CHAPTER 1

COLLISIONAL-RADIATIVE
MODEL IN NON EQUILIBRIUM HIGLY IONIZED PLASMAS

1.1 Introduction

The collisional-radiative (CR) model is an effective theoretical basis for the calculation of the excited level populations (atomic or ionic), volume recombination and ionization coefficients and relaxation times necessary for establishing quasi-stationary state population in non equilibrium, partially (or highly) ionized plasmas. A self-consistent solution for the excited level populations and the quantities mentioned above requires a simultaneous solution of the system of the rate equation for the level populations and the Boltzmann equation determining the electron energy distribution function (EEDF).

To obtain a generalized solution of the problem indicated it is necessary to impose some simplifying assumptions on the coupling of the rate
equations and the Boltzmann equation. One of the fundamental assumptions made in almost all extensive computations based on realistic atom models is the use of the Maxwellian EEDF [12]-[15]. However, it is shown by many authors that this assumption is not justified for a wide range of physically conditions in various gases.

The EEDF is obtained by the solution of the Boltzmann equation. In this approach, the effects of electric and magnetic fields, space gradients and flow conditions on free electrons can be investigated. In this work, only the electric field is considered. The parameter which characterizes the shape of the distribution function is the reduced electric field, E/N, where E is the electric field and N is the plasma density. The electric field, or a generic external force, in fact, accelerates free electrons giving them a privileged motion direction. The effect is the generation of anisotropy of the velocity distribution function. On the other hand, collisions with heavy particles tend to redistribute the motion of free electrons in all space directions reducing the anisotropy. Many other terms can influence the shape of distribution function. The electron-electron collisions, for example, play a very important role because are responsible of a redistribution of the total electron kinetic energy and tend to establish the Maxwell distribution. In contrast, inelastic collisions cause loss of energy and can be treated as sinks. When the anisotropy of the velocity distribution function is small, the two-terms spherical harmonic expansion of the distribution function is applicable. This approximation limits the simulation conditions at plasmas with low rates of E/N (about $10^3$ Td, where $1\text{Td} = 10^{-17}\text{V/cm}^2$) [1]-[11]. When the distribution function is calculated, the transport coefficients, as drift velocity, ionization coefficient and electron mobility, can be evaluated.
1.2 The Boltzmann equation

The quantity of interest in Boltzmann’s equation is the one-particle distribution function $f = f(\bar{v}, \bar{x}, t)$. The function $f$ is defined so that $n_0 f \bar{d} \bar{x} \bar{d} \bar{v}$ is the number of particles in the phase-space volume element $d \bar{x} d \bar{v}$ at a time $t$. The normalization condition is that the local probable number density of particles at a point in space is

$$n(\bar{x}, t) = n_0 \int f(\bar{v}, \bar{x}, t) d \bar{v} \quad (1.1)$$

where for non uniform systems, $n_0$ is the average particle density. For homogeneous systems, the (1.1) becomes:

$$\int f(\bar{v}, \bar{x}, t) d \bar{v} = 1 \quad (1.2)$$

Let’s consider the number of particles $dn = n_0 f(\bar{v}, \bar{x}, t) \bar{d} \bar{x} \bar{d} \bar{v}$ in the phase-space volume. In the absence of interparticle interactions, the particle coordinates in a time $\delta t$ change to

$$\begin{cases} 
\bar{x}' = \bar{x} + \bar{v} \delta t \\
\bar{v}' = \bar{v} + \left( \frac{\bar{F}}{m} \right) \delta t
\end{cases} \quad (1.3)$$

where $\bar{F}$ is any external force field that acts to the particles (gravity, electromagnetic forces).
In the time $\delta t$ several collisions occur, some of which scatter particles into the velocity interval $d\vec{v}$ and some out of $d\vec{v}$ (see figure 1.1).

![Figure 1.1 - Schematic representation of the motion of an infinitesimal volume element in single-particle phase space volume.](image)

Writing the rate at which the collisions change $f$ and taking into account the effect of the collisions, the following equation is derived:

$$\frac{\partial(nf)}{\partial t} + \vec{v} \cdot \text{grad} (nf) + \frac{\vec{F}}{m} \cdot \text{grad} (nf) = \sum \left( \frac{\delta (nf)}{\delta t} \right)_{\text{coll},j}$$ (1.4)

This is the **Boltzmann equation** and determines the velocity distribution of the particles. The right-hand term is called *collision integral*. The sum is extended at each type of collision (electron-electron collisions, ionizations, excitations, ...) considered.

Once that the Boltzmann equation is solved and the distribution function is calculated, some plasma properties, as mean velocity $v_m$ (or
mean energy) and drift velocity $v_{d,\alpha}$ expressed by the following equations (1.5), are evaluated:

$$v_m = \int_{-\infty}^{+\infty} v f(v) d^{-1}v$$

$$v_{d,\alpha} = \int_{-\infty}^{+\infty} v_d f(v) d^{-1}v$$

(1.5)

(1.6)

1.3 The collision integrals

1.3.1 Elastic collisions: general formulation

For elastic collisions between neutral particles or between neutral and charged particles, the evaluation of the collision terms is straightforward, since it is sufficient consider only two-body collisions. For particle densities, in fact, less than standard density ($2.7 \times 10^{19} \text{ cm}^{-3}$), it is possible to assume the hypothesis of "molecular chaos," that is no correlation exists between the initial velocities of the two particles in a collision. For collisions between charged particles the long-range nature of the Coulomb potential is in contradiction to the previous condition, but, if the Coulomb potential is regarded as shielded or "cut-off" at the Debye length, the charged-body interactions can be treated as two-body collisions.

