Non-equilibrium as the cornerstone of collisional low-temperature plasmas: cross sections, kinetic phenomena and real world applications*

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1. Introduction

Low temperature plasmas have been the basis of a vast number of applications, ranging from light sources, nano-electronics structures to new medical and agricultural procedures. The key ingredient opening doors to so many different applied technologies and techniques is the non-equilibrium nature of such plasmas. Manifestations of non-equilibrium are numerous and very different. As general laws cannot be developed, low temperature plasmas have often been considered as lacking the fundamental nature. That view is, however, equivalent to absolute application of reductionism as a principle in seeking the fundamental. With any two non-equilibrium plasmas being so different, one must seek the intellectual underpinnings of the LTPs in the search for the elementary data (mostly scattering cross sections), understanding and reshaping collective kinetic phenomena and using them to tailor different plasma sources for specific applications. In other words, the common fundamental thread is in learning how to predict controlled plasma sources with desirable properties. In this presentation we shall first return to the swarm technique of obtaining the cross sections and how those affect some specific applications. Furthermore we shall observe how electron collisions establish properties of the breakdown in RF fields where production of secondaries in collisions with surfaces is not required to achieve a self-sustained discharge. We shall address systems where ionization is due to the presence of free positrons, namely the gas filled positron traps.

Kinetic phenomena have been defined in the physics of non-equilibrium plasmas as the manifestation of their non-equilibrium nature. We may illustrate the complexity of non-equilibrium in one example of plasma, the atmospheric pressure plasma jet. For example, it has been shown to be effective in controlling production of reactive species needed to activate the immune response of the human immune system cells to tumour cells. The fundamental understanding of kinetic phenomena provides ample opportunities for a large number of applications of low-temperature plasmas that are at the front of modern technologies.

2. Equilibrium with the local electric field

This is the most common form of non-equilibrium that is employed in plasma models and is represented as hydrodynamic equilibrium. In its root is the applicability of the hydrodynamic expansion of the Boltzmann equation and the equilibrium between the energy gained from the local field and lost in collisions with gas molecules. Hydrodynamic expansion provides the foundation for the definition of transport coefficients. Essentially the very presence of transport implies some form of non-equilibrium driven by the external field. It appears to be a physical situation similar to the transition of the initial form of universe that has been initially in thermodynamic equilibrium (TE) for around 200 000 years. The additional gravitational field converted almost uniform TE plasma into lumps of matter that gave rise to the proto galaxies (and furthermore stars and other interstellar objects).

In a similar fashion, external field affects the electron, ion and non-thermal neutral ensembles into seemingly organized entities called swarms. In its zero space charge limit, physics of swarms provides low temperature plasmas (LTP) with the description of the local field driven equilibrium that is a form of non-equilibrium exactly calculable by Boltzmann equation or Monte Carlo simulations for infinite (and uniform) systems.

Calculated rates and transport coefficients may be employed in fluid models of the LTP. These coefficients are directly shaped by the cross sections and thus their measured values may be used to obtain the cross sections by employing the so-called 'swarm technique'. Advantage of that technique is that it provides complete sets of cross sections that satisfy number, momentum and energy balances defined by the transport coefficients. In Figure 1. we show a fit of calculated to experimental data for drift velocities in mixture of 2% tetrafluoroethane mixture in argon. Interestingly, there is a region where drift velocity decreases for increasing *E/N*, a phenomenon known as negative differential conductivity (NDC). That is one of the better known multifaceted kinetic phenomena that arise due to changing degrees of relaxation of momentum and mean energy as *E/N* changes.

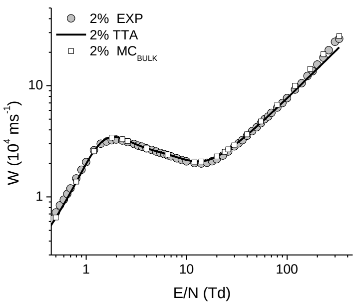

Figure 1. Drift velocities in 2% mixture of tetrafluoroethane in Ar.

