TOPICAL REVIEW

Kinetic phenomena in charged particle transport in gases, swarm parameters and cross section data

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Abstract
In this review we discuss the current status of the physics of charged particle swarms, mainly electrons. The whole field is analysed mainly through its relationship to plasma modelling and illustrated by some recent examples developed mainly by our group. The measurements of the swarm coefficients and the availability of the data are briefly discussed. More time is devoted to the development of complete electron–molecule cross section sets along with recent examples such as NO, CF₄ and HBr. We extend the discussion to the availability of ion and fast neutral data and how swarm experiments may serve to provide new data. As a point where new insight into the kinetics of charge particle transport is provided, the role of kinetic phenomena is discussed and recent examples are listed. We focus here on giving two examples on how non-conservative processes make dramatic effects in transport, the negative absolute mobility and the negative differential conductivity for positrons in argon. Finally we discuss the applicability of swarm data in plasma modelling and the relationship to other fields where swarm experiments and analysis make significant contributions.

1. Introduction
Where has all the swarm physics gone? The swarm experiments, which were quite numerous in 1970s and 1980s (Huxley and Crompton 1974, Dutton 1975), seem to have almost disappeared with only a few groups continuing measurements (Šašić et al 2005, Malović et al 2003, Nakamura 1991). The conversions of the transport data and normalizations of the cross sections based on the swarm data are also rare (Sakai 2002, Kurihara et al 2000, Bordage et al 1999). Yet swarm physics represents the basis of the models of collisional non-equilibrium (low-temperature) plasmas (Robson et al 2005, Makabe and Petrović 2006) and as such it is present in a much broader sense than before. The aim of this paper is to review the current status of the physics of swarms, its relationship to discharge modelling and to present some recent results describing kinetic phenomena, new sets of cross sections and transport data. In doing so we make no attempts to give a comprehensive review as the space allocated to this paper is limited so we shall confine examples to those that were contributed recently by our group. A comprehensive article covering new advances in the physics of swarms, in analysis and evaluation of the data and in the new modes of its application is certainly long overdue but it would require much more space.

In particular we will show some examples of the cross section sets that were recently obtained and employed in plasma modelling, discuss the data needs and what are the best strategies to improve the availability of the data and quality of swarm experiments and analyses. We will cover examples of the data for crossed electric and magnetic fields, for time
varying fields and for pulsed fields. Finally we will discuss how studies of kinetic phenomena may add physical insight into the data and swarm techniques and how these may be important for numerous plasma phenomena.

In principle, the definition is that a swarm of charged particles is an ensemble of particles moving through the background gas under the influence of an external electric field. The density of charge is so low that charged particles do not affect the electric field and the Coulomb interaction between the charged particles is negligible. Finally, the charged particles have no chance of colliding with products or the remnants of previous collisions such as ions and excited molecules. Swarms may be regarded as the low current limit of gas discharges and as such the data are appropriate to normalize the scattering cross sections and verify the collisional parts of the plasma models.

2. The swarm technique

2.1. The basis of the swarm technique and key examples

The foundations for swarm physics were built by developing very accurate experiments producing transport coefficients such as drift velocities ($v$), characteristic energies ($D/\mu$) or diffusion coefficients ($D$) and ionization coefficients ($\alpha$). The first two coefficients were often used to unfold the cross sections in the region below few electronvolts where vibrational energy losses dominate the energy balance in molecular gases. With the closing of the laboratory at the Australian National University (Huxley and Crompton 1974) the shortage of high accuracy sources of transport data has become critical. The low energy region has been covered very well for most of the basic gases that serve as targets of scientific relevance processes. The problem of non-uniqueness appeared in independent data sets is equal to or greater than the number of characteristic energies so basically the technique itself is able to provide unique results provided that the number of the swarm analysis to include all relevant processes; in other words, the swarm derived cross section is too low. The fact that the swarm derived result was confirmed by a completely independent set of data (drift velocities in a hydrogen helium mixture) shows that the problem is not merely a completely independent set of data (drift velocities in a hydrogen helium mixture) shows that the problem is not merely the adequacy of the data for characteristic energy (Petrović and Crompton 1987). In this experiment only drift velocity was used and the analysis was based on the knowledge of the cross sections for helium and rotational excitation and elastic processes in hydrogen. Numerous attempts to solve this problem included tests of the Townsend–Huxley technique to determine characteristic energies (Braglia 1992), fitting of the cross sections by optimization algorithms (Morgan 1993), considerations of basic methodologies of collision theory and classical kinetic theory (Robson et al 2003, White et al 2002).