Let us consider collisions between particles of species 1 and 2. The rate of depleting collisions, (collision in which the particles are scattered out form the velocity volume element) is given directly by the collision frequency of particles of the velocity class in question with particles of species 1.
The differential rate per unit volume of depleting collisions is given by the following relation:

\[
dR^- = n_1n_2f_1(c)f_2(w)gI_{12}(g, \chi)d\Omega d^3wd^3c
\]  

(1.7)

where \( I_{12}(g, \chi)d\Omega \) is the differential cross section for scattering, \( g \) is the relative velocity and \( \chi \) is the scattering angle. The most convenient way of ordering replenishing collisions is through the consideration of inverse collisions. An inverse collision is defined as the collision in which the initial velocities of the two particles are equal to the final velocities of the direct collision. Furthermore, the velocity plane of the inverse collision is the same plane as that of the original collision and the deflection angle is taken as equal to the original scattering angle \( \chi \). Under these conditions, the velocities after the inverse collision will be equal to the velocities before the original collision. If \( c \) and \( w \) are the velocities before the inverse collision, the differential rate of the inverse collision is:

\[
dR^+ = n_1n_2f_1(c')f_2(w')gI_{12}(g, \chi)d\Omega d^3w'd^3c'
\]  

(1.8)

where for elastic collisions \( g = g' \). Combining equation (1.7) and (1.8), the collision integral for elastic collisions is:

\[
C_{12} = n_1n_2 \int \int \left[ f_1(c)f_2(w) - f_1(c')f_2(w') \right] gI_{12}(g, \chi)d\Omega d^3w
\]  

(1.9)

where \( d^3w'd^3c' = d^3wd^3c \).
The calculation of this collision integral is not trivial. The equation (1.9), in fact, as well depends of the distribution function $f_2$ of particles of type 2, and without any simplifications this term must be considered. In the next sections, the particle species referred as 1 are electrons.

1.3.2 Elastic electron-electron collisions: the Fokker-Plank term

The effects of charged-particle collisions result mainly from collisions in which the deflections, and hence velocity changes, of the particles are small. The predominance of small deflections in charged-particle collisions gives rise to the Fokker-Planck collision term. A first simplification in equation (1.9) is the expression of the cross section $I_{12}$ that assumes the Rutherford form:

$$I_{12}(\chi, g) = \left(\frac{|q_1 q_2|}{2 \pi e_0 m_{12}}\right)^2 \frac{1}{g^4 \sin^4\left(\frac{\chi}{2}\right)}$$

where $m_{12}$ is the reduced mass and $q_1, q_2$ are the electric charges. Since the effects of charged-particle collisions result mainly from collisions where the change in particle velocities is small, the functions $f_1(\vec{c})$ and $f_2(\vec{w})$ are expanded in a Taylor's series as follows:

$$f_1(\vec{c}) = f_1(\vec{c}) + \frac{\partial f_1}{\partial c_\beta}(c'_\beta - c_\beta) + \frac{1}{2} \frac{\partial^2 f_1}{\partial c_\beta \partial c_\gamma}(c'_\beta - c_\beta)(c'_\gamma - c_\gamma) + ...$$

$$f_2(\vec{w}) = f_2(\vec{w}) + \frac{\partial f_2}{\partial w_\beta}(w'_\beta - w_\beta) + \frac{1}{2} \frac{\partial^2 f_2}{\partial w_\beta \partial w_\gamma}(w'_\beta - w_\beta)(w'_\gamma - w_\gamma) + ...$$

(1.11)
Substituting the equations (1.11) into (1.9) and after some manipulations the usual term of the electron-electron collisions is obtained:

\[ C_{12} = n_1 n_2 \Gamma_{12} \left\{ -\frac{\partial}{\partial c_\beta} \left( f_1 \frac{\partial H}{\partial c_\beta} \right) + \frac{1}{2} \frac{\partial^2}{\partial c_\beta \partial c_\gamma} \left( f_1 \frac{\partial^2 G}{\partial c_\beta \partial c_\gamma} \right) \right\} \]  

(1.12)

where the function \( G \) and \( H \) are the so-called Rosenbluth potential and are defined as:

\[ H \equiv \frac{m_1}{m_{12}} \int g f_2 d^3 w \]  

(1.13)

\[ G \equiv \int g f_2 d^3 w \]

and \( \Gamma_{12} \equiv \frac{m_{12}^2}{m_1^2} g^4 Q_{i2}^{(1)} = \frac{m_{12}^2}{m_1^2} g^4 4\pi \left( \frac{q_1 q_2}{4\pi\varepsilon_0 m_{12} g^2} \right)^2 \log \Lambda \)

It should be noted that \( \Gamma_{12} \) is independent of the relative velocity \( g \). \( Q_{i2}^{(1)} \) is the momentum-transfer cross section. Equation (1.12) is the Fokker-Planck collision term.

**1.3.3 Elastic collisions: electron-heavy particles**

In an elastic collision between an electron and a heavy particle, as a result of the difference of mass of the two particles, the changes in the energy of the electron and in the velocity of the heavy particle are small. In addition since the electron velocity is typically much greater than that of the heavy particle, the relative velocity \( g \) is nearly equal to the electron
velocity \( \vec{c} \). The velocities of the two particles after a collision, expressed in terms of peculiar velocities, are

\[
\vec{c}' = \vec{c} - \frac{2m_h}{m_h + m_e}(\vec{g} \cdot \vec{k})\vec{k} = \vec{c} - \frac{2}{1 + m_e/m_h}(\vec{g} \cdot \vec{k})\vec{k}
\]  

(1.14a)

\[
\vec{w}' = \vec{w} + \frac{2m_e}{m_h + m_e}(\vec{g} \cdot \vec{k})\vec{k} = \vec{w} + \frac{2m_e/m_h}{1 + m_e/m_h}(\vec{g} \cdot \vec{k})\vec{k}
\]  

(1.14b)

where the subscript \( h \) denotes the heavy particle. The vector \( \vec{k} \) is a unit vector directed along the external bisector of the relative velocities \( \vec{g} \) and \( \vec{g}' \) before and after the collision (see figure 1.2).

