Modelling of Anomalous Doppler broadened Lines, Thermalization of Electrons and the role of Radicals in Discharges at high E/N

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Abstract. In this paper we show how Monte Carlo technique developed for swarm studies may be applied to model some real discharges or to provide data for realistic plasma models. In all cases discussed here the Monte Carlo technique without self consistent field is driven to a much greater level of complexity than usually found in swarm studies. We discuss three conceptually quite different situations that require exact modelling by Monte Carlo Simulations (MCS). The first is the case of transport in gases where degree of dissociation is large and thereby radicals formed by the discharge may affect the transport coefficients. Based on recent calculations for electron CF₄ radical cross sections we calculated how transport coefficients would be affected by the presence of radicals in pure CF₄ and CF₄/Ar mixtures covering range of abundances often found in plasma etching devices. The second case studied here is modelling of thermalization of high energy electrons in the atmospheric gases as an attempt to provide the basis for detection of very high energy cosmic particles. In that case pressure dependent emission efficiency is studied as a function of electron energy and the system is developed to an arbitrary degree of secondary electron production. Finally we give some recent advances and current status of modelling of high E/N discharges operating in Townsend’s regime in hydrogen where anomalous broadening was observed and explained by fast neutral excitation in both directions along and against the acceleration due to electric field.

1. Introduction
Non-equilibrium nature of plasmas [1, 2] makes them especially suited for numerous applications ranging from plasma etching of integrated circuits through treatment of materials, light sources to biomedical treatments and large scale modification of the atmosphere. Perhaps the most promising future applications of non-equilibrium plasmas include massively parallel production of nanostructures for nanotechnologies (top down approach) and for medical treatments. Monte Carlo simulations are the best way to model such plasmas as they allow realistic treatment of complex boundary conditions [3], inclusion of recently found complex kinetic phenomena [4] and essentially 3 dimensional treatments of complex geometries. In this paper we show three examples of how extension of standard and exact Monte Carlo procedure as developed for studies of charged particle swarms [5] may be extended by making the model more complex by one step to include new phenomena required to explain realistic discharges in gases.

The first example involves complexity due to presence of radicals created by the discharge itself and now, thanks to recent calculations of cross sections it has become possible to answer the question
of just how much do the radicals change the transport in gases. The second example is that of emission caused by very high energy charged particles in the atmosphere where most of the emission is produced by secondary electrons. Complexity added here is due to very large initial energy and the need to follow a large number of secondary electrons produced by the primary particle. Finally we address and even more complicated situation where both the primary electrons are in runaway, the length of the particle becomes comparable to the mean free path so the energies change form one point to another and most of the excitation is produced by fast neutrals which are generated in charge exchange collisions of ions with gas molecules or in neutralization and reflection of fast ions hitting the cathode.

Observations of anomalously broadened hydrogen lines in gas discharges were made in 60s and the explanations that followed were mainly based on dissociative processes. However, some observations, especially those of Benesch and Li [6] could not be explained without evoking the directionality of the motion of ions. First full explanation of the effect and observations of energies exceeding few tens of eV were made on the basis of a swarm experiment carried out by Petrović et al. [7] which revealed the need to include a new effect, that of the reflection of fast neutrals from the cathode with sufficient energies to produce hydrogen radiation. The model that was developed although having a correct physical phenomenology was based on approximate treatment of non-hydrodynamic transport, i.e. essentially on a beam like treatment of energy distribution functions with the mean energy calculated from the energy balance. In the meantime the set of pertinent atomic collisions has become much more complex and we have based the calculations on a Monte Carlo simulation which gives exact energy distributions. We will present the results on all details of kinetics of relevant particles, from electrons to ions, molecules and atoms. We will also stress the need to model more accurately the heavy particle collisions, especially the angular anisotropy of scattering.

Thermalization of electrons produced by cosmic rays from very high energies and the resulting emission of nitrogen radiation has been proposed as a means to detect properties of extremely high energy elementary particles. The process is exactly the opposite to that taking place in modeling of high E/N discharges and may be treated exactly by a similar Monte Carlo code if the applied cross sections are correct.

Finally we will discuss how dissociated fragments affect the transport properties of electrons having in mind applications such as plasma etching of SiO₂ where abundances of radicals of CFₓ are of the order of several percent. The principal effect of radicals on electron transport in pure CF₄ or in CFₓ/Ar mixtures is through very different attachment rates which lead to orders of magnitude different effective attachment rate for the mixture with radicals as compared to the properties of pristine buffer gas. Thus one may conclude that even the electronegative nature of the plasma may be changed due to the presence of different radicals, especially of CF₂.