Interestingly, while for hydrogen beam (binary collision experiment) and theoretical results agree at the lowest energies where disagreement with the swarm result is significant, in the case of nitrogen swarm and beam results agree for vibrational excitation below the resonance while theory gives a significantly smaller result (Crompton 1994). It is hard to say whether other molecular gases such as O$_2$, D$_2$, NO, CO and CO$_2$ are not subject to similar disagreements between the theory and swarm experiment or perhaps they were not subjected to such detailed analysis.

2.2. Limitations and advantages of the swarm technique

Limitations of the swarm technique are well known and well analysed. Those include:

- non-uniqueness;
- limited resolution;
- averaging over angular distribution;
- complexity and indirect nature of the procedure.

The advantages compared with the binary collision technique (experimental) are numerous and also well analysed. These include:

- completeness;
- good pressure calibration and determination of the absolute cross sections;
modification (dashed curve) of the model rotational cross section lines) produce exactly the same transport data. Clearly, the resulting cross sections (solid lines and a combination of solid and dashed result and the predictions of the binary collision theory. Both sets of satisfies the changes similar to the difference between the swarm modification of the vibrational cross section (order to have exactly a factor of 5 difference) were selected and similar to parahydrogen (but with thresholds somewhat changed in non-uniqueness of swarm cross sections. Model cross sections that it would be impossible to obtain differential cross sections for inelastic processes. While this modification maintains losses of the two processes. This may be accomplished only for inelastic processes. While this modification maintains the energy balance the momentum transfer balance is not maintained. This balance is dominated by elastic collisions which are typically one to two orders of magnitude larger than the inelastic processes and therefore momentum balance would need experimental data of infinite accuracy matched by equally good numerical technique in order to resolve the non-uniqueness. The limited resolution is often sufficient to yield important information and at low \( E/N \) at 77 K the resolution of the entire electron energy distribution function (EEDF) may be as low as 5–6 meV. One such example is shown in figure 2, where we show the EEDF for electrons in NO, where it has been established that the first two peaks of the resonant vibrational excitation cross section are significantly lower than the other peaks. However, the resolution decreases with increasing mean energy and the entire ensemble plays a role, or at least the part of the ensemble that is above the threshold for inelastic processes. The fact that EEDF averages over all angles merely means that it would be impossible to obtain differential cross sections but the transport data are sometimes very sensitive to angular distribution of electrons after the collisions. It is especially so in the case of non-hydrodynamic situations such as those that may occur in sheaths or when runaway is possible. Of the advantages of the swarm technique we shall first mention the completeness. The term should only imply that the solution of the Boltzmann equation provides balance of the number of particles, of the momentum transfer and of the energy transfer. If a swarm-derived set of cross sections provides a good fit to the experimental swarm data it means that all these balances are satisfied and that the EEDF is accurate in the energy range that was covered by the data. If a set of cross sections is compiled from the binary collision experiments or theories there are no guarantees that all processes would be included. Although with major advances in binary collision experimental techniques the advantages of the swarm technique are being reduced, the distinction still exists and will persist for a while. Thus, we are yet to see a cross section set that was compiled based on experimental (and theoretical) cross section data only, that would predict properly all transport coefficients for all relevant energy ranges. The cross section sets compiled by Christophorou and Olthoff come close (e.g. for CF, see Christophorou et al. (1996)) but usually the prediction of ionization coefficients was not good (Bordage et al. 1999) even though ionization cross sections are known to be extremely accurate (Stephan et al. 1985). Since even the best compilations rely on several sources, it is quite possible, or to be more precise probable, that some process will not be included because it has not been measured directly in binary collision experiments. Typically dissociation into the ground state neutrals is missing. On the other hand the cross section sets compiled by the late Hayashi, that typically included some form of swarm normalization depending on the available data, were able to predict transport coefficients over very broad energy ranges.

Figure 1. An example chosen to show the problem of non-uniqueness of swarm cross sections. Model cross sections similar to parahydrogen (but with thresholds somewhat changed in order to have exactly a factor of 5 difference) were selected and modification of the vibrational cross section \( \Delta \sigma_{v1} \) was made to satisfy the changes similar to the difference between the swarm result and the predictions of the binary collision theory. Both sets of cross sections (solid lines and a combination of solid and dashed lines) produce exactly the same transport data. Clearly, the resulting modification (dashed curve) of the model rotational cross section \( \Delta \sigma_{i1} \) is in disagreement with its expected shape. The effect of the changes on the summed (total) momentum transfer cross section is negligible (Petrović 1985).

