Challenges in plasma modelling for environmental applications: electron kinetics and transport

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Computer models are a powerful tool for advancing scientific and technological investigation of plasmas for environmental applications. However, developing such tools is a great challenge due to the complex chemical network and multiple time scales. Moreover, these models are strongly dependent on the choice of atomic and molecular data, such as cross sections and rate coefficients. In this work, electron kinetics and transport in gases and plasmas is studied using different computational approaches. First, the importance of anisotropic scattering of electrons with molecules on calculations of electron transport parameters is investigated using Monte Carlo simulations. Finally, a 2-D fluid model is presented which is being developed to study electron kinetics and transport in surface dielectric barrier discharges for water treatment. As a result of the models, insights into optimization of electron impact cross sections which are used as input to the fluid model are derived.

Introduction

Atmospheric pressure plasma sources have been widely studied in recent decades for application in medicine, agriculture, aerospace engineering, and plasma processing of materials and surfaces [1, 2, 3]. As an example, the dielectric barrier discharge (DBD) is a practical and low-cost configuration, where the plasma is generated by a time-varying high voltage (several kVs) between two electrodes; the dielectric barrier is to prevent arcing between electrodes which could otherwise occur following electrical breakdown of the gas. Recently, surface DBDs in ambient air have found applications in agriculture for plasma indirect treatment of water [4, 5]. The uniqueness of this process is the adjustability of the pH with one system which can be used for sanitation purposes. Additionally, the technology can be used on-demand for production of nitric acid, and therefore nitrates, in a plant-usable form of water. However, despite an excellent capability, most of the currently available plasma sources for water treatment still have several shortcomings such as scalability, durability of the electrodes, and possible requirements for carrier gases or other chemicals [6]. Moreover, comprehensive understanding of the main physical and chemical mechanisms as a function of operational parameters is still limited [7]. Similar considerations for microwave discharges for CO_2 conversion are applicable.

Numerical modelling of atmospheric pressure plasmas operating with molecular gases is still challenging, mainly due to the complex chemical network and multiple timescales. So far, many studies have relied on lower-dimensional (0-D) models where a large number of species and chemical reactions are taken into account [8, 9]. The use of these models is also motivated by the large disparity of timescales, ranging from electron impact ionization ($1-10$ ns) to slower neutral reactions and gas-phase mass transport ($\sim$ s timescale), as shown in Fig. 1. However, 0-D models typically neglect the transport of charged and neutral species in the plasmas, the interactions of the plasma with surfaces, and the spatial non-uniformity of the discharge. Moreover, kinetic and fluid models are strongly dependent on the choice of atomic and molecular data, such as cross sections and rate coefficients. Such coefficients are usually calculated from collision cross-section data by solving numerically the electron Boltzmann equation (EBE). Requirements of accuracy, consistency, and completeness of such cross sections sets significantly affects the predictive capability of these models, not only in the estimation of macroscopic plasma parameters, but also in the determination of the main chemical mechanisms [10].

In this presentation, electron kinetics and transport in molecular gases and plasmas is investigated using different numerical methods. First, Monte Carlo simulations of electron swarm in gases are presented to assess the accuracy of the available sets of cross sections. The importance of anisotropic

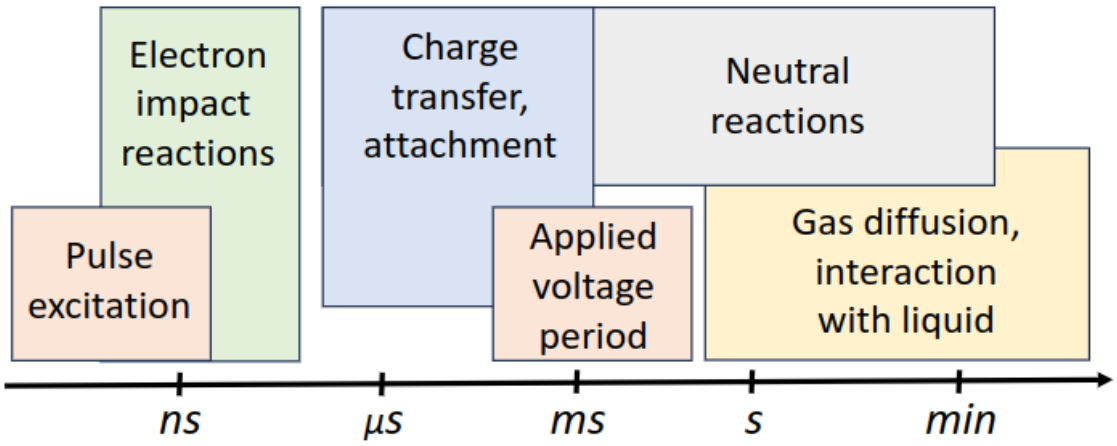

Fig. 1: Multiple timescales in surface DBDs for water treatment.

scattering of electrons is emphasized. Finally, an application for surface DBD for water treatment is given. The emphasis is on the fluid model development and assessment of the accuracy in the assumptions that are usually taken for description of electron kinetics and transport in atmospheric pressure plasmas.

Monte Carlo simulations of electron swarm in gases

The first part of the presentation focuses on several aspects of anisotropic scattering of electrons in gases. A Monte Carlo simulations code for electrons has been developed to study the effect of scattering dynamics in electron rate and transport coefficients [11]. First, the accuracy of the implementation and treatment of anisotropic scattering is assessed through benchmarking calculations of two-term, multi-term Boltzmann solver, and Monte Carlo simulations [14]. Fig. 2 shows results obtained with isotropic, forward, and screened Coulomb angular scattering models in electron-neutral collisions with the Lucas-Salee ideal gas model. The impact of scattering on electron swarm parameters is demonstrated in both conservative and non-conservative model gases using Monte Carlo simulations and 10-term solutions of the electron Boltzmann equation showing excellent agreement between the two codes.