1.1. Monte Carlo simulation technique

The MC code has been developed based on null collision technique and has been tested against all known benchmarks [3, 8]. The code has a facility to use energy dependent differential cross sections defined specially for each process and it also has a facility to follow sequentially products such as ions, fast neutrals, secondary and reflected electrons. We typically follow 100 000 electrons through hundreds of thousands of collisions and we have means to reproduce all observables with accuracy limited only by the quality of the cross sections and by statistical uncertainty.

2. The effect of CFₓ radicals on electron transport in CF₄

Carbon tetrafluoride is commonly used in today's semiconductor industry for etching of dielectric materials, such as SiO₂ [1, 2] and also for deposition of fluorinated polymer films. CF₄ has also an important role in a number of technological applications. CF₄ belongs to the Freon group of gases that unfortunately significantly contribute to the global warming of our planet with a lifetime of 50 000 years.

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In industrial applications a large number of radicals are produced in plasmas, and in etching reactors the densities of radicals may reach several percent [9]. In CCP (capacitively coupled plasma) [10] and ICP (inductively coupled plasma) [11] etching reactors in fluorine-poor gas mixtures the dominant reactive radical is CF₂. The effect of these radicals has already been studied in the literature [12].

Recent advances in electron scattering theory [13] made it possible to calculate the cross sections for electron scattering on CFₓ radicals in the energy domain relevant to non-equilibrium plasmas. Some of the cross sections for electron- CX radical scattering can be significantly larger than the cross sections for CF₄ itself especially in the region of the Ramsauer Townsend minimum and for the attachment cross section [13]. Until recently [14] no direct experimental measurements of these cross-sections have been performed.

Of all the CFₓ radicals the CF₂ molecule may be present at the level of several percent [9, 15] in industrially relevant plasmas. As a result it could play a significant role even at the level of electron transport that determines the electron energy distribution function (EEDF) and the basic kinetics.

In this work we have calculated the electron transport coefficients for mixtures consisting of CF₄/CF₂ [16] and of CF₄/Ar/CFₓ [17]. Argon was present at 10% while the abundance of the radical was varied from 0.01% to 10% thus covering realistic abundances found in plasma applications. We have also performed calculations for all possible radicals CF, CF₃, F, F₂ but those, while present in significant amounts are never found at densities greater than CF₂. In general we have used a two term code for calculations and verified them by a Monte Carlo simulation (MCS).

2.1. Calculated transport coefficients in mixtures with radicals

Our calculations [16, 17] indicate that the addition of radicals even at the level of 10% does not affect very much the mean energy and the EEDF (see figure 1). On the other hand the effect on the drift velocity is significant and one example is shown for the mixture that includes argon in figure 2. The comparison between the two figures means that while mean energy is not perturbed much by the presence of radical and the shape of EEDF is not affected the elastic cross section for radicals which does not have a minimum fills the cross section in the region of the Ramsauer Townsend minimum in
CF₄ and it changes the optimum conditions for the negative differential conductivity [16, 18]. This is a proof that by selecting a mixture one may control independently the momentum and the energy balance and in particular the number balance.

The dominant number changing process in the discharge for energies of practical gas discharges is the attachment. It is a characteristic of the cross sections for electron scattering in CF₂ [19] that attachment has a threshold at a relatively high energy. On the other hand some of the radicals, CF₂ and F₂ in particular have a threshold at lower energies [13, 20].

In figure 3 we show the effective rate coefficients for attachment for two abundances of the radicals one 1% and 10% [16] in pure CF₄. The cross sections for F₂ and F were taken from [20, 21]. Since CF₃ does not have the attachment the curve for 1% of CF₃ is close to that for pure CF₄ while the reduced attachment as the abundance is increased to 10% is due to dilution of the attaching gas in the mixture.

On the basis of our calculations one could conclude that even for the abundances of radicals CF₂ of few percent the effect on the transport coefficients of electrons is significant and requires consideration in plasma modeling. Apart from momentum balance and the presence of the negative differential conductivity the most important effect is on the effective attachment rate. The operating point of plasma will certainly change as the abundance of radicals grows and even the nature will change from almost electropositive plasma to electronegative plasma with all the consequences and changes in the nature and anatomy of the discharge.

