# Monte Carlo Flux simulations of electrons for plasma modelling

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**Abstract:** A powerful Monte Carlo approach, the Monte Carlo Flux, has been implemented with the aim of calculating the electron velocity and energy distribution function in non-thermal plasmas. The method is applied to an atomic system and results are compared with solutions of the Boltzmann equation under two-term and multi-term expansion in Legendre series. The current implementation can be considered as a highly efficient alternative to the conventional Monte Carlo for a detailed description of electron kinetics.

Keywords: Monte Carlo Flux, electron Boltzmann equation, electron kinetics.

## 1. Introduction

Modelling of intermediate pressure plasmas far from thermodynamic equilibrium is extremely challenging, due to the complex plasma chemistry and the different time scales involved. One example is the study of plasmas for CO<sub>2</sub> activation, where a strongly structured electron energy distribution function (eedf) is expected [1]. From the eedf, it is possible to determine fundamental quantities such as rate coefficients and transport coefficients (mobility, diffusion, etc.) that are needed for a complete characterization of the discharge. For this reason, fast but accurate calculations of the eedf are important to properly evaluate the contribution of electron impact processes in the overall plasma chemistry. In current approaches, eedfs are usually obtained by solving the Boltzmann equation under the two-term assumption in which the velocity dependence of electron distribution is isotropic. This approximation, however, is not valid for gases at field strengths which facilitate the onset of inelastic collisions [2]. Another approach is to predict the evolution of the eedf probabilistically using Monte Carlo calculations in which individual trajectories of a large number of electrons are simulated [3]. Despite being equivalent to an exact solution of the Boltzmann equation, this method appears to be computationally inefficient due to a vast number of trajectories that has to be taken into account to achieve an acceptable statistical noise level. These limitations can be overcome by the use of the Monte Carlo Flux (MCF) method [4, 5]. The MCF method is a highly efficient example of variance reduction technique, faster than conventional Monte Carlo, but with similar versatility. It is useful for a calculation of the eedf with uniform statistical accuracy (and much more than this, the velocity distribution function) even in the high energy region. In this work, an implementation of MCF is presented and results are validated against the widely used two-term Boltzmann solver BOLSIG+ [6] and the multi-term MultiBolt [7]. The potentialities of this method are also discussed.

#### 2. Transport equations and Monte Carlo Flux

The eedf is generally calculated by solving the Boltzmann equation for electrons:

$$\left[\frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla}_r + \vec{a} \cdot \vec{\nabla}_v\right] f(\vec{r}, \vec{v}, t) = J[f(\vec{r}, \vec{v}, t)].$$
(1)

This equation gives the rate of change of the electron distribution function  $f(\vec{r}, \vec{v}, t)$  in terms of space and velocity gradients, the acceleration  $\vec{a} = -e\vec{E}/m$  and the effect of collisions, described by the operator  $J[f(\vec{r}, \vec{v}, t)]$  at the right hand side of Eq.(1). In this context, we consider a homogenous case in which spatial variations are neglected and the velocity distribution function in stationary condition  $f(\vec{v})$  is determined by the action of a constant external electric field and binary elastic and inelastic collisions. Because of the axial symmetry of the problem along the direction of the electric field, the velocity distribution function in a series of Legendre polynomials  $P_i(\cos \theta)$  [8]:

$$f(\vec{v}) = \sum_{j=0}^{\infty} f_j(v) P_j(\cos \theta).$$
(2)

Where v is the magnitude of the velocity vector,  $\theta$  is the angle between the velocity vector and the direction of the electric field and  $f_j(v)$  is the Legendre polynomial coefficient in the expansion. Usually only two terms in the expansion are taken into account, such that the first term  $(f_0)$  is associated with the isotropic part of the distribution and the second term  $(f_1)$  takes into account the angular dependence. The calculation of the aforementioned velocity distribution is then performed by converting the partial differential equation (1) into a set of ordinary differential equations, one for each term of the Legendre expansion. This description is referred in literature as two-term approximation. At the cost of computational complexity, it is also possible to include higher order terms

in the Legendre polynomials expansion [7, 8]. In order to calculate the electron distribution function without any approximation and with high accuracy, we used the Monte Carlo Flux. The method is based on a statistical analysis of a finite number of electrons, initially distributed uniformly in the velocity space. The simulation is initiated by partitioning the total velocity space of interest into N equally spaced intervals:

$$\Delta \vec{v}_n = [\vec{v}_n, \vec{v}_{n-1}], \qquad n = 1, 2, \dots, N.$$
(3)