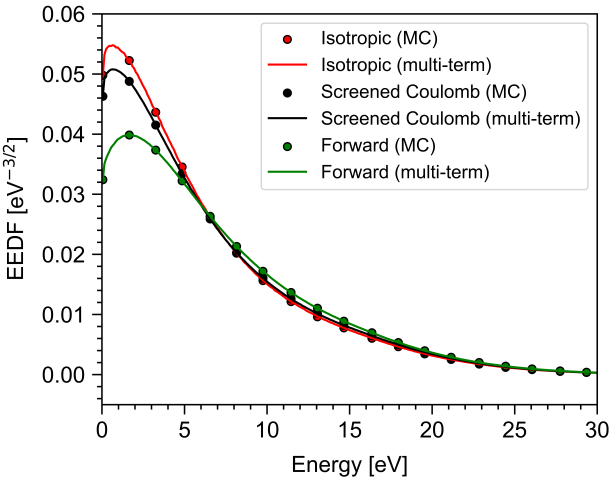

Fig. 2: Electron energy distribution function calculated at 100 Td with Lucas-Salee ideal gas model using Monte Carlo simulations (dots) and multi-term Boltzmann solver (lines) [14]. Three different angular scattering models have been used: isotropic (red), screened-Coulomb (black), and forward scattering (green).

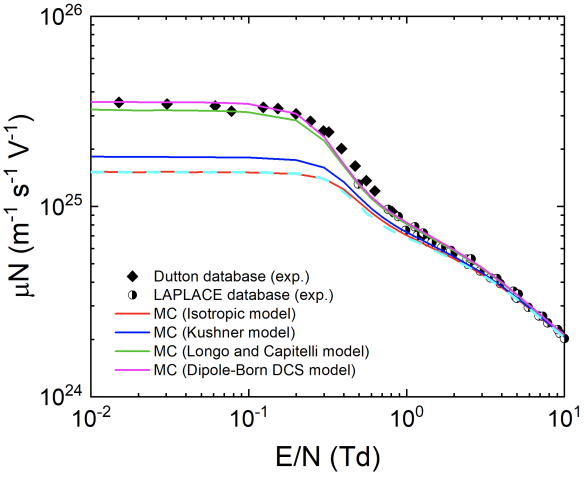

Fig. 3: Electron reduced mobility measured (dots) and calculated (lines) using Monte Carlo simulations in CO with different angular scattering models and Biagi's set of cross sections, as a function of the reduced electric field.

Then, the importance of anisotropic scattering of electrons in real gases is assessed. Specifically, an anisotropic scattering model for dipole rotational collisions of electrons has been derived based on the dipole-Born differential cross sections. Results of electron reduced mobility obtianed with Monte Carlo simulations using different angular scattering models is compared with measured transport parameters in Fig. 3. It has been found that the application of anisotropic scattering of electrons in rotational collisions affects significantly the calculated electron transport parameters in molecular gases, such as CO [11], NO [12], and H_2O [13]. The consequences in the electron swarm derived cross sections are also discussed. Finally, the application of Monte Carlo simulations of electrons in arbitrary mixture of gases is presented. As an example, electron transport parameters calculated in air with variable concentrations of H_2O vapor are presented and compared with experiments [15]. These results are important for estimation of three-body attachment cross sections of electrons in air with variable admixture of water vapor, which is often neglected in plasma chemistry models at atmospheric pressure [15]. It is demonstrated that insights provided by Monte Carlo simulations of electron swarms in gases are important for accurate optimization of electron impact cross sections that are used as input to fluid models of the plasma.

Fluid modelling of plasmas for environmental applications

A 2-D fluid model for surface DBDs is being developed to study the influence of operational parameters in plasma formation and production of reactive oxygen and nitrogen species. The model couples fluid discharge equations for a four fluid mixture including neutrals, electrons, positive ions, and negative ions, with the Poisson equation. The electron rate and transport coefficients are derived from Monte Carlo simulations of electrons. The transport of charged particles has been described using the drift-diffusion approximation. Results of the fluid model have been benchmarked against PIC/MCC simulations and Full-Fluid Moment Model results for a 1-D DC breakdown in Ar [16]. Furthermore, the correctness of the implementation has been tested against analytical and manufactured solutions. As an example, the model is applied to study discharge formation in surface DBDs operated with air. As a perspective, results obtained from the fluid model can be used to inform lower dimensional (0-D) chemistry models to accurately describe the gas heating, ion wind, and neutral species transport effects on the chemical reactions occurring in the plasma and gas phase.

Challenges and future outlook

Despite electron transport in gases has been studied since decades, we conclude that modelling and simulations of electrons in arbitrary mixture of gases are still challenging. This is mostly due to the lack

of experimental electron transport parameters and accurate cross sections of electron impact dissociation of molecules. Comparison between electron swarm measurements and calculations can provide valuable insights into the collision dynamics and cross sections magnitude and shape. Apart from electron swarm, modelling of surface DBDs with complex chemistry is still limited to timescales much shorter than the typical treatment time, that is in the order of minutes. Methods to bridge longer timescales and integrate experimental data into modelling frameworks is sought after for quantitative understanding of plasma formation and dynamics.

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