Kinetic Monte Carlo simulations of plasma chemistry

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This work presents a Kinetic Monte Carlo algorithm to solve the gas-phase chemistry in plasmas, as a first effort to achieve a self-consistent and unified formulation of the electron and heavy-particle kinetics in low-temperature plasmas based on Monte Carlo techniques. The implemented algorithm is successfully validated from the comparison with the traditional deterministic description using rate-balance equations. Besides, we propose a modification in the standard stochastic method that strongly reduces the statistical fluctuations on the concentrations of the minor species.

Several plasma-chemistry models adopt a deterministic description to couple the solution of the electron Boltzmann equation to a system of rate-balance equations describing the heavy-species kinetics. The most common method to solve the electron Boltzmann equation relies on a low-anisotropy approximation, keeping only two-terms in an expansion in Legendre polynomials, which stands only for low reduced electric fields, *E/N*. In addition, there is a rather generalized use of "quasi-stationary" solutions to the electron Boltzmann equation, in which the electron energy distribution function (EEDF) is solved at each time-step for the instantaneous value of *E/N*. This strategy has been used successfully in a variety of discharges. However, it is not suitable for nanosecond pulsed discharges, subject of a growing interest in the last few years. These discharges operate with very high reduced electric fields (of the order of 200 Td and above) and in the nanosecond time-scale. This is clearly a poor approximation due to the violation of the low-anisotropy assumption and because the time-scales of the changes in the EEDF can become comparable with the time-scale of variation of *E/N*.

The difficulties with the two-term and quasi-stationary approximations can be avoided with a self-consistent and unified formulation of the model based on Monte Carlo (MC) techniques. The MC description of the electrons does not require an expansion in the velocity space and it includes from the very formulation the time-dependence of the electric field [1]. The simultaneous MC description of the heavy-species kinetics enables the inclusion of the time-dependent influence of different excited states of atomic and molecular species in the electron kinetics and vice-versa. In this work, we focus on the development of a stochastic MC method to study the heavy-species chemistry. In future works we will address the MC solution of the electron kinetics and the proper coupling with the chemical kinetics.

To the best of our knowledge, gas-phase chemistry in plasmas was never described with a MC approach, despite the success of the stochastic methods in describing relatively complex surface kinetics [2] and biochemical systems [3]. Here, we solve the heavy-species kinetics using the Kinetic Monte Carlo (KMC) algorithm developed by Gillespie [4] to simulate the temporal evolution of coupled chemical reactions. KMC simulations are exact, in the sense that they follow the time-evolution of one element of the statistical ensemble, simulated without any subjacent approximations. They provide the answers to the questions 'when and what', determining the dynamics of the chemical species. In short, it is considered that the system may undergo k reactions $\{R_1,\ldots,R_k\}$, characterized by transition rates $\{r_1,\ldots,r_k\}$, and that the number of particle combinations capable of experiencing a given reaction are $\{n_1,\ldots,n_k\}$. Upon the successful choice of 'what' (which reaction), time is advanced by randomly selecting an increment τ from an exponential distribution with parameter $\lambda=\Sigma_i n_i r_i$, namely $\tau=(1/\lambda)\ln(1/r)$, where r is a random number drawn from the uniform distribution in the unit interval.

The kinetic KMC algorithm used here was validated by Gillespie in [5] through a comparison of the MC results with deterministic calculations. However, this comparison was performed only for very simple chemical systems with few species and reactions. In this work, we use a realistic and much more complex system for the validation of the KMC algorithm: the heavy-species kinetics in an O_2 glow discharge. The simulation conditions used in the model are: p = 1 Torr, T_g = 396 K, E/N = 48 Td and $n_e = 6.5 \times 10^{15}$ m^{-3} (corresponding to a current of 40 mA). The deterministic simulations are performed using the 0-D chemistry solver of the LisbOn Kinetics (LoKI) tool suit [6,7], for the conditions and using the same kinetic scheme [8] as in the KMC calculations.