Electrons undergo a deterministic motion under the effect of electric field that is distorted by collisions with the background gas. Collisions of electrons are simulated by Poisson stochastic processes using a Monte Carlo procedure. The effect of collisions is the randomization of particle trajectories and velocities. Throughout this randomization, the electron history is erased and the process evolution is determined only by the current status of the system, not the previous ones. This is known as *Markov property* that allows to rewrite Eq.(1) in the following general (discretized) form [9]:

$$n_i(t + \Delta t) = \sum_j p_{ji}(\Delta t)n_j(t) - n_i(t)\sum_j p_{ij}(\Delta t).$$
 (4)

Where  $n_i$  is the number of electrons found in the *i-th* velocity-space interval and  $\Delta t$  is the time step chosen for the calculation of conditional transition probabilities  $p_{ij}(\Delta t)$  of electrons going from *i-th* to *j-th* interval. In the MCF, the transition probabilities between velocity-space intervals are calculated by means of short Monte Carlo simulations, such that

$$\tau_{coll} \ll \Delta t \ll \tau_{eedf}.$$
 (5)

Where  $\tau_{coll}$  is the characteristic time for electron-neutral collisions and  $\tau_{eedf}$  is the relaxation time of the eedf.

After calculating the transition probabilities, the stationary solution of the eedf can be obtained by iterative application of Eq.(4) to the initial distribution of electrons. The advantage of this procedure is twofold: the Monte Carlo simulations are limited to a short time  $\Delta t$  that is usually orders of magnitude lower than the relaxation time for the eedf. Moreover, since as many electrons can be initially introduced in the high energy part as in the low one, the method allows a uniform statistical accuracy of the eedf that is not achieved by conventional Monte Carlo techniques without a significant computational cost.

# 3. Druyvesteyn distribution

To highlight differences between MCF and Conventional Monte Carlo (CMC), a first model is run under considering only isotropic elastic scattering with a constant cross section of  $2 \times 10^{-20}$  m<sup>2</sup>. In this model, electrons collide with a background gas of atomic mass A = 4 amu. A background gas number density of  $3.2 \times 10^{22}$  m<sup>-3</sup> is

assumed. CMC and MCF simulations were performed under same physical and numerical conditions (i.e. 10<sup>7</sup> sample electrons and energy resolution of 0.3 eV). Results of the simulations showing stationary eedfs for different values of reduced electric field are presented in Fig. 1. As expected, the Druyvesteyn distribution is obtained. Moreover, MCF allows calculations of eedfs at values exceedingly lower than the ones obtained by CMC simulations and results of MCF show a uniform accuracy over all the energy range for several orders of magnitude of the distribution function values. In those conditions, MCF calculations need around one minute in a laptop, whereas the same CMC calculations could require up to several hours.



Fig. 1. Stationary eedfs calculated at different reduced electric fields (from left to right: 2, 5, 10, 20 Td) with CMC and MCF for isotropic elastic scattering.

#### 4. Argon model

To test the effect of different chemical processes implemented in MCF, simulations in the case of an Argon gas have been performed. Cross sections are taken from the Biagi database in LXCat [10] and include the following electron impact processes: elastic momentum transfer for ground state Argon, 44 different electronic excitation processes with thresholds ranging from 11.548 eV to 15.660 eV and single ionization from ground state with threshold 15.760 eV. Even if in MCF it is possible to include different scattering models, for the sake of comparison with other codes, here only isotropic elastic scattering is assumed using the elastic momentum transfer cross section. For what concerns inelastic collisions, all processes are treated with an isotropic angular model and equal energy sharing is assumed after an ionization collision between the primary and secondary electron. For anisotropy studies, the dimensionality of the system is 2D  $(\varepsilon, \theta)$  or  $(v_r, v_z)$ , where  $\varepsilon$  is the kinetic energy of the electrons,  $\theta$  is the angle between the velocity vector and the direction of the electric field and  $(v_r, v_z)$  are the electron velocity components perpendicular and parallel to the direction of the electric field respectively. In these conditions, an example of electron velocity distribution is

shown in Fig. 2 for a constant uniform reduced electric field of 1000 Td.



Fig. 2. Velocity distribution function in cylindrical coordinates  $(v_r, v_z)$  calculated for Argon at a constant reduced electric field of 1000 Td.

The contour plot in Fig. 2, shows that the maximum of the distribution is slightly shifted opposite to the electric field. In fact, the effect of the external force will set a preferential direction in the electron motion, enhancing the anisotropy of the distribution. Additional information about electron motion in velocity space can be obtained from the current description, such as drift and diffusion. The importance of a 2D description of the velocity distribution function can also be appreciated by analysing the coefficients of the Legendre expansion (Eq. (2)), whose accurate calculation is fundamental for the determination of reliable transport parameters and for anisotropy studies. Calculation of coefficients from MCF can be validated against results obtained by two-term or multi-term Boltzmann solvers.

In Fig. 3, calculations of the isotropic  $(f_0)$  and first anisotropic component  $(f_1)$  of the electron velocity distribution function obtained from MCF and the two-term code BOLSIG+ are shown. Different simulations are performed at reduced electric fields ranging from 2 to 2500 Td. In BOLSIG+, temporal growth model and equal energy partition after ionization are used.

