................................... 48
Table 3: Experimental Results Obtained For The Fine Structure Relaxation And Excitation Of Aluminum By Atomic Argon Between 44.5 K and 137 K . ................................................................................................................. 48
Table 4: Fitting Parameters Used To Calculate Photoionization Cross Section ........................................ 60
CHAPTER 1

INTRODUCTION

1.1 Introduction

In the early sixties of the last century, shortly after the invention of the pulsed ruby laser in 1960, two big challenging branches of plasma science have been evolved; Laser Induced Breakdown Spectroscopy (LIBS) by Brech and Cross in 1962[1] and Collisional-Radiative Modeling by Bates et al.[2] in the same year.

The simplicity, accuracy, reproducibility of LIBS techniques and feasibility of rapid any multi-elemental analysis made LIBS as one of the most important elemental analysis techniques in industrial and environmental applications and in situ qualitative elemental analysis [3-7]. where it has been proved to be one of the most powerful techniques that can be used to perform surface analysis, it is capable of performing trace element measurements in any kind of solid material [8, 9] as well as in liquids [10,11]. The technique can be characterized as a non-destructive one and features high sensitivity and minimal sample preparation.

Optical fibres can be used to transfer the laser beam to the sample and the emitted light back to the spectrometer, so LIBS can be characterized today as a remote analytical technique that recently finds a lot of applications in
hostile environments, e.g. where radioactivity [12] or toxic samples [13] might be harmful to the working personnel.

Laser Induced Breakdown Spectroscopy in principle is the analysis of the spectra obtained from the evaporated elements of the plasma generated by a powerful pulsed laser focused on a surface, these spectra consist of lines corresponding to the evaporated elements present in the plume [14].

The process starts by evaporation of a tiny amount of the material by a powerful pulsed laser, and then the ionization process and plasma formation starts after further photon absorption.

Plasma emission is dependent on laser parameters and geometry [15] that has to be optimized in each individual case, and also on surface condition and thermal properties of the sample. The latest ones are known as “matrix effects” and affect the line intensity of an element embedded in a particular matrix.

The interaction of laser with solid targets consists of four different stages: the laser ablation of the target; plasma generation; laser interaction with the plasma and plasma expansion. The initiated expanding atomic plasma at high temperature (6,000 – 20,000 K), is ionized by the inverse bremsstrahlung and the photoionization processes, expanding rapidly (approximately at 10^6 cm/s) perpendicularly to the target surface [16]. During the expansion, the main mechanism of transition of bound electrons from the lower levels to the upper levels and vice versa is driven by inelastic collisions of electrons with heavy particles, while the concentration of charged particles is controlled by the electron impact ionization and three-body recombination of electrons with ions.
Radiative processes such as re-absorption, spontaneous and stimulated emission are also important in determining the concentration of emitting levels [17]

The results obtained from LIBS techniques are based on the assumption of existence of Local Thermodynamic Equilibrium (LTE) and optically thin plasma [18-20], considering the LTE condition for thermal plasma in stationary conditions is common approach but it cannot be applied without care to laser plasma, where the fast dynamics play a fundamental role. In laser induced plasma (LIP) all the energy is delivered during the laser pulse (a few ns) and then the system evolves spontaneously for several microseconds. The most part of initial energy is converted into kinetic energy so that the LIP expands with supersonic velocities (10⁵–10⁷ cm/s). Under these conditions the plasma parameters can change due to the expansion in a shorter time with respect to that necessary for the establishment of elementary processes balances [21]. The knowledge of the deviations from LTE is really important to understand the constraints and the corrections on theory to be taken into account for practical applications [22,23], this calls for the need of considering collisional-radiative models while studying the LIBS [24].

On the hand, collisional-radiative model was essential to obtain quantitative information about the elementary processes, kinetics of the population of atomic levels in plasma and distribution of population density of the different species of the plasma plume [25]. Binding both findings from LIBS and collisional-radiative model will give profound understanding on the plasma systems and the deviation of the excited levels populations from the LTE conditions.
1.1.1 Collisional-Radiative Model

Collisional and radiative reactions are the main factors affecting the population of the atomic and ionic levels of the different species in the plasma [26], each reaction is characterized by a respective cross-section signifying the strength of this reaction which in turn is function of different parameters controlling such reactions.

Studying these reactions together for the most relevant processes is the so called collisional-radiative models (CRM), which gives extensive diagnosis for the plasma as it provides great details for several aspects of the population kinetics for various regimes of the plasma parameters, for example it gives us the rate coefficient for each reaction, the population of exited levels and the factors affecting the departure of equilibrium state of plasma.

Modeling of the emission from laser-produced plasma is performed either with a co- or post-processor to the hydrodynamic codes or simply by assuming a single set of plasma parameters (i.e. electron density and temperature). Example of the co- or post-processor codes are FLY (time-dependent), RATION (steady state) and NMP [27], in the presented model we will use the plasma parameters assumption approach.

The main objective of the collisional-radiative models is to determine the population density distribution of a system in thermodynamic non-equilibrium. In the case of thermodynamic equilibrium, density distribution is well known and precisely given by Saha equation [28].
1.1.2 Aluminum Industrial Application

Aluminum is an essential contributor in the industry evolution as it has many industrial applications; for example, plasma coated aluminum engine blocks are being used by big car companies like Ford and Nissan instead of heavy cast iron sleeves. The plasma coating technique used a single conductive wire as "feedstock" for the system, a supersonic plasma jet melts the wire, atomizes it and propels it onto the substrate [29].

