It's all About Monte Carlo

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Kinetic Monte Carlo (KMC) algorithms have been effectively used in recent years to study atomic recombination and molecule formation on surfaces [1-3]. KMC simulations are exact, in the sense that they follow the time-evolution of one element of the statistical ensemble, simulated without any subjacent approximation. They provide the answers to the questions 'when, where and what', determining the dynamics of the surface. In short, it is considered that the system may undergo k transition events, $\{e_1,\ldots,e_k\}$, characterised by transition rates $\{r_1,\ldots,r_k\}$, and that the number of particles capable of experiencing a given event are $\{n_1,\ldots,n_k\}$. Upon the successful choice of 'what' (which event) and 'where' (on each position on the surface), 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, as initially proposed in [4].

Despite the success of KMC algorithms in describing relatively complex surface kinetics [1-3], the coupling with gas phase chemistry remains tenuous. The large differences in the characteristic timescales, which can vary over several orders of magnitude, makes the situation even worse regarding a full MC description including the electron kinetics as well. This work points out how to achieve a common formulation of KMC algorithms capable of addressing simultaneously, in a fully coupled way, the surface, chemical and electron kinetics. It focuses on the recent progress made in the KMC description of surface kinetics [1-3] and reviews the current state of KMC algorithms for gas phase chemistry [5], using oxygen discharges as a test case. In addition, a new KMC method to study the electron kinetics is outlined. The new approach is suited to study the coupled kinetics in nanosecond discharges [6], where the high values of the reduced electric fields limit the accuracy of the calculation of the electron energy distribution function using a 2-term Boltzmann solver and where the influence of collisions with different excited states and of the atomic kinetics can be significant.

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