Unified Monte Carlo formulation of plasma-chemistry in nanosecond-pulsed discharges

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This work presents a unified Monte Carlo formulation of plasma-chemistry, potentially relevant for the accurate modelling of nanosecond-pulsed discharges. This approach avoids the problems of the typical models that use the two-term and quasi-stationary approximations. We start by generalizing the formulation of the electron kinetics to time-dependent electric fields and we benchmark it against a two-term time-dependent solver. Then, we move on to the self-consistent inclusion of the gas-phase chemistry. Finally, the differences from the typical plasma-chemistry models are quantified.

Low-temperature plasmas are surprisingly efficient for chemical conversion processes with relevance in industry, medicine, agriculture and environment. However, their potentiality comes together with a high level of complexity and a detailed study of the fundamental processes in the discharge is necessary to find the most efficient configuration for a determined application. The interest in a special kind of plasmas - nanosecond-pulsed discharges (NPD) - has been growing quickly in the past years due to the remarkable non-equilibrium properties inherent to these systems. NPD are characterized by very high reduced electric fields, *E/N* (~1000 Td), with rising times on the nanosecond timescale, which turns their modelling deeply challenging.

The usual plasma-chemistry models couple the deterministic solution of the electron Boltzmann equation (EBE) to a system of rate-balance equations that solves the heavy-species chemistry. Moreover, very often two assumptions are used: the low-anisotropy approximation, where only the first two terms in a Legender expansion over the electron velocity space are kept; and the quasi-stationary approximation, which identifies the solution of the instantaneous EBE as the steady-state calculation for the instantaneous *E/N*, being valid when the electron energy relaxation time is much smaller than the characteristic time of the pulse. This approach was applied with success in a variety of discharges. However, it may fail to describe fast-pulsed discharges, since the intense values of *E/N* break down the two-term approximation, due to the appearance of important anisotropies, and the temporal evolutions of the electron energy and the electric-field pulse can no longer be decoupled.

The difficulties associated with the two-term and quasi-stationary approximations can be avoided with a self-consistent and unified formulation of a plasma model based on Monte Carlo techniques. Due to the simplicity and generality of the Monte Carlo methods, the electrons, the heavy species and the surface kinetics can be embedded in the same formulation, with no strong approximation. In short, the Monte Carlo method consists on advancing the physical system according to the frequencies associated to each process (of any type). The time is randomly advanced according to the sum of the process frequencies. The processes occurring along time are stochastically chosen, depending on their probability. Such universality in the physical description is very difficult to achieve using differential equations.

In previous works, we developed a Kinetic Monte Carlo algorithm to study gas-phase chemistry [1]. Recently, we presented the Lisbon Kinetics Monte Carlo (LoKI-MC) code for the simulation of steady-state electron transport in an arbitrarily complex gas mixture, which will be released as open source [2]. Here, we join the previous knowledge to achieve the coupled Monte Carlo formulation of electron and heavy-species kinetics. This description enables a rigorous inclusion of the time-dependent influence of different excited states in the electron kinetics and vice-versa.

As a first step, we start by generalizing the Monte Carlo solution of the electron kinetics in time-dependent fields, keeping the heavy-target densities constant. The most relevant details, such as the temporal integration of the electron motion during the free-collision flight and the continuous update of the electron collision frequency, will be discussed at the conference. The results of this formulation were compared with the two-term time-dependent solver, LoKI-B [3], in conditions where the low-anisotropy assumption is reasonable. Figure 1 presents the *E/N* pulse considered for the simulation of the electron transport in 80%N_2 - 20%O_2 at a pressure of 10^5 Pa. The electric field increases quickly from 0 up to 40 Td, followed by a relatively slow decrease. Figure 2 shows the temporal evolution of the electron mean energy, where we find a good agreement between the two approaches, despite the small deviation at the end of the pulse rise. The accordance for other swarm parameters is also good. However, as it will be shown in the conference, significant differences are found in conditions of strong values of *E/N*.

Concerning the self-consistent inclusion of the gas-phase chemistry, we explore two possible paths. The first and most elegant solution is to describe electrons and heavy species through a full Monte Carlo approach, which in practice consists on adding the Kinetic Monte Carlo algorithm developed in [1] for the heavy-species chemistry to the time-dependent electron transport formulation. On the other hand, we can use a hybrid approach, where we join the stochastic/discrete description of the interactions between electrons and heavy species to a continuous deterministic evolution of the reactions between heavy particles. The pros and cons of both methods will be presented at the conference. Furthermore, the differences from the typical plasma-chemistry modelling will be quantified.

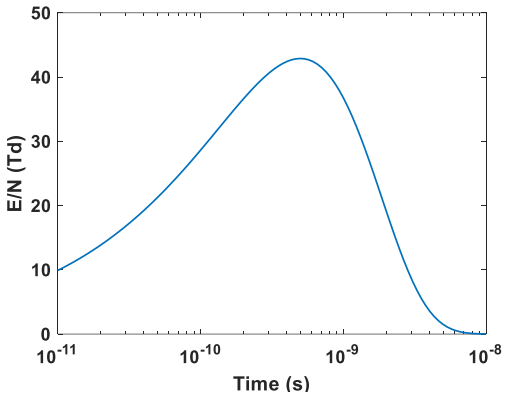

Figure 1: Reduced electric field pulse.

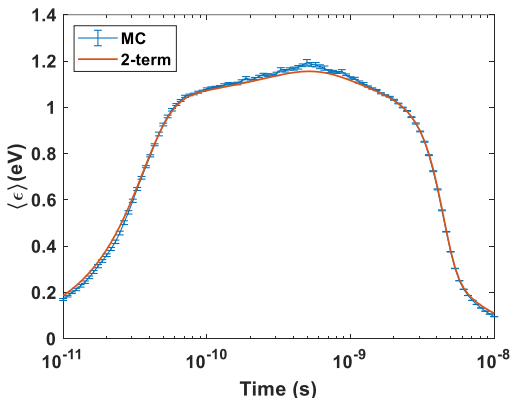

Figure 2: Temporal evolution of the electron mean energy, comparing Monte Carlo and two-term solvers.

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References
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