Figure 1 shows the temporal evolution of the most abundant species in the discharge ($O_2(X)$, $O_2(a)$ and $O(^3P)$), comparing the KMC (with 10^5 particles) and LoKI simulations. The agreement is remarkable, which indicates that the two methods are equivalent in this case. However, a substantial factor for the smoothness of a MC simulation is the initial number of molecules in the system. To analyze this effect, we performed simulations with the same input conditions but with a different number of simulation particles. Figure 2 presents the time-evolution of the $O_3(X)$ fraction, where it can be observed that the more particles we put in the simulation, the smaller are the fluctuations of the results. Figure 2 reveals a major drawback of the standard KMC method: when we want to describe accurately the rare species in a discharge we need a large number of particles in the simulation, which may become very expensive in terms of CPU time. The (unphysical) statistical fluctuations on the calculation of the densities of the rare species are larger because the associated transition rates are much smaller and the associated reactions are rarely chosen. In this work, we propose a variance reduction method, where the reaction selection is uniform: instead of having different intervals for each reaction i with length $L_i = n_i r_i/\lambda$, we consider a single interval for each reaction given by $L'=1/k$. However, when a reaction i is chosen, we have to correct its weight (importance) with the factor L_i/L'. Figures 3 and 4 present the fractions of two minority species (O_3(exc) and O_2^+), comparing our approach with the standard one. For a similar CPU time, we can reduce significantly the fluctuations using the new method. Different variance-reduction techniques to achieve an efficient and accurate time-evolution of all the species, including the minority ones, will be presented and discussed at the conference.

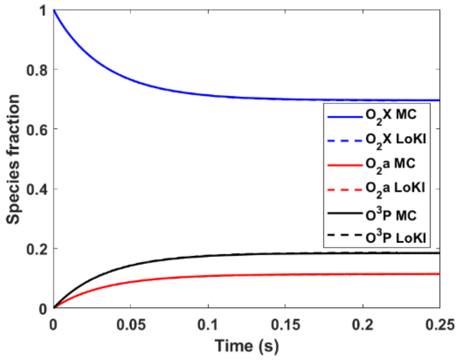


Fig. 1: Comparison between KMC (10^5 particles) and LoKI.

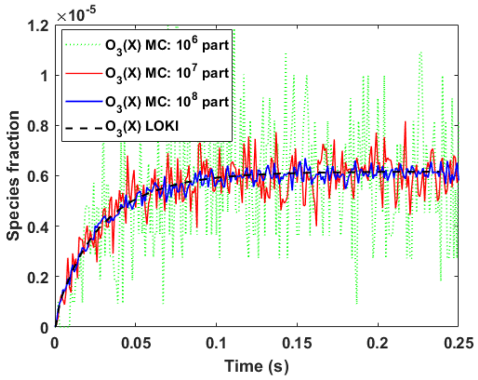
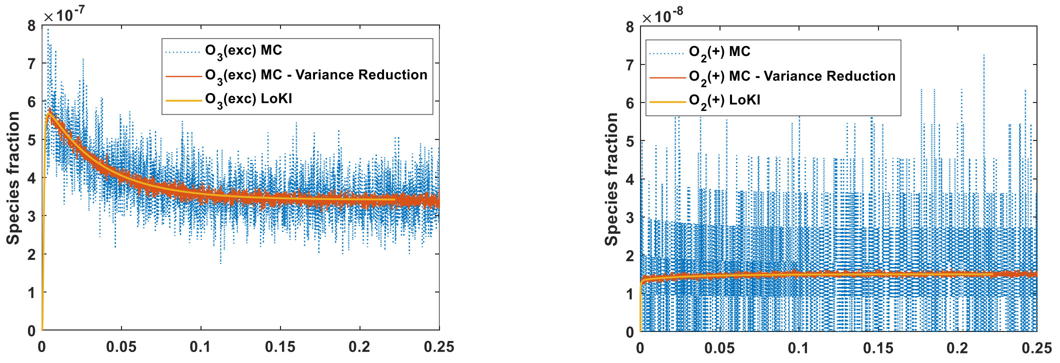


Fig. 2: Comparison between KMC and LoKI, varying the number of particles in the simulation.



b) O_3(exc) **a)** O_2^+

Fig. 3: Comparison between KMC (10^8 particles) and LoKI, using both standard and new methods.

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