Comparison between results of MCF and BOLSIG+ shows a good agreement between solutions obtained at values of reduced electric fields lower than 200 Td. Above this value, deviations from two-term solutions are clearly visible and higher values of the tail of the distribution functions are obtained using MCF. As expected, in those conditions, the small anisotropy assumption used in the two-term model breaks down due to the onset of a strong preferential direction given by the external electric field. In this condition of strong anisotropy in velocity space, calculations performed by a multi-term expansion in Legendre series or (alternatively) Monte Carlo simulations are necessary.



Fig.3. Comparison between zeroth (top) and first (bottom) order Legendre polynomial coefficients from MCF and BOLSIG+ calculations for an Argon system at constant reduced electric fields (from left to right: 2, 5, 50, 200, 1000, 2500 Td).

To test the accuracy of the eedf calculations even at high values of reduced electric field, results from MCF are validated against the multi-term Boltzmann solver MultiBolt. In this work, the MultiBolt solver is used to solve the Boltzmann equation (1) under hydrodynamic condition [7], where the velocity distribution function is expanded in a series of 10-term Legendre polynomials. Results of the calculations are shown in Fig. 4 for a constant, uniform electric field of 2000 Td. From this figure, it is possible to see that MCF results overlaps with calculation of the multi-term code. Moreover, every integral calculated over the eedf in order to obtain kinetic and transport parameters for plasma modelling (or swarm studies) will result inevitably higher than the corresponding ones obtained from BOLSIG+. The possibility of calculating the eedf with uniform statistical accuracy beyond a two-term approximation is important, for example, in order to accurately evaluate rate coefficients of inelastic and ionization processes.



Fig.4. Eedf calculated in Argon at 2000 Td from BOLSIG+, MultiBolt and MCF.

The accuracy in the calculation of ionization rate coefficients in Argon is shown in Fig. 5, by comparing results obtained using BOLSIG+ and MCF. The percent error between ionization rate coefficients  $k_{iz}$  calculated with BOLSIG+ and MCF is defined as:

$$E_p = \left(1 - \frac{k_{iz}[BOLSIG+]}{k_{iz}[MCF]}\right) \cdot 100\%. \quad (6)$$

In the Argon system considered, the deviation from a twoterm model are mainly due to the strong external electric field and the impact in the calculation of ionization rate coefficient is below 4% for a range of reduced electric field up to 3000 Td. Larger deviations up to 70% are reported for calculation of transport parameters like bulk mobility and longitudinal diffusion [7].



Fig.5. Percent error for the ionization rate coefficient in Argon between BOLSIG+ and MCF.

## 5. Conclusions

In this work, a Monte Carlo Flux code has been developed from scratch and validated against the two-term Boltzmann solver BOLSIG+ and multi-term MultiBolt. The code was implemented to obtain efficient calculations of the velocity distribution function with an accuracy not comparable with conventional Monte Carlo approaches. Furthermore, while the capability to obtain uniform statistical accuracy can be matched by more complex Monte Carlo methods using variance reduction techniques, the MCF method differs from any Monte Carlo solution in the possibility of avoiding the calculation of a sometimes huge number of collisions until eedf relaxation is achieved. With MCF, a detailed description of the distribution function in velocity space can be obtained. This allows accurate calculations of kinetic rate coefficients and swarm transport parameters for electrons in atomic and molecular gases even at high reduced electric fields. Next steps will involve the application of MCF to the study of molecular systems, like CO<sub>2</sub>, and embedding it in a comprehensive plasma chemistry model, including vibrational and chemical kinetics.

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# 7. References

[1] M. Capitelli et al., *Plasma Sources Sci. Technol.* **26**, 055009 (2017).

[2] R. D. White et al., J. Phys. D: Appl. Phys. 36, 3125-3131 (2003).

[3] S. Longo, *Plasma Sources Sci. Technol.* **15** S181-S188 (2006).

[4] G. Schaefer and P. Hui, J. Phys. D: Appl. Phys. 1 1567-1568 (1990).

[5] S. Longo and M. Capitelli, *Plasma Chem. Plasma Process.* 14, 1-13 (1994).

[6] G. J. M. Hagelaar and L. C. Pitchford, *Plasma Sources Sci. Technol.* 14, 722-733 (2005).

[7] J. Stephens, J. Phys. D: Appl. Phys. 51, 125203 (2018).

[8] L. C. Pitchford et al., *Phys. Rev. A* 23, 294-304 (1981).

[9] M. Capitelli et al., *Fundamental aspects of plasma chemical physics: Kinetics*, Vol. **85**, Springer (2015).

[10] Biagi database (Magboltz versions 8.9 and higher), www.lxcat.org, retrieved November 5<sup>th</sup> 2018.