**Figure 1.2** - Schematic representation of the collision plane.
Since \( \frac{m_e}{m_h} \) is small and \( g = \tilde{c} - \tilde{w} \equiv \tilde{c} \), the equations (1.14) are written by means of binomial series as:

\[
\begin{align*}
\tilde{c} &= \tilde{V} + 2 (\tilde{w} \cdot \tilde{k}) \tilde{k} + 2 \frac{m_e}{m_h} (\tilde{c} \cdot \tilde{k}) \tilde{k} + \ldots \\
\tilde{w} &= \tilde{w} + 2 \frac{m_e}{m_h} (\tilde{c} \cdot \tilde{k}) \tilde{k} - 2 \frac{m_e}{m_h} (\tilde{w} \cdot \tilde{k}) \tilde{k} + \ldots
\end{align*}
\]

(1.15a) (1.15b)

where the velocity \( \tilde{V} \) is defined by \( \tilde{V} \equiv \tilde{c} - 2 (\tilde{c} \cdot \tilde{k}) \tilde{k} \). As done for the electron-electron collision term, the functions \( f^e_1(\tilde{c}) \) and \( f^e_2(\tilde{w}) \) are expanded in a Taylor's series in term of \( \frac{m_e}{m_h} \). Finally, in order to eliminate the dependence from the relative velocity in the term \( g I_{eh}(g, \chi) \), it is necessary to write an expansion for this factor also. Substituting these expansions in the (1.9) and after some manipulations and simplifications, the following expression is obtained:

\[
C_{eh} = n_e \left[ f^e_1(\tilde{V}) - f^e_1(\tilde{c}) \right] \left[ \nu_{eh} - u_{h, \beta} \frac{\partial \nu_{eh}}{\partial c_{\beta}} + \frac{1}{2} \frac{k T_h}{m_h} \frac{\partial \nu_{eh}}{\partial c_{\beta} \partial c_{\beta}} \right] d\Omega_k - \\
- 2n_e \int_{\Omega_k} \frac{k_{\beta}}{\partial c_{\beta}} u_{h, \beta} \cdot \tilde{k} \nu_{eh} d\Omega_k + \\
+ 2n_e \frac{m_e}{m_h} \frac{\partial}{\partial c_{\beta}} \left[ \int_{\Omega_k} k_{\beta} f^e_1(\tilde{V}) \left[ c_{\gamma} + \frac{k T_h}{m_e} \frac{\partial f^e_1(\tilde{V})}{\partial c_{\gamma}} \right] \nu_{eh} d\Omega_k \right].
\]

(1.16)

The first part of the first term on the right-hand side of equation (1.16) represents the effect on \( f^e_c \) of scattering by infinitely massive heavy particles. The terms that involve \( k T_h \) and \( u_{h, \beta} \) reflect the effect of the thermal and diffusive motions of the heavy particles. The first part of the last term
represents the effect of the recoil of the heavy particles, which is a consequence of their finite mass. For practical purpose, several terms (in particular the derivatives of $\dot{\nu}_{ch}$) in equation (1.16) give no contribution, so that the application of $C_{ch}$ is less complicated.

### 1.3.4 Inelastic collisions: excitations

If the solution of Boltzmann equation is devoted to the determination of the distribution function of free electrons, an important simplification in the evaluation of the inelastic collision terms occurs. Because of the difference of mass of the two particles (electron and heavy particle), the velocity of the electrons is much higher than that one of heavy particles. So, the differential rate per unit volume for the excitation is:

$$dR^- = n_j N_j \int \sigma_j(v, \chi) v f(v) d\Omega d^3v$$

(1.17)

where $\sigma_j(v, \chi) d\Omega$ is the differential excitation cross section. After the collision, the electrons are scattered out of the velocity volume element $d^3v$. So, the equation (1.17) corresponds to the depleting term.

At the same way, considering the electrons that are scattered into $d^3v'$, the following expression is obtained:

$$dR^+ = n_j N_j \int \sigma_j(v', \chi) v' f(v') d\Omega d^3v'$$

(1.18)

Equation (1.18) is the replenishing term. The electron velocity before and after the collision are related by means the following relation:
\[
\frac{mv'^2}{2} - \frac{mv^2}{2} = \varepsilon_j 
\]  
(1.19)

where \(\varepsilon_j\) is the excitation energy. Substituting equation (1.19) into (1.18) the excitation collision term is obtained:

\[
\left( \frac{\delta(nf)}{\delta \varepsilon} \right)_{exc} = n_e N_j \int_{\Omega} \left[ \sigma_j(v', \chi) \frac{v'^2}{v} f(\bar{v}) - \sigma_j(v, \chi) v f(\bar{v}) \right] d\Omega 
\]  
(1.20)

(Note that differentiating (1.19) \(v dv = v' dv'\) is obtained)

### 1.3.5 Inelastic collisions: ionizations

With analogous approach, it is possible to write the depleting term for ionization that is:

\[
dR^- = n_e N_j \int_{\Omega} \sigma_i(v, \chi) v f(\bar{v}) d\Omega d^3v 
\]  
(1.21)

where \(\sigma_i(v, \chi) d\Omega\) is the differential ionization cross section. In order to write the replenishing term, it is convenient to split up the electron in primary and secondary. The first one is the electron incident. The other is the electron that becomes free after the collision. So, the energy conservation law gives:

\[
\left( \frac{mv'^2}{2} - \varepsilon_i \right) \quad \text{energy of the two electrons after the collision} 
\]  
(1.22a)
\[ \Delta \left( \frac{mv^2}{2} - \epsilon_i \right) \] primary electron energy with \( 0 \leq \Delta \leq 1 \) \hspace{1cm} (1.22b)

The velocity at which the primary electron enters in the element volume \( d^3v \) is:

\[ \Delta \left( \frac{mv^2}{2} - \epsilon_i \right) = \frac{mv^2}{2} \] \hspace{1cm} (1.23)

Differentiating equation (1.23) it can be found that \( v' dv' = \frac{1}{\Delta} v dv \).

In the same way, replacing \( \Delta \) with \((1-\Delta)\) and \( v' \) with \( v'' \), the contribution of the secondary electron is carried out. So, the replenishing term is:

\[ dR^+ = n_e N_i \int_{\Omega} \left[ \sigma_i(v', \chi) \frac{v'^2}{\Delta \cdot v} f(v') + \sigma_i(v'', \chi) \frac{v''^2}{(1-\Delta) v} f(v'') \right] d\Omega d^3v \] \hspace{1cm} (1.24)

Finally, the ionization collision term becomes:

\[ \left( \frac{\delta(nf)}{\delta t} \right)_{\text{ion}} = n_e N_i \int_{\Omega} \left[ \sigma_i(v', \chi) \frac{v'^2}{\Delta \cdot v} f(v') + \sigma_i(v'', \chi) \frac{v''^2}{(1-\Delta) v} f(v'') - \sigma_i(v, \chi) v f(v) \right] d\Omega \] \hspace{1cm} (1.25)
1.4 The two term approximation