A possibility of direct applicability of the distribution functions, swarm and transport data in plasma modelling and analysis of diagnostic data.

Non-uniqueness is illustrated in figure 1. It merely means that if we have one inelastic process with the cross section that has been modified by \( \Delta \sigma \), it is still possible to achieve a good energy balance by modifying another cross section by \( \Delta \sigma (\varepsilon_1/\varepsilon_2) \), where \( \varepsilon_1/\varepsilon_2 \) is the ratio of energy losses of the two processes. This may be accomplished only for inelastic processes. While this modification maintains the energy balance the momentum transfer balance is not maintained. This balance is dominated by elastic collisions which are typically one to two orders of magnitude larger than the inelastic processes and therefore momentum balance would need experimental data of infinite accuracy matched by equally good numerical technique in order to resolve the non-uniqueness.

The limited resolution is often sufficient to yield important information and at low \( E/N \) at 77 K the resolution of the entire electron energy distribution function (EEDF) may be as low as 5–6 meV. One such example is shown in figure 2, where we show the EEDF for electrons in NO, where it has been established that the first two peaks of the resonant vibrational excitation cross section are significantly lower than the other peaks. However, the resolution decreases with increasing mean energy and the entire ensemble plays a role, or at least the part of the ensemble that is above the threshold for inelastic processes.

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Figure 2. The low energy part of the \( \nu = 0–1 \) vibrational excitation cross sections for electron–NO collisions are shown together with the energy distribution function obtained by the two-term theory (smooth curve–TTT) and Monte Carlo simulation (the curve with statistical fluctuations–MC). One can see that at 10 Td the first two peaks predominantly overlap with the EEDF giving information on their relative contribution (Novaković et al. 2006). In spite of the similarity the between TTT and MC curves there are appreciable discrepancies between the two especially at somewhat higher \( E/N \).
of the missing processes when agreement has been achieved effective excitation cross section therefore includes the effects and ionization cross section can be accurately measured. An cross section. At the same time both the ionization coefficient is a very sensitive function of the effective excitation done using the fact that the calculated Townsend ionization dissociation in case of molecules) cross sections is often specific line intensities.

if one needs to calculate the specific channels of excitation or (30–40 specific excitation channels) but it is only necessary sections with higher and lower thresholds. We have also used separate electronic excitation in different groups of cross sections. Those coming from the binary collision com- have been recently carried out (Šašić et al 2004, Strinić et al 2004).

Finally, one may apply mixtures to provide additional reasonably independent data to improve uniqueness. For example hydrogen has been added to helium as mentioned above (Petrović and Crompton 1987) to take advantage of the well known elastic scattering cross section for electrons in helium to use the drift velocities in a He/H$_2$ mixture in order to establish vibrational excitation for electron hydrogen collisions. On the other hand, the well established rotational excitation in hydrogen together with relatively accurately known elastic scattering cross section were the basis for using Ar/H$_2$ mixtures to thermalize very low energy electrons and obtain the low energy transport data and cross section for electrons in argon without relying on very high pressures which is necessary in pure Ar (Petrović et al 1995). Classic examples of the application of the mixture technique are:

- to transfer the sensitivity to inelastic processes to drift velocities in mixtures with the buffer gas with Ramsauer Townsend minimum (e.g. Ar–N$_2$ or Ar–H$_2$: Haddad and Crompton (1980), Haddad (1984)),
- to study very specific reaction channels such as attachment with EEDF determined by the buffer gas (Christophorou and Hunter 1984, Hunter et al 1989),
- to verify semi-analytic techniques to predict transport data for gas mixtures such as Blanc’s law (Šašić et al 2005) and the analogous law for ionization coefficients (Marić et al 2005).

### 3. Examples of the electron scattering cross section sets (recently obtained by applying the swarm technique)

Recently there have been several attempts to provide sets of cross sections. Those coming from the binary collision community are quite numerous and some of those include critical evaluations of the available data so they provide a valuable source of information (e.g. Buckman and Brunger 1997, Zecca et al 1996). Even collections of the bibliography are of great use (e.g. Hayashi 2004) as some sources of data are not easy to find or, even more so, are easy to overlook. The compilations of Christophorou, Olthoff and coworkers (e.g. Christophorou et al 1996) fall mainly into the category of compilations based

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**Figure 3.** A set of cross sections for argon including two electronic excitation cross sections and ionization.