3. Nonequilibrium plasmas (NEP) at atmospheric pressure

Thermal plasmas (TP) have all temperatures equal ($T_e >> T_i > T_{gas}$) as opposed to the NEP ($T_e = T_i = T_{gas}$). With an increasing space charge, the exchange of energy between electrons and ions increases and so does the transfer from ions to the background neutrals. Under those conditions energy put into plasma is redistributed mainly to heating ions and consequently the background gas (and walls) rather than electrons. The desired mode for plasma medical applications is to have the NEP so that heating of the substrate (made up of living cells) does not cause thermal necrosis. The increase of charged particle density *n* is defined by

$$n = n_0 e^{\alpha d} = n_0 e^{\frac{\alpha(E/N)}{N} dN} .$$

Here, high gas number density *N* leads to a rapid growth of space charge over a limited space or time. Therefore in order to promote the NEP one needs to control the space charge growth. Control can be achieved by: Inhomogeneous fields (corona); Dielectric barrier- interrupt the field on the dielectric surface; Temporal modulation; Microwave; Pulsed; RF; Gas mixture (make plasma in He/Ar and mix it into the air); Micro scale discharged (using jd^2 scaling); and through Combined methods. Over many decades, only the following atmospheric pressure plasmas have been implemented: dielectric barrier discharge (DBD); sparks and streamers and corona discharges (positive and negative corona). Recently, however, new sources have been developed including: plasma needle; atmospheric pressure plasma jets, micro jets, plasma bullets; atmospheric pressure rf discharges and glow discharges; atmospheric pressure -microwave discharges and more. These plasma sources have the properties allowing applications on thermally unstable materials and living tissue and on inorganic materials that may suffer from the unwanted thermal effects. Typical kinetic phenomena at atmospheric pressure include self-propagating ionization fronts (plasma bullets); and many more.

4. Temporal and spatial relaxation of swarm properties and lack thereof

In moments after the initiation of the field/swarm, close to the electrodes or walls and in time varying fields there is a constant struggle for the swarm properties to relax. Electron, ion and super-thermal neutral swarms relax at quite different timescales. Ionization takes place on a different timescale altogether and excited species and chemically active radicals may linger on for quite a long time. Different energy domains will have different relaxation times with significant differences between high energy tail and the bulk of distribution. Choosing frequency we may choose that time varying field may affect electrons and not ions. Using two frequencies independently applied to the plasma we may achieve a functional separation between the field that produces plasma and the field that controls flux of ions towards the surface. Importance of such control for plasma etching devices cannot be overemphasized and modern day procedures use tailor made pulses (rather than a combination of two RF fields) for fine tuning energy profile of the ion beam and its other properties. The RF breakdown itself has its peculiarities from a double valued breakdown (Paschen like) curve to extension of the swarm either well in-between electrodes never touching them to electrode to electrode oscillations of fast electrons whereby most of the ionization occurs right in front of the electrodes. As for infinite gas swarms, the focus may be on different relaxations leading to a number of kinetic phenomena including time resolved NDC, anomalous time dependent diffusion, anomalous diffusion as the field goes through the zero value, and many more.

5. Towards surfaces, non-neutral plasma, gas phase chemistry and applications

At times when phase of the repetitious signal passes through zero values of the field and changes of direction, relaxation, if not equally completed for all properties, leads a range of kinetic phenomena each bringing in a different aspect of non-equilibrium: anomalous RF diffusion, RF NDC, RF negative absolute conductivity, anomalous RF diffusion and more. After initiation of the field/swarm or close to the electrodes, properties of the cross sections may lead to selective particle losses due to diffusion/attachment heating/cooling. Those losses function in much the same way as hole burning in populations of excited atoms in lasers albeit with a more complex profiles and kinetics. The same occurs in gas filled positron traps where employing Maxwell Boltzmann distribution often cannot fit the complex distribution functions that develop. Finally, separation of electrons and ions leading to formation of sheaths provides functionality to plasma etching. On the other hand transition of ions to fast neutrals either on surfaces or in charge transfer collisions allows us to control charging in dielectric trenches and contact holes and reduce damage and limitations such as etch stop.

6. Instead of conclusion

All the mentioned kinetic phenomena give an insight into balances leading to some form of non-equilibrium. Plasmas are equipped with enough of different tools to be able to provide the most complex of tasks such as plasma medicine or even the initial formation of life. One just needs to find ways to tailor their properties in a predictable and controlled fashion.

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