In a wide range of physical situations in collision-dominated plasmas, a particular representation of the electron Boltzmann equation is carried out. The idea is to express the distribution function $f(\vec{v})$ in terms of a spherical-harmonic expansion (or Legendre’s orthogonal polynomials $P_n(\cos \Theta)$) that can be written as:

$$f(\vec{v}) = \sum_{n=0}^{\infty} f_n(v) P_n(\cos \Theta)$$  \hspace{1cm} (1.26)

where the functions $f_n$ are all isotropic and $\Theta$ is the angle between the generic force $\vec{F}$ and $\vec{v}$ direction. When the anisotropy of the velocity distribution function not negligible ($f_0 >> f_1 >> f_2, ...$), only the first two polynomials are considered, so the equation (1.26) becomes:

$$f(\vec{v}) = f_0(v) + \cos \Theta f_1(v) = f_0(v) + \left( \frac{v_z}{v} \right) f_1(v)$$  \hspace{1cm} (1.27)

in which $\vec{F} = (0,0,F)$. This approximation is called two-terms spherical harmonics expansion. Substituting equation (1.27) in both of (1.5) and (1.6), the following equations are obtained:

$$v_m = \langle v \rangle = 4\pi \int_0^{\infty} v^3 f_0(v) dv$$  \hspace{1cm} (1.28)

and
\[ v_d = \langle v \cos \Theta \rangle = \frac{4}{3} \pi \int_0^\infty v^3 f_1(v) dv \] (1.29)

From these equations it can be observed that the function \( f_0 \) governs the plasma properties that depend on the mean velocity, as mean energy and viscous stress. By the other hand, \( f_1 \) is responsible of the directional properties. So, \( f_0(v) \) and \( f_1(v) \) are called respectively isotropic and anisotropic term.

Finally, substituting equation (1.27) in (1.2), the normalization condition becomes:

\[ 4\pi \int_0^\infty v^2 f_0(v) dv = 1 \] (1.30)

### 1.5 Effects of the two term approximation in the Boltzmann equation

In the case of stationary plasma, substituting the expansion (1.27) into the Boltzmann equation (1.4), two scalar equations for \( f_0 \) and \( f_1 \) are obtained:

\[
\begin{align*}
\frac{\partial (nf_0)}{\partial t} & - \frac{Een}{3m} \frac{d}{dv}(v^2 f_1(v)) + \alpha \frac{v}{3} nf_1(v) = \sum C_0 \\
\frac{\partial (nf_1)}{\partial t} & - \frac{Een}{m} \frac{df_0}{dv} + \alpha v nf_0(v) = \sum C_i
\end{align*}
\] (1.31)
where the unique external force acting on electrons considered is the electric field $E$, directed only along the 0-z axis. The parameter $\alpha$ is the first Townsend coefficient and takes into account of the variations of electron density along the $z$ axis. The terms $C_0$ and $C_1$ are the collision integral expressed by:

$$C_0 \equiv \frac{1}{2} \int_{-1}^{1} \left( \frac{\delta(nf)}{\delta \alpha} \right)_{\text{coll.}} d(\cos \Theta) \quad (1.32a)$$

$$C_1 \equiv \frac{3}{2} \int_{-1}^{1} \left( \frac{\delta(nf)}{\delta \alpha} \right)_{\text{coll.}} \cos \Theta d(\cos \Theta) \quad (1.32b)$$

In the evaluation of the electron-electron collision term from the Fokker-Planck expression (1.12), it is sufficient to consider only the contribution of $f_0(v)$ in the expansion (1.27), since $f_0 \gg f_1, f_2, \ldots$ With this condition the following expression is obtained:

$$C_{ee}^0 = n_e^2 \Gamma_{ee} \frac{1}{v^2} \frac{\partial}{\partial v} \left[ 4\pi f_0^2 \int v^2 f_0 dv + \frac{4\pi}{3} v \frac{\partial f_0}{\partial v} \int v^3 f_0 dv + \frac{4\pi}{3} v^2 \frac{\partial^2 f_0}{\partial v^2} \int v^4 f_0 dv \right] \quad (1.33)$$

If the electron-electron collisions play a fundamental role (for example fully ionized plasmas) also in the reducing the anisotropy caused by the electric field, the $C_{ee}^1$ term has to be considered. In the evaluation of the electron-heavy particle collision term, both the $f_0$ and $f_1$ functions have to be considered. In fact, the principal role of these collisions is to redistribute in all space directions the motion of free electrons reducing the anisotropy. Introducing the expansion (1.27) into the
equation (1.16) and after some manipulations, the two terms $C^{0}_{eh}$ and $C^{1}_{eh}$ are obtained:

$$C^{0}_{eh} = n_p \frac{m_e}{m_h} \frac{1}{\nu^2} \frac{\partial}{\partial \nu} \left[ (f_0 + \frac{kT_h}{m_e} \frac{1}{\nu} \frac{\partial f_0}{\partial \nu}) \cdot \nu \right]$$  \hspace{1cm} (1.34)$$

$$C^{1}_{eh} = -n_h \nu^{(i)}_{eh} \frac{1}{\nu} \frac{\partial f_0}{\partial \nu}$$  \hspace{1cm} (1.35)$$

where $\nu^{(i)}_{eh} = n_h g Q^{(i)}_{eh}(g)$ and $Q^{(i)}_{eh}(g)$ is the momentum transfer cross section.

If the mean velocity of the heavy particles is low, the second term of equation (1.35) is negligible.