In aerospace/aeronautical industry, weight reduction and improved damage tolerance characteristics were the prime drivers to develop new family of materials. Aiming this objective, aluminum has been used in a new lightweight Fiber/Metal Laminate (FML).

The combination of aluminum and polymer composite laminates can create a synergistic effect on many properties. The mechanical properties of FML show improvements over the properties of both aluminum alloys and composite materials individually. Due to their excellent properties, FML are being used as fuselage skin structures of the next generation commercial aircrafts.

The moisture absorption in FML composites is slower when compared with polymer composites, even under the relatively harsh conditions, due to the barrier of the aluminum outer layers. Due to this favorable atmosphere, recently big companies such as Embraer, Aerospatiale, Boing, Airbus, and
so on, start to work with this kind of materials as an alternative to save money and to guarantee the security of their aircrafts [30].

Metal Matrix Composites (MMCs), as the name implies, have a metal matrix, aluminum is considered as an important component in such composites[31] where different plasma technologies have been utilized to improve the surface properties of fiber-reinforced composites, Rongzhi et al. studied the feasibility and characteristics of plasma technologies applied to fiber-reinforced polymer composites, the influence of various plasma treatments on the chemical and mechanical properties of different fibers as well as fiber-reinforced composites [32].
1.1.3 Local Thermodynamic Equilibrium

Plasma in complete thermodynamic equilibrium never happen in laboratories, rather it normally exists in interior of stars. Radiation usually escapes readily from plasmas thus leading to radiation fields inside the plasma below the Planckian radiant energy density. Nevertheless, at high plasma densities collisions will be so frequent, that they maintain steady-state population densities according to Boltzmann relation and a distribution of the ionization stages given by the Saha equation leading to the local thermodynamic equilibrium (LTE) [33,34].

Under the condition of local thermodynamic equilibrium and as mentioned above the radiation escape leading to loss in radiative energy within the system, but this loss is small compared to the energy exchange between material particles, so that Maxwell, Boltzmann and Saha relations are still valid locally. For the LTE condition only small variations of the system are admitted so that the times associated to the establishment of kinetic balances are smaller than that of the plasma variations [35]. Plasmas in LTE are sometimes synonymously referred to as collision dominated (CD). For complete LTE in steady-state plasma to prevail for the population densities of all levels of an ion, Griem [36] suggested that the electron collisional rate across the largest energy gap in the term system should be higher than the corresponding radiative rate by at least a factor of ten.

As the electron collision is the main process maintaining the plasma in the LTE state through balanced excitation and de-excitation reactions, the decrease of electron density decrease the collisions processes rate and the population of exited levels start to deviate from equilibrium starting with the
lower levels of large energy gaps, the higher excited levels will still be populated and show more equilibrium according to Saha equation more than the lower levels maintaining the Partial Local Thermodynamic Equilibrium (PLTE).

1.1.4 Saha Decrement

Comparing the population number density calculated by the presented model and by Saha equation representing the local thermodynamic state will delineate the onset of local thermodynamic equilibrium (LTE).

The ratio between both numbers for each level is known as Saha decrement, calculating such value will help us know the condition affecting the deviation from the equilibrium state and how each level will respond to these conditions as a function of electron density and temperature [37].

1.1.5 Model Assumption

In the presented model we are targeting the steady-state rather than the time-dependent regime, so time factor will not be considered for population density calculations.

Furthermore, we are considering the stationary-state approximation. This approximation is essentially a statement that the convection of excited-state
species is slow compared to the local rates of collisional and radiative processes [38].

Since electron collisions are much faster than atom collisions, they will establish and control the equilibrium, and hence we will neglect the effect of atom-atom collisions in our proposed model; atom-atom collision has to be considered if the condition

\[ n_a < \sigma_a^{a} v_a > \gg n_e < \sigma_e^{a} v_e > \]

is fulfilled [39], while this condition is not satisfied in the presented work.

*Where:*

- \( n_a \rightarrow \) density of atomic species
- \( \sigma_a^{a} \rightarrow \) atom/atom collision cross section
- \( v_a \rightarrow \) velocity of the atomic species
- \( n_e \rightarrow \) electron density
- \( \sigma_e^{a} \rightarrow \) electron/atom collision cross section
- \( v_e \rightarrow \) velocity of the electrons
1.2 Collisional Radiative Processes

Collisional and radiative processes are the basic of any collisional-radiative model, here we will go through each process in details, illustrating the transition process and the parameters controlling the rate coefficient for each reaction.

In typical CRM the following reactions are considered:

- **Electron collisional excitation** reactions out of level (i) to all other levels (j) where j>i
- **Electron collisional de-excitation** reactions out of level (j) to all other levels (i) where j>i
- **Electron collisional ionization** reactions out of level (i) to the ground state of the next ionization stage
- **Electron collisional three-body recombination** reactions from the ionization stage to level (i) of the neutral atom.
- **Radiative decay** reactions out of level (j) and into all other levels (i) where j>i
- **Radiative recombination** reactions from the ionization stage to level (i) of the neutral atom.

1.2.1 Electron Collision Reactions

Electron collision with different species is the most effective reaction controlling the population of the different levels of such species;