2.3. Strategies for extending the applicability of the swarm technique

There are several ways to solve the problem of the lack of uniqueness in situations where a large number of cross sections exists. All of these are the basic strategies of implementing the swarm technique.

The first method to improve the uniqueness of the swarm data is to seek some additional information about the relative magnitude of the cross sections or about their shape either from electron scattering theory or from electron beam experiments. In this case swarm experiments were used often in the past to provide accurate normalization of the relative cross sections. One such example, determination of vibrational excitation cross section for NO, will be discussed later. With increasing accuracy of the binary collision data (both theoretical and experimental) swarm analysis should be used more often to provide information on the missing processes by producing effective cross sections. Such an approach has been used in the past (usually applied to the monatomic gases) to produce a single effective electronic excitation cross section (Jacob and Mangano 1976, Specht et al 1980). Many cross sections were derived more recently for rare gases that fall into the same category (Phelps ftp://jila.colorado.edu/collisiondata/electronneutral/electron.txt). For example, the cross section set for electrons in argon shown in figure 3 consists of two effective cross sections for electronic excitation and one for ionization. Even though the set is quite simple it is complete as it represents the total energy and momentum transfer exchange (as well as the number conservation). Other available sets separate electronic excitation in different groups of cross sections with higher and lower thresholds. We have also used a set with all (available) specific electronic excitation channels (30–40 specific excitation channels) but it is only necessary if one needs to calculate the specific channels of excitation or specific line intensities.

Generation of effective electronic excitation (and dissociation in case of molecules) cross sections is often done using the fact that the calculated Townsend ionization coefficient is a very sensitive function of the effective excitation cross section. At the same time both the ionization coefficient and ionization cross section can be accurately measured. An effective excitation cross section therefore includes the effects of the missing processes when agreement has been achieved between the calculated and experimental data for the ionization coefficients. This approach should be applied more frequently together with compilations of the data from binary collision experiments and recently it has been applied for CF$_2$ (Kurihara et al 2000).

If one wants to study separate channels of excitation one has to measure excitation coefficients for particular channels and then include the analysis of the cascading effects. The third approach has been exploited only partially and only recently: for electronic levels that radiate in the easily accessible visible and near infrared spectral range (Tachibana and Phelps 1979, Urošević et al 1983), for metastable electronic levels (Božin et al 1983, Lawton and Phelps 1978) and for vibrational levels (Bulos and Phelps 1976, Buckman and Phelps 1985). Application of excitation coefficients to normalize the cross sections of excitation of CH$_4$ and Xe by electrons have been recently carried out (Šašić et al 2004, Strinić et al 2004).
on binary collision data, but they make a further step to calculate the transport data. The compilations of the late Hayashi (which are being taken over by Nakamura), the work on compiling the cross section sets at Hokkaido University (Sakai 2002), the work of Morgan (2000) and above all the continuous work of Phelps (ftp://jila.colorado.edu/collisionsdata/electronneutral/electron.txt) are mainly based on the standard swarm analysis. Classical compilations of the swarm transport data such as those of Dutton (1975) and Gallagher et al (1983) have not been updated recently.

In recent years we have made several contributions to the available cross section data. Determination of the vibrational excitation cross sections for electrons in NO was achieved by combining the characteristic energies $eD/\mu$ which were not available up to that point in the required energy range with the information from the total cross sections and the data for similar gases that have strong resonances, such as O$_2$ and N$_2$. Without the additional information from experiments and theory it was not possible to resolve complex energy dependence of the cross section as partly seen in figure 2. The derived cross section (Josić et al 2001) was a factor of 40 greater than the previously available binary experiment result and has been subsequently confirmed by new binary collision experiments and theory (Jelisavčić et al 2003, Trevisan et al 2005, Allan 2005). Recently the cross section set has been extended to higher energies and to include a differential cross section (Novaković et al 2006).

A different approach was adopted for the electron cross sections with CF$_4$. As it was not possible to obtain binary cross section data for all processes, an effective cross section for dissociation mainly into the ground state was used to fit the ionization rate data (Kurihara et al 2000). This set has been the basis for many plasma models including the work of Georgijeva and Bogaerts (Georgijeva et al 2003) and for a separate study of the transport data (Dujko et al 2005) in dc electric and $E \times B$ fields. In figure 4 we show the dependence of the components of the electron drift velocity as a function of the magnetic field (reduced magnetic field $B/\sqrt{N}$ is given in units of Huxley, 1 Hz = $10^{-27}$ T m$^3$) for different values of $E/N$.