When the inelastic collisions are not too frequent, it is sufficient to consider only the first contribution of the expansion (1.27) and place $f \approx f_0$ in their evaluation. As consequence, the integral collision $C^{1}$ is zero. For excitation and ionization processes the $C^{0}$ term reads:

$$C^{0}_{exc} = n_e N_i \left[ Q_j(v') \frac{\nu^2}{\nu} f_0(v') - Q_j(v) vf_0(v) \right]$$  \hspace{1cm} (1.36)$$

$$C^{0}_{ion} = n_i N \left[ Q(v') \frac{\nu^2}{\Delta \nu} f_0(v') + Q(v'') \frac{\nu^2}{(1-\Delta)(\nu)} f_0(v'') - Q_i(v) vf_0(v) \right]$$  \hspace{1cm} (1.37)$$

where $Q(v) = \int_{\Omega} \sigma(v, \chi) d\Omega$ is the integral cross section of the generic process.
1.6 The electron energy distribution function (EEDF)

The substitution of the two term expansion in the Boltzmann equation allows to write a system of two scalar equations in \( f_0 \) and \( f_1 \). Introducing the second expression of the equation (1.31) into the first one and substituting the collisional terms previously described, an integro-differential equation for \( f_0(\nu) \) is obtained. Usually, the problem is re-formulated in the electron kinetic energy domain \( u=mv^2/2 \). As consequence, the Boltzmann equation for the electron energy distribution function (EEDF) \( f(u) \) takes the following second order non-linear integro-differential form:

\[
K(u)\frac{d^2 f(u)}{du^2} + U(u)\frac{df(u)}{du} + \gamma(u)f(u) + \sum_\varepsilon v_\varepsilon(u_{\varepsilon})f(u_{\varepsilon}) = 0
\]  

(1.38)

with the normalization condition, from equation (1.2), expressed as

\[
\int_0^\infty f(u)\sqrt{u} \, du = 1
\]  

(1.39)

The expressions of the coefficients in the (1.38) are the following:

\[
K(u) = -\frac{2}{3}\left(\frac{Ee}{m}\right)^2 \frac{u}{A} - \frac{4kT_h}{m_n m}Au^2 - \frac{2}{3} B \left[ \int_0^\infty u^3 fdu + u^3 \int u fdu \right]
\]  

(1.40a)

\[
U(u) = -\frac{2}{3}\left(\frac{Ee}{m}\right)^2 \frac{d}{du} \left( \frac{u}{A} \right) + \frac{4 \alpha Ee}{3 m^2} - \frac{4}{m_n m} Au^2 - \frac{4kT_h}{m_n m} \frac{d}{du}(Au^2) - 
\]

\[
- B \left[ \int_0^\infty \sqrt{u} fdu + \sqrt{u} \int \sqrt{u} fdu \right]
\]  

(1.40b)
\[ \gamma(u) = \frac{2}{3} \frac{\alpha E_e}{m^2} \frac{d}{du} \left( \frac{u}{A} \right) - \frac{2}{3} \frac{\alpha^2}{Am^2} u - \frac{4}{m_i m} \frac{d}{du} \left( A u^2 \right) - B(\sqrt{u} f) + \]

\[ + \frac{2}{m^2} \sum_j N_j u Q_j(u) + \frac{2}{m^2} \sum_i N_i u Q_i(u) \]

\[ \sum_i \varphi_i(u_i) f(u_i) = \frac{2}{m^2} \sum_j N_j \left[ Q_j(u + u_j) \cdot (u + u_j) \right] f(u + u_j) + \]

\[ + \frac{2}{m^2} \sum_i N_i \left( \frac{u}{\Delta} + u_i \right) Q_i \left( \frac{u}{\Delta} + u_i \right) f \left( \frac{u}{\Delta} + u_i \right) + \]

\[ + \frac{2}{m^2} \sum_i N_i \left( \frac{u}{(1 - \Delta)} + u_i \right) Q_i \left( \frac{u}{(1 - \Delta)} + u_i \right) f \left( \frac{u}{(1 - \Delta)} + u_i \right) \]

in which \( A(u) \equiv \sum_n Q_{\text{eh}}^{(n)}(u) n_n \) and \( B(T_e) \equiv n_e \Gamma_{ee} \).

The solution of the equation (1.38) allows to evaluate the EEDF \( f(u) \). Afterwards, the electron temperature \( T_e \) is evaluated in terms of the electron mean energy as:

\[ T_e = \frac{2}{3k} \langle u_m \rangle = \frac{2}{3k} \int_0^\infty u f(u) \sqrt{u} \, du \] (1.41)

Finally, the other parameters of interest, as the drift velocity (expressed by (1.29)) and the first Townsend coefficient \( \alpha \), are evaluated:

\[ v_d = \frac{8 \pi}{3m^2} \int_{u=0}^\infty u f_i(u) \, du \] (1.42)
\[ \alpha = \frac{\nu_i}{\nu_d} \quad (1.43) \]

where \( \nu_i \) is the ionization frequency defined as:

\[
\nu_i = \sum_{i} \int_{0}^{\infty} N_i Q_i(v) f_i(v) dv = \sum_{i} \sqrt{\frac{2}{m_0}} \int_{0}^{\infty} N_i Q_i(u) f_i(u) u du \quad (1.44)
\]

### 1.7 Solution of the Boltzmann equation

#### 1.7.1 Discretization of the energy domain

The discretization in the energy domain has been carried out by means of a finite difference formulation. If \( u_{i-1}, u_i, u_{i+1} \) are the kinetic energy of the generic points \( i-1, I, i+1 \) and \( f_{i-1}, f_i, f_{i+1} \) are their function values, the second order expansion in a Taylor's series gives:

\[
\begin{align*}
\begin{cases}
  f_{i+1} = f_i + f_i' \Delta u_+ + \frac{1}{2} f_i''(\Delta u_+)^2 \\
  f_{i-1} = f_i - f_i' \Delta u_- + \frac{1}{2} f_i''(\Delta u_-)^2
\end{cases}
\end{align*}
\quad (1.45)
\]

Substituting these expansions in the equation (1.38) the following expression for the generic point \( i \) is derived:

\[
a_{i-1} f_{i-1} + a_i f_i + a_{i+1} f_{i+1}
\quad (1.46)\]
with

\[ a_{\text{c},i} = \frac{1}{\Delta u_{-}(\Delta u_{-} + \Delta u_{+})} \left( 2 - \frac{U}{K} \Delta u_{+} \right) \]

\[ a_i = \frac{1}{\Delta u_{-} \Delta u_{+}} \left[ 2 + (\Delta u_{-} - \Delta u_{+}) \frac{U}{K} - \frac{\gamma}{K} \Delta u_{-} \Delta u_{+} \right] \quad (1.47) \]

\[ a_{\text{c},i+1} = \frac{1}{\Delta u_{+}(\Delta u_{-} + \Delta u_{+})} \left( 2 + \frac{U}{K} \Delta u_{-} \right) \]