3. Thermalization of high energy electrons in nitrogen

The kinetics of excited species at higher altitudes has been often connected to the kinetics of electrons. Emission from the higher layer of the atmosphere has been proposed as a probe of the particles of cosmic origin with extremely high energies [22, 23]. In their papers Blanco and Arqueros [23, 24] have applied a Monte Carlo technique to calculate the emission due to thermalization of very high energy electrons in nitrogen at low pressures that correspond to the conditions in the upper atmosphere. These authors have initially assumed that the cross section may depend on the pressure if one needs to model the low pressure and the high pressure limits. The cross section is a description of a binary collision event and therefore it is independent of the pressure. What was required to fit the experimental results at higher pressures is to model the effective emission/excitation coefficient and the effect of secondary electrons.
These authors have eventually adopted modeling of secondary electrons and effective emission but they confined themselves to a single excitation by each of the secondary electrons and they limited their simulation to a certain escape radius R. In this paper we have performed calculations without such limitations and we based ourselves on a complete set of cross sections and differential cross sections [3] that were tested against standard swarm experiments at high E/N [8]. The MC code used here has representation of the detailed kinetics of primary and secondary electrons, ions and fast neutrals built in together with detailed representation of collisional events (differential cross section, treatment of non-conservative processes). For many years high altitude studies have focused on observation of emission from nitrogen and details of the cross sections from thermal to high energies have been compiled and analyzed [25, 26].

It is important to note that the swarms at very high E/N are a good laboratory equivalent of electrical processes in the upper atmosphere and our codes have been tested against those experiments [27] including the runaway phenomena in the EEDF [28]. Finally it is worth noting that with runaway effects being in the main phenomenology of lightning discharges [29, 30] these models are applicable to study lightnings as well as similar atmospheric electrical phenomena such as sprites, elves and blue jays.

In this paper we shall present our results modeling deposition of energy in nitrogen at low pressures that are analogous to and also test the results of Blanco and Arquieros [23]. We have extended the calculations [31] to produce results for spatial profiles of emission that may easily be measured in practice and applied to analyze the effect of cosmic rays in the upper atmosphere.

3.1. Cross section data
The cross sections set for electron scattering on N2 was the same one as in [3]. It consists basically of the data due to Phelps and Pitchford [32] for the total inelastic cross sections, while the total cross section was determined on the basis of their momentum transfer cross section and our collection of differential cross sections. The set was extended by the available data and high energy analytic formulae to 10 keV [3]. Our studies of high E/N data revealed that at high mean energies exceeding several hundred eV it is essential to define very well the differential cross sections as under those conditions of electron runaway it is essential to model properly the energy gain which is not properly calculated by using for example a momentum transfer cross section with isotropic scattering. Therefore our code has an option to use different differential cross sections not only for the elastic cross section which dominates at low energies. Other Monte Carlo codes limit their facility to deal with anisotropic scattering only to elastic scattering. In addition we have employed a number for different differential cross sections for different energy ranges in our code.

3.2. Thermalization of high energy electrons at low pressures of nitrogen
The effective macroscopic cross section may be determined from the effective emission. In Ref [23, 24] it is defined as:

\[ \varepsilon \propto (e) = N \sigma_{\text{apparent}} (e) \]

where cross sections refer to: \( v \rightarrow v' \)-transition between two vibrational sublevels of an excited state, inel- total cross section for all inelastic processes, ion- ionization; where \( e \) is the electron energy and \( R \) is the effective range as introduced in [23]. We may fit the results of simulation or experiment by using (2) and \( R \) as a fitting parameter. The effective cross section may be determined from:

\[ \varepsilon_{\text{apparent}} (e) = N \sigma_{\text{apparent}} (e) \]

where effective emission is the result of simulations. In our study [31] we sample directly the emission coefficient and therefore we can also sample the effective cross section.
In figure 4 we show results for the second positive state of nitrogen (337 nm emission). In addition to the basic cross section there is an extension to higher energies due to production of secondaries and subsequent excitation. The secondary electrons have lower energies than the primary beam and therefore they produce emission even at high energies when direct cross section by the primary electron is negligible. We agree with the data from [23] but there is some disagreement just at the maximum of the contribution of the secondaries for energies from 30 eV to 100 eV.

It is hard to separate which effect is due to different assumptions and which due to different cross sections so we have performed a calculation with the assumption of only one generation of secondaries [31]. A relatively good agreement with the data of [23] is also achieved if we fit our results with their formula and with R= 0.17 cm that is close to 0.2 cm used in [23]. At higher energies we see that discrepancy between our data and that from [23] is by a factor of 10 which is due to multiple excitations by secondaries.

The effects for the first negative band and the ionization are smaller but it is still significant to use multiple generations of secondary electrons [31].

3.3. Range of primary and secondary electrons
In addition to spatial emission profiles we may directly sample the range of electrons both primary and secondary. This quantity is well defined as the mean distance traveled by a group of electrons that have some common property. In this case the condition for declaring the end of sampling would be when electron energy drops down below the threshold for excitation. This time may be connected somehow to the time required for thermalization to be achieved but again both depend on the definition of the condition for ending the procedure...

The dependence of the calculated range $<R>$ as a function of the energy of the beam of electrons is shown in figure 5. We are able separate the range defined by the single excitation collision of the primary electrons and the range allowing multiple excitation collisions and the difference is up to a factor of 5. The calculated range was found to scale with pressure (as expected) so the value assumed...
in [23] is valid only for a narrow range of pressures around 1 Torr. It is also possible to compare the spatial profile of emission due to electrons with and without production of secondaries. While the range is greater if no secondaries are formed, the overall emission with secondaries is larger.

3.4 Conclusion
The effect of runaway electrons in high E/N experiments is fully analogous to the thermalization of high energy particles. Thus we propose that the high E/N experiments may be used to benchmark the codes for thermalization. While our results are directly applicable to compare with the results of papers [23, 24] it is also important to note that the upper atmosphere lightning's also involve high energy runaway electrons [29, 30]. In addition our results are relevant to other studies of thermalization of electrons [33] and positrons [34, 35] that in addition to atmospheric phenomena may include biomedical applications and radiation damage.

4. Modelling of Doppler broadened line profiles
The first interpretations of unusually high Doppler broadening of hydrogen lines in non-equilibrium plasmas [6, 7, 36-38] were based on possible dissociative processes, recombination and excitation. Experiments with dc fields revealed a large asymmetric component with energies exceeding the energy available from the repulsive potentials of the dissociating molecules [6, 7]. The explanation of such results was found in a specially designed high E/N swarm experiment [7, 39] which gave a proof that, to the largest degree the excitation is due to collisions of fast neutrals formed in charge transfer collisions of the buffer gas with ions accelerated by the electric field. At high E/N ions gain high energies and consequently create through charge transfer collisions very fast neutrals with comparable energies. In addition it is possible to have reflection and neutralization of ions with reflection as fast neutrals, which leads to different components in blue and red wings of the Doppler profile [7]. Anomally broadened profiles were observed in hydrogen lines in pure hydrogen and in hydrogen containing molecules such as methane [40] and especially the effects were pronounced in mixtures of such molecules with argon [39]. Here we show the latest results obtained by detailed modeling based

Figure 5 Effective mean range of particles for a single excitation collision (red) and for multiple collisions (black) [31].
on the most recent cross sections of A.V. Phelps [41] expanded with the analysis of the role of vibrational energy losses and anisotropy of the cross sections on the experimental observables.

4.1. Procedure of simulation
The Monte Carlo code [12] based on null collision technique was used to follow electrons and heavy particles (H\(^+\), H\(_2^+\), H\(_3^+\), fast H and fast H\(_2\)) in pure H\(_2\). Processes at cathode and anode surfaces such as secondary electron production, reflection, neutralization, elastic and inelastic collisions were also included based on the available experimental data and models of scattering without any adjustment. Simulations were performed for the conditions of high E/N Townsend experiments. We followed trajectories of all reaction fragments until they neutralized or thermalized below the H\(_2\) excitation energy.

4.2. Results for line and spatial profiles
In figure 6 we show profiles of the Balmer H\(_2\) line and the axial emission profile. A good representation of the profile is obtained with the best available data without any additional adjustments of the cross sections. Only a slightly better fit was obtained if inelastic energy losses due to vibrational excitation are introduced. We have used the suggestion of A.V. Phelps to include vibrational excitation only for H\(^+\) ions colliding with H\(_2\). We have also analyzed the role of anisotropy of scattering on the final results. It is essential to use forward scattering as EEDF will be very different and in disagreement with experiment if one assumes isotropic scattering (even when proper transition from total to momentum transfer cross section is made). However, the details of the differential cross section are open to discussion and may be used to fit the experimental data better.

4.3. Distribution function functions and fluxes
The Monte Carlo code can also provide all the details that are impossible to measure for example the energy distribution functions of fast neutrals at the cathodes (since they are not affected by field the

![Figure 6](image-url)
fast neutrals may fly in both directions. In figure 7 we show the distribution function of fast neutrals at the anode and at the cathode and at the figure 8 the axial profile of fluxes of different species in the gap between electrodes. The negative values for fast H mean that more particles flow backwards (as expected from the experimental profile due to reflection with neutralization and with dissociation of molecular ions at the cathode.

Calculations were made for two different yet sets of cross sections.

4.4. Conclusion
A similar degree of success was achieved in modeling of Doppler profiles in rare gas hydrogen (methane) mixtures and in pure methane [40].

One can conclude that the whole phenomenology is well developed and that even without any adjustments good fits of swarm like experiment are achieved. Therefore one may be free to pursue this further either to modify further and achieve a better fit or to proceed to model more complex gas discharges.

In all cases discussed in this text Monte Carlo simulation codes (in one case supplemented by a two term code) provide full description. It also shows a large number of situations where swarm phenomenology as represented by the

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**Figure 8** Energy distribution functions of fast H atoms at two electrodes.

**Figure 9** Fluxes of different heavy particles in the gap.

Use of transport coefficients [41] may provide full description.
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