A combination of measurements of the excitation coefficients and the standard sets of the cross section data were used in order to renormalize cross sections for specific channels. This was done for ionic and atomic lines of rare gases such as Xe and Ar (Sirinič et al 2004) and for dissociative excitation of H$_2$, H$_6$ and CH(A–X) bands of CH$_4$ (Šašić et al 2004). The idea was to normalize the cross sections for dissociative excitation of methane in order to be able to use them as the benchmarks (Crompton 1994) for testing theories that would be subsequently used to calculate the dissociative excitation into the ground state products or cross sections for electron–radical collisions.

Finally we have compiled a set of cross sections combining binary collision results from theory and experiment and their combination in producing a complete set for electron scattering in HBr. The importance of this gas in plasma processing meant that the data for modelling are needed to develop chemical processes and plasma tools and yet there were no sets for this gas. Presumably the lack of transport data is due to the very reactive nature of this gas but recent advances in theory and experiment have made it possible to base the set on the binary experiments which suffer from fewer problems from reactive gases since their operating pressure is significantly lower. In order to complete the set (Šašić and Petrović 2006) some extrapolations based on the data for electron HCl scattering had to be made.

The data for cross sections are shown in figure 5. Since the total cross section is quite similar to a constant collision frequency cross section the drift velocities (see figure 6) do not show a significant structure. The effects of non-conservative processes are quite large due to the enormous attachment cross section as seen in figure 6 where we show the transport coefficients calculated by the two-term theory and by the Monte Carlo technique.

### 4. Ion swarms and fast neutrals

One may safely conclude that we still suffer from a great shortage of data for electron molecules and in particular for electron–radical collisions. An even worse situation exists for the transport and cross section data for ions that are both positive and negative. On the other hand the situation there is simpler as the low energy region may be covered by a smaller number of processes and ions seldom reach energies much higher than the thermal energy. For thermal energies there
are numerous results though the ions often found in reactive plasmas were seldom covered by swarm investigations as they cannot be easily produced.

Yet the need to model processes in sheaths, in particular for plasmas used for etching of SiO$_2$, requires cross sections in the range up to 1 keV. The control of negative ions in the off phase of the plasma in order to reduce charging of high aspect ratio nanostructures in dielectrics (Matsui et al 2001) poses similar requirements even for the negative ions (Petrovic et al 2006).

Which kind of data are required to model ions in plasmas is still an issue. One certainly needs transport data (mobilities and diffusion coefficients) for fluid codes. Nevertheless, to cover the higher energies or for kinetic techniques of modelling one needs to use the cross sections. It was shown that low energy scattering of parent gas ions should be represented by both isotropic and backward scattering in order to properly describe the low energy transport dominated by the resonant charge transfer (Phelps 1994, Jovanovíc 2004). Recent studies of ion scattering cross sections developed through the swarm procedure include the work on the analysis of positive ions in rare gas mixtures (Piscitelli et al 2003), of negative ions in SF$_6$ (Benhenni et al 2005) and atmospheric gases and a review of the data for negative ions has been prepared recently (Petrovic et al 2006). One example of the cross sections that have been derived recently is shown in figure 7.

In the analysis of the ion swarms it was customary to bypass the cross sections and involve interaction potentials in the calculations of data (Buchachenko et al 2005) which is not practical for modelling of non-equilibrium plasmas. Recently Nanbu and coworkers have developed a technique to calculate the differential cross sections for elastic and reactive collisions which was implemented as an integral part of the particle in cell simulation scheme (Nanbu and Kitatani 1995, Denpoh and Nanbu 1998). The technique has been employed for both positive and negative ions. The problem is that insufficient data (low energy mobility in the range of thermal energies) have been used to normalize the parameters and therefore the results may suffer from a degree of non-uniqueness. Unfortunately there is a shortage of experimental data especially at somewhat higher energies that are needed to establish the reactive cross sections. Thus a combination of a beam experiment and high $E/N$ Townsend discharge study (which is essentially a swarm experiment) was a good strategy to provide the data for reactive gases and for somewhat higher energies (Peko et al 1999).