In order to represent the inelastic collision terms in the energy domain, it is necessary to add the coefficients resulting from the approximation of the generic function \( f(ku_i + u_k) \) in which \( u_k \) is the threshold energy. This function is expanded in a second order Taylor's series around the nearest domain point \( u_v \). The coefficients of this expansion are:

\[ d_i = \frac{\Delta u}{\Delta u_{-}(\Delta u_{-} + \Delta u_{+})} \left[ -\Delta u_{+} + (\Delta u)^2 \right] \]

\[ e_i = \left[ 1 + \left( \frac{1}{\Delta u_{-}} - \frac{1}{\Delta u_{+}} \right) \Delta u - \frac{(\Delta u)^2}{\Delta u_{-} \Delta u_{+}} \right] \quad (1.48) \]

\[ f_i = (\Delta u_{-} + \Delta u) \frac{\Delta u}{\Delta u_{-}(\Delta u_{-} + \Delta u_{+})} \]

Due to a strong dependence of the discretization step by the input parameters (electric field, density and temperature), a step by step calculation of the coefficient \( K \) and \( U \) is performed. The discretization step \( \Delta u \) adopted has to satisfy the stability condition \( \Delta u \leq 2K/U \). Another more
restrictive condition is adopted taking into account that the coefficient \( \gamma \neq 0 \) and (1.38) is not homogeneous.

1.7.2 Boundary conditions

The boundary conditions adopted are the following:

\[
\begin{align*}
\int_{0}^{\infty} f(u) \sqrt{u} \, du &= 1 \\
\text{Separation of the energy domains}
\end{align*}
\]  

(1.49)

The first of the (1.49) is the already described normalization condition (1.39). The integral is calculated by means of the “trapeze rule”. The other one illustrates that all the collisional events having electron energy greater than the maximum value of the domain (for example 100 eV) are not considered. This condition is expressed by setting \( a_{n+1} = 0 \) in (1.47), if \( n \) are the number of the discretization points.

1.7.3 Solution of the system

The non linear system is solved iteratively by the FORTRAN routine DLSLXG that solves a system of linear algebraic equations having a real sparse coefficient matrix. It first uses the routine DLFTXG to perform an LU factorization of the coefficient matrix. The solution of the linear system is then found using DLFSXG. The routine DLFTXG by default uses a symmetric Markowitz strategy to choose pivots that most likely would
reduce fill-ins while maintaining numerical stability. In the figure 1.3 the basic structure of the numerical code is shown.

*Figure 1.3 - Flux diagram of the numerical code solving the Boltzmann equation.*
1.8 Application of the model at monatomic weakly ionized plasmas

The model is firstly applied at stationary and homogeneous argon weakly ionized plasma, with ionization degree less than $10^{-3}$. In this way, the calculated electron energy distribution functions are compared with the results presented in reference [1] and the transport parameters with reference [2]. The following anelastic and elastic collision processes are considered:

$$\text{Ar}_1(1) + e \rightarrow \text{Ar}_1(j) + e$$ \hspace{1cm} (excitations to a level \(j\) from ground level) \hspace{1cm} (I)

$$\text{Ar}_1(1) + e \rightarrow \text{Ar}_2(1) + e + e$$ \hspace{1cm} (ionization from ground level) \hspace{1cm} (II)

$$\begin{align*}
\text{Ar}_1 - e \\
\text{Ar}_2 - e \\
e - e
\end{align*}$$ \hspace{1cm} (elastic collisions) \hspace{1cm} (III)

In the equation (I) \(j\) is referred at the neutral argon levels indicated in table 1.1.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Excitation energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4s [3/2]_2</td>
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</tr>
<tr>
<td>4s [3/2]_1</td>
<td>11.624</td>
</tr>
<tr>
<td>4s [1/2]_0</td>
<td>11.723</td>
</tr>
<tr>
<td>4s [1/2]_1</td>
<td>11.828</td>
</tr>
</tbody>
</table>

*Table 1.1 - Energy levels of neutral argon considered.*
Following the same approach used by Vleck [1] on the solution of the equation (1.38), the distribution function \( f(u) \) is replaced by the corresponding Maxwellian function \( f_M(u) \) in the coefficients containing the Fokker-Plank term. In figure 1.4 the numerical results of the ratio \( f(u)/f_M(u) \) for electron temperature \( T_e = 20000 \, ^\circ\text{K} \) are shown. The simulations are performed at \( N_h = 1.61 \times 10^{23} \, \text{m}^{-3} \), at two values of heavy particle temperature (\( T_h = 300 \, ^\circ\text{K} \) and \( 1000 \, ^\circ\text{K} \)) and with electron density in the range of \( 10^{14} \div 10^{20} \).

![Figure 1.3 - Calculated EEDF at \( T_e = 20000 \, ^\circ\text{K} \).](image)

The calculated EEDF is nearly Maxwellian up to the first argon excitation level (11.55 eV) in all cases investigated. On the other hand, the high-energy tail is underpopulated. If the electron density is increased, the tail is more populated and the deviations from the Maxwellian distribution are less evident. These results are in excellent agreement with those presented by Vleck.
Figure 1.4 - Calculated drift velocity at different E/N ratios.

Figure 1.5 - Calculated ionization coefficient at different E/N ratios.
In the figures 1.4 and 1.5 the drift velocity $V_d$ and the ionization coefficient $\alpha/N$ are shown. An excellent agreement with the experimental data of $V_d$ measured by Robertson and Lucas [2] (figure 1.4) is obtained when the ionization degree is varied with the ratio $E/N$. A good agreement with the calculated values of by Puech-Torchin [2] is also obtained for $\alpha/N$ (figure 1.5).

1.9 EEDF at MPD plasma conditions

The application of the model solving the Boltzmann equation to these type of plasmas is not trivial. These plasmas are characterized by very high $E/N$ ratios ($10^3$ Td, or more, where $1$ Td $= 10^{-21}$ V/m$^2$) with strong electric field ($E = 200 \div 800$ V/m) and low density ($N = 10^{19} \div 10^{20}$ m$^{-3}$). Moreover, due to the fully ionized condition (see chapter 3) the electron-electron collisions become the leading term and the approximation used in the previous section is not longer valid. Finally, due to the probable high energy of the heavy particles, their mean velocity in the equation (1.35) could be considered. Due to these considerations, the following anelastic and elastic collision processes are considered:

$$Ar_i(1) + e \rightarrow Ar_i(j) + e$$  \hspace{1cm} (excitations to a level j from ground level) \hspace{1cm} (I)

$$\begin{cases}
Ar_i(1) + e \rightarrow Ar_z(1) + e + e \\
Ar_z(1) + e \rightarrow Ar_z(1) + e + e
\end{cases}$$  \hspace{1cm} (ionizations from ground level) \hspace{1cm} (II)
\[ \text{Ar}_1(1) + e \rightarrow \text{Ar}_2(1) + e + e \quad \text{(direct excitation from the ground level of neutral argon)} \]

\[
\begin{align*}
\text{Ar}_1 - e \\
\text{Ar}_2 - e \\
\text{Ar}_3 - e \\
e - e
\end{align*}
\]

(elastic collisions)

In the equations (I) and (IV) \( j \) is referred at the following argon levels indicated in table 1.2.

<table>
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<tr>
<th>Designation</th>
<th>Excitation energy [eV]</th>
</tr>
</thead>
<tbody>
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<td>Ar I 4s [3/2]</td>
<td>11.548</td>
</tr>
<tr>
<td>Ar I 4s [3/2]</td>
<td>11.624</td>
</tr>
<tr>
<td>Ar I 4s [1/2]</td>
<td>11.723</td>
</tr>
<tr>
<td>Ar I 4s [1/2]</td>
<td>11.828</td>
</tr>
<tr>
<td>Ar I 4d [1/2]</td>
<td>14.710</td>
</tr>
<tr>
<td>Ar I 6p' [1/2], 6p' [3/2], 6p' [3/2]</td>
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</tr>
<tr>
<td>Ar II 3p6 (2S)</td>
<td>29.240</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4s (2P)</td>
<td>33.000</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4p (4P*5/2)</td>
<td>34.984</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4p (4D*5/2)</td>
<td>35.310</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4p (2D*5/2)</td>
<td>35.524</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4p (2P*1/2)</td>
<td>35.562</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4p (2P*3/2)</td>
<td>35.628</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4p (4S*)</td>
<td>35.728</td>
</tr>
<tr>
<td>Ar II 3p4(3P)4p (2S*)</td>
<td>35.734</td>
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<tr>
<td>Ar II 3p6 (2S)</td>
<td>13.481</td>
</tr>
<tr>
<td>Ar II 3p4 (3P)4s (2P1/2)</td>
<td>17.267</td>
</tr>
</tbody>
</table>

**Table 1.2** - Energy levels of neutral argon considered.

Figure 1.6 shows the numerical results of the \( f(u)/f_M(u) \) ratio in the case of \( E = 100 \) V/m and \( N_e = 10^{19} \) m\(^{-3}\). The calculated electron temperature \( T_e \) is 33.400 °K. The form is slightly Maxwellian up to approximately 20 eV after that the tail overpopulated.
The same considerations are valid also if the electric field is increased (E = 200 V/m). The results are shown in figure 1.7 ($T_e \approx 70.000 \, ^\circ \text{K}$).

**Figure 1.6** - Calculated EEDF at $E = 100 \, \text{V/m}$ and $N_e = 10^{20} \, \text{m}^{-3}$.

**Figure 1.7** - Calculated EEDF at $E = 200 \, \text{V/m}$ and $N_e = 10^{20} \, \text{m}^{-3}$.
All these simulations are performed with $\alpha = 0$ and with percentage of ArIII density less than 0.1%. The role the e-ArIII collisions are more evident if this percentage is increased up to 1%. The results are shown in figure 1.8 with $E = 100$ V/m and $N_e = 10^{19}$ m$^{-3}$ ($T_e \approx 110.400$ °K).

![Figure 1.8 - Calculated EEDF at $E = 100$ V/m and $N_e = 10^{19}$ m$^{-3}$](image)

The calculated EEDF is not too different from the Maxwellian distribution with the high energy tail less populated than the case of figure 1.6. The decrease near the higher boundary is probably caused by numerical effects.

An indication of the validity of the two term approximation to solve the Boltzmann equation in plasmas characterized by high E/N ratio is given by the behaviour of the $f_1/f_0$ ratio, reported in figure 1.9 in the same simulation conditions of figure 1.6. The ratio stays less than unity up to 30 eV and then increases. So the high energy tail of the EEDF could not be sufficiently well described. On the other hand, it is necessary to note that the inelastic processes and the e-e collisions are described only by the $f_0$
function and the role of $f_i$ should be taken into account. However, these considerations do not compromise the validity of the model developed, but they have to be intended as the basis for the future work.

![Figure 1.9 - Calculated $f_i/f_0$ ratio at $E = 100$ V/m and $N_e = 10^{20}$ m$^{-3}$.](image)

1.10 Collisional-radiative model of ArII system

1.10.1 Formulation of the problem

The equation describing the population/depopulation mechanisms of the excited generic level $k$ is the following continuity equation:

$$
\frac{\partial n_k}{\partial t} + \text{grad}(v_k n_k) = P_k - D_k
$$

(1.50)
where $P_k$ and $D_k$ are the terms that describe the population and the depopulation of the level $k$ by the collisional and radiative processes. The distribution function of the particles in the level $k$ is taken Maxwellian. Usually, the collisional and radiative phenomena dominate over the transport phenomena and the so-called quasi steady-state solution (QSSS) is applicable and the equation (1.50) becomes:

$$P_k - D_k = 0$$  \hspace{1cm} (1.51)

The model is applied to the singly ionized argon system (ArII). The collisional and radiative processes, for the ArII, are the following:

$$ArII(1) + e \overset{C_{kj}, F_{kj}}{\rightarrow} ArII(j) + e$$

$$ArII(k) + ArII(1) \overset{K_{kj}, L_{kj}}{\rightarrow} ArII(j) + ArII(1)$$

$$ArII(k) + e \overset{S_{kj}, Q_{kj}}{\rightarrow} ArIII(1) + e + e$$

$$ArII(k) + ArII(1) \overset{V_{kj}, W_{kj}}{\rightarrow} ArIII(1) + ArII(1) + e$$

$$ArII(k) + h\nu_{kj} \overset{(1-L_{kj})A_{kj}, A_{kj}}{\rightarrow} ArII(j)$$

$$ArII(k) + h\nu \overset{(1-L_{kj})B_{kj}}{\rightarrow} ArIII(1) + e$$

Here, $C_{kj}$ and $K_{kj}$ are the rate coefficients for collisional excitation by electrons and by the ground state of the ArII respectively. $F_{kj}$ and $L_{kj}$ are respectively the rate coefficients for the inverse processes (collisional de-excitation). $S_{kj}$ and $V_{kj}$ are corresponding collisional ionization rate coefficients while $Q_{kj}$ and $W_{kj}$ are the rate coefficients for the inverse three-
body recombination and $R_k$ is the radiative recombination rate coefficient. $A_{kj}$ is the transition probability, $\Lambda_{kj}$ and $\Lambda_k$ are the optical escape factors for bound-bound and free-bound transitions.

Writing a balance for the population and the depopulation of the level $k$ the equation (1.52) is derived:

$$\sum_{j=1}^{p} a_{kj} n_j + \delta_k = 0$$  \hspace{1cm} (1.52)

The coefficients are given by:

$$a_{kj} = n_e C_{kj} + n_i K_{kj} \quad \text{for } j < k \quad (1.53a)$$

$$a_{kj} = n_e F_{kj} + n_i L_{kj} + \Lambda_{kj} A_{kj} \quad \text{for } j > k \quad (1.53b)$$

$$a_{jj} = - \left( n_e S_j + n_i V_j + \sum_{j \neq k}^{p} a_{kj} \right) \quad \text{for } j = k \quad (1.53c)$$

$$\delta_k = n_e n_i \left( n_e O_k + n_i W_k + \Lambda_k A_k \right) \quad (1.53d)$$

In the present model, the collisions with the ArII(1) are not considered. Furthermore, the plasma is considered optically thin for all the radiations and then is set $\Lambda_{kj} = \Lambda_k = 1$. The expressions for the rate coefficients are given by:

$$C_{kj} = \sqrt{\frac{2}{m u_{ij}}} \int_{m u_{ij}}^{\infty} \sigma_{kj}(u) n_f(u) du \quad (1.54a)$$
\[ F_{kj} = \sqrt{\frac{2}{m}} \frac{g_k}{g_j} \sigma_{kj}(u)u f(u - u_{kj}) du \]  
(1.54b)

\[ S_k = \sqrt{\frac{2}{m}} \int_{u_k}^{\infty} \sigma_k(u)u f(u) du \]  
(1.54c)

\[ Q_k = \sqrt{\frac{2}{m}} \frac{g_k}{2g_+} \left( \frac{h^2}{2\pi n k T_e} \right)^{3/2} \int_{u_k}^{\infty} \sigma_k(u)u f(u - u_k) du \]  
(1.54d)

\[ R_k = \sqrt{2} \frac{g_k}{2g_+} \frac{1}{c^2} \left( \frac{h^2}{m} \right)^{3/2} \int_{u_k/h}^{\infty} \sigma_k^p(v)v^2 f(hv - u_k) dv \]  
(1.54e)

The expressions of the cross sections are reported in the Appendix A.

The boundary conditions are given by the following conditions:

\[
\begin{align*}
N_e &= N_{ArIII} + \sum_{k=1}^{p} n_k & (1.55) \\
N_{ArIII} &\text{ constant}
\end{align*}
\]

The first equation is the condition of global neutrality of the electrical charge in the plasma.

The QSSS approximation is no longer valid for the doubly ionized argon particles in the ground state (also for the singly ionized argon) because the transport phenomena are not negligible. So, the continuity equation reads:
\[ \frac{\partial n_k}{\partial t} + \text{grad}(v_k n_k) = n_e N_{ArII} S_{CR} - n_e N_{ArIII} \alpha_{CR} = I_{\text{eff}} \] (1.56)

where the coefficients are given by:

\[ S_{CR} = S_1 + \frac{1}{N_{ArII}} \sum_{k=2}^{p} n_k S_k \] (1.56)

\[ \alpha_{CR} = n_e \sum_{k=1}^{p} Q_k + \sum_{k=1}^{p} \Lambda_k R_k \] (1.57)

The equation (1.56) allows to classify the excitation space of the ArII system in:

- \( I_{\text{eff}} > 0 \) ionizing system
- \( I_{\text{eff}} < 0 \) recombining system
- \( I_{\text{eff}} = 0 \) ionization-recombination equilibrium

### 1.10.2 Results and discussions

The level of the ArII system are grouped in \( p = 78 \) effective excited states. These levels are reported in the table 1.4 with information on their configuration and the statistical weight values.
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<th>Energy [eV]</th>
<th>Configuration</th>
<th>Statistical weight</th>
</tr>
</thead>
<tbody>
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<td>6</td>
</tr>
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<td>13.4798</td>
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<td>2</td>
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<tr>
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<td>20</td>
</tr>
<tr>
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</tr>
<tr>
<td>16.7485</td>
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<td>4</td>
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<tr>
<td>16.8125</td>
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The distribution of the population over the energy excited levels in the conditions of figure 1.6 is shown in figure 1.10.
In this figure, only the population density of the energy levels being to the most intense ArII transitions in the wavelength range of the OMA system used in the experimental investigation of the MPD thruster are shown. The population density is characterized by two different excitation temperatures. The low-lying levels temperature \( T_L \) is approximately 1.2 eV (1 eV = 11,600 °K) while the high-lying levels temperature \( T_H \) is 2.5 eV. So, in these conditions, the ArII system is not in pLTE. The radiative decay from the higher levels is an significant contribution of the low-lying levels. On the other hand, the high-lying levels (over 20 eV) are mostly populated by collisions with electrons. \( T_H \) is 4-5 times lower than the calculated \( T_e \) and gives a rough estimation of it. The separation level between the two population groups corresponds to the energy where the calculated EEDF departs from the Maxwellian form. Finally, by means of the equation (1.56), the flux \( I_{\text{eff}} \) over the levels is calculated. \( I_{\text{eff}} \) is approximately \( 3.5 \times 10^{23} \text{ m}^3/\text{s} \) and the ArII system is classified as ionizing.