One should mention a standard drift tube technique applied by de Urquiijo and coworkers (Piscitelli et al 2003, Benhenni et al 2005) which provides a lot of data for both ions and electrons in the moderate and higher energy range. The most important source of recent low energy transport data is the so-called FAIMS technique (High-field asymmetric waveform ion mobility spectrometry Guevremont et al 2001). Most comprehensive reviews of the cross sections for ions and also for fast neutrals for several gases have been prepared by Phelps (e.g. Phelps 1991).

As fast neutrals play a considerable role in plasma processing and as fast neutral based etching is considered (Petrovic and Stojanovic 1998, Panda and Economou 2001 and Samukawa et al 2002) the cross section data for the fast neutrals are required and may be sought through swarm experiments and their analysis (Petrovic et al 1992, Petrovic and Stojanovic 1998). One example of recent results along the lines first...
measurements and analysis of the effect of fast neutrals in phenomena that occur even in hydrodynamic situations. One may be described as non-hydrodynamic but there are plenty of more complex phenomena. It is easy to predict that there will be a lot of phenomena associated with boundary effects that order. It is one of the examples as to why more fundamental essence one needs to resort to a phenomenology of a higher basis of individual collision events and effect of the fields. In modelling low-pressure high-E/N swarms where most of the particles are not in equilibrium with the local field throughout the entire drift length. This situation is labelled as non-hydrodynamic in swarm theory and it is actually reflected in plasma physics as non-local transport. Modelling of such situations is well established in the physics of swarms and some benchmarks may be easily developed to test the plasma models. Non-hydrodynamic situations lead to a number of complex phenomena and Frank–Hertz experiment is one such example (Li et al 2002). Studies of spatial and temporal relaxation of electron swarms may be carried out using well established swarm numerical codes (Winkler et al 2002) but also some of the experiments have been carried out such as the measurements of the transient mobility or spatial profiles of emission close to the electrodes.

Term kinetic phenomena may be used for a class of phenomena associated with behaviour of an ensemble of charged particles that may not be trivially predicted on the basis of individual collision events and effect of the fields. In essence one needs to resort to a phenomenology of a higher order. It is one of the examples as to why more fundamental phenomenologies may fail to provide full description of the more complex phenomena. It is easy to predict that there will be a lot of phenomena associated with boundary effects that may be described as non-hydrodynamic but there are plenty of phenomena that occur even in hydrodynamic situations. One can certainly remember the explanation of the anisotropy of diffusion that could be regarded as a new level of maturity of the swarm physics (Parker and Lowke 1969). The phenomena that were analysed recently and not so recently include the following.

- Negative differential conductivity (NDC)
- Anisotropic diffusion due to magnetic field
- Negative absolute mobility (NAM)

All these phenomena have their much more complex counterparts in the case of rf fields which also induce new phenomena such as anomalous diffusion which occurs for the longitudinal component of the diffusion tensor whenever the field changes sign (Petrović et al 2002, White et al 2002). Finally there is a whole range of effects due to the non-conservative nature of collisions (attachment and ionization) which will be significant for both dc and rf fields. The work of the leading groups on some of the kinetic phenomena was revised recently (Petrović et al 2002, White et al 2002) and we shall not aim for a comprehensive review here; the field will be illustrated by some of the recent examples including some unpublished results.

5. Kinetic phenomena and time dependent swarms

The data for the fast neutrals are usually obtained by measuring the spatial profile of absolute excitation/emission coefficients in a Townsend discharge in CH4 at 10 kTd. The peak in front of the anode (A) is excited by electrons and the peak in front of the cathode (C) is excited by fast neutrals while contribution due to ions is negligible (Nikitović et al 2006).

developed by Phelps and coworkers (Petrović et al 1992) are measurements and analysis of the effect of fast neutrals in CH4 where recent measurements have been fitted very well (Nikitović et al 2006) by the earlier still unpublished cross sections of Petrović and Phelps (1991). The point of these results (see figure 8) is that fast neutral effects occur in a wide range of molecules and especially in mixtures of molecular and some atomic gases. These effects are also quite common in sheaths of gas discharges (Marić et al 2003) and therefore swarm studies are needed to provide the quantitative data.

Figure 8. The spatial profile of absolute excitation/emission coefficients in a Townsend discharge in CH4 at 10 kTd. The peak in front of the anode (A) is excited by electrons and the peak in front of the cathode (C) is excited by fast neutrals while contribution due to ions is negligible (Nikitović et al 2006).
solutions of the Boltzmann equation for rf fields has led medical applications and particle detectors. Physics may be used in the modeling of positron transport in techniques developed to satisfy the requirements of the swarm best way to test the codes and at the same time Monte Carlo such processes. Swarm benchmarks and experiments are the non-conservative nature of collisions and one should bear in mind that velocity space (flux) coefficients are different by an order of magnitude. This is due to the enormous degree of the number change which is energy dependent and therefore affects the spatial profile of particles. Even more so, the bulk drift velocity has NDC even though flux drift velocity is nowhere near the conditions for NDC (Vrhovac and Petrović 1996). This is another dramatic display of the way transport coefficients are affected by the non-conservative nature of collisions and one should bear in mind that most plasma models are not equipped to deal with such processes. Swarm benchmarks and experiments are the best way to test the codes and at the same time Monte Carlo techniques developed to satisfy the requirements of the swarm physics may be used in the modeling of positron transport in medical applications and particle detectors.

5.2. Transport of electrons in rf fields

The development of accurate Monte Carlo techniques and solutions of the Boltzmann equation for rf fields has led to the observation of a wide range of kinetic phenomena including anomalous longitudinal diffusion and anisotropic diffusion in crossed electric and magnetic fields (Raspopović et al 2000) and time resolved negative differential and absolute negative mobility (Petrović et al 1995). Representation of such phenomena in plasma modeling has led to the understanding of some aspects of rf plasmas such as maintenance of inductively coupled plasmas (Tadokoro et al 1998, Vasenkov and Kushner 2003) and their wider inclusion in the plasma models is expected and welcome. Thus, in addition to providing the basic transport data and normalized sets of cross sections one of the major contributions of swarm physics to plasma modeling would be to develop benchmark models which will test both the accuracy and the ability to represent some aspects of physics related to the transport of charged particles in rf fields.

6. Applicability of the swarm data in plasma modelling

The destiny of swarm physics was mainly associated with atomic and molecular collision physics as it was able to provide data on numerous processes. Application in plasma modelling, mainly through zero dimensional models was secondary. With the major advances of binary collision techniques swarm methods are less important in atomic physics but have become increasingly important in plasma modeling and in the development of elementary particle detectors. The issue of application of swarm parameters in plasma modeling was addressed recently by Robson et al (2005) and Hagelaar and Pitchford (2005).

In particular, swarm data are directly used for fluid models (see Makabe and Petrović 2006) and also for the fluid parts of the hybrid models (e.g. Donko et al 2006). These data are used to model low energy particles trapped by the plasma and mostly it is assumed that transport coefficients are constant in space and time. Quite often simple relationships such as the Nernst–Townsend (or Einstein) relations are used to determine the values of the coefficients. This illustrates that either the situation is so complex that transport coefficients make little difference or that fluid codes cannot handle the possible complexities some of which have been described in this paper. For example, even for plasmas with relatively strong magnetic fields often the data for pure electric fields are used. Even the basic effects such as the $E \times B$ drift yield new physical phenomena that may provide a major contribution to plasma maintenance (Tadokoro et al 1998, Vasenkov and Kushner 2003). In applying data to fluid models one should bear in mind that velocity space (flux) coefficients should be used and that experiments provide mainly the real space (bulk) data. With the importance of strongly attaching gases in numerous applications it may be expected that non-conservative effects, so far neglected, will be considerable (see Hagelaar and Pitchford 2005). As for the time dependent transport coefficients that show tremendous complexity, it is unlikely that such data may be used directly in the fluid models. However, one should bear in mind the temporal developments of transport coefficients, especially longitudinal diffusion and drift velocity components and be able to check where and when significant effects may be expected. At the same time the kinetic schemes should be tested against rf swarm benchmarks as well.
With the predominance of particle-in-cell schemes (and other kinetic treatments) and also keeping in mind the kinetic part of the hybrid codes one could claim that transport data and therefore swarm physics are not necessary for plasma modelling. However, as described above the application of cross sections in plasma modelling kinetic schemes should necessarily include swarm normalization, at least to make sure that all important processes are included in the cross section set. Thus, only the swarm normalized sets provide proper distribution functions.

However, in plasmas one faces numerous additional processes not existing in the realms of swarm physics (or to be more precise, swarm physics and its experiments were designed in such a way to simplify the situation and make these processes negligible). For example, collisions with excited molecules may become a significant contributor to the high energy tail of electrons and therefore to ionization through superelastic collisions (for example, in the abnormal glow discharges). Thus stepwise ionization may become one of the key processes in sustaining some types of discharges. The effect of superelastic collisions on EEDF (Petrović et al 1997) in gas discharges has been studied in great length by groups in Bari and Lisbon (Capitelli and Bardsley 1990, Guerra et al 2004). In addition to electron-excited molecule collisions, there could be a lot of collisions between the excited states or Penning-type collisions that could lead to additional ionization and such processes have been known to contribute to the sustaining of plasmas. At the same time supereleastic collisions and even Penning-type collisions have been studied in swarm experiments and have been represented accurately by the models so the experience from swarm models is directly applicable to non-equilibrium plasmas.

In discharges, the non-local (non-hydrodynamic) effects are dominant for electrons that provide most of the ionization, i.e. in the sheath regions. While one could regard that such effects are as far away from the swarm physics as possible, since most swarm experiments were designed to reduce to negligible the non-hydrodynamic effects, it is a fact that non-local processes have been studied under swarm physics. Most importantly under swarm physics, it is also possible to set up benchmark situations that could be used to verify plasma models. One such example are the luminous layers at the edge of the non-hydrodynamic section of steady state Townsend discharges that are well known in excitation coefficient measurements and which have been also used to normalize the cross sections.

The intrinsic property of non-equilibrium EEDF as a solution to the Boltzmann equation (BE) is that it is very sensitive to the presence of cross sections which affect its energy dependence. By definition a Maxwell–Boltzmann (M–B) energy distribution function is unaffected by the cross sections. As shown in figure 10 for the same mean energy the BE and M–B distribution functions are considerably different. Most importantly the high energy tail of the M–B function is unaffected by the inelastic processes at high energies, while the BE distribution function has a rapid depletion of the high energy tail due to inelastic processes (figure 11). This is the primary reason for non-equilibrium plasmas being so effective in many applications; it is possible to design their properties by selecting a gas mixture that would favour the desired processes.

At the same time numerous measurements of the distribution functions show Maxwellian or, most frequently, two temperature Maxwellian distributions. This by no means implies that these plasmas are in thermal equilibrium. As a matter of fact one could easily see why one could regard the BE distribution shown in figure 10 as a two temperature Maxwellian. The electron–electron (e–e) collisions will work in such a way as to turn the EEDF into a Maxwell–Boltzmann distribution. However, at the same time the mean energy will drop down (Hagelaar and Pitchford 2005). Thus in order to make a proper comparison we should deal with the distribution functions for the same mean energy. Also, one needs really high degrees of ionization of the order of $10^{-2}$ to turn the EEDF into a Maxwell–Boltzmann distribution (Hagelaar and Pitchford 2005) and for typical values of $10^{-6}$–$10^{-4}$ the effect exists but it is small. This fact gives the basis for application of swarm data in a wide range of plasmas. However, the e–e collisions also lead to new kinetic phenomena as analysed by the Troitsk group (Dyatko and Napartovich 2003) such as e–e induced NDC and a bistable distribution function.

![Figure 10](image_url)

**Figure 10.** Drift velocities for electrons and positrons in argon. One can see a major difference between the drift velocities of electrons and positrons and also a major difference between flux and bulk drift velocities for positrons. The NDC that is observed for bulk velocity even though the flux drift velocity is not even near the conditions for NDC. This is a dramatic display of the non-conservative nature of positronium formation which changes the shape of the positron swarm very much and induces the NDC in the bulk drift velocity.

### 7. Conclusion

Returning to swarm physics for its own sake, the primary need is to initiate a wider range of experiments. In particular one would prefer to be able to cover reactive gases even with accuracy that does not have to match that of Crompton and coworkers (while experiments with predominantly excited molecules and radicals have to remain a long term goal...
coefficients for ionization (solid) and metastable excitation (dashed). There are considerable for the MB distribution. In (b) we have shown rate coefficients for ionization (solid) and metastable excitation (dashed), or perhaps even a pipedream). New challenges for swarm physics lie in developing experiments with radio frequency fields to match the recent theoretical and numerical predictions (Petrović et al 1995) and to venture to higher mean energies to cover the energy region that is of interest for plasma modelling. Surprisingly, very high energies have been covered better than the range of moderate energies by low pressure high $E/N$ experiments (Petrović et al 1992). The moderate energy range should take advantage of a wide range of ionization coefficients and of the excitation coefficients. Continuation of the measurements of these coefficients for a wide range of gases is necessary.

It is not often appreciated that if one wants to calculate the transport coefficients one needs a more or less complete set of cross sections. A combination of even the most accurate cross sections will lead to wrong results if one of the critical processes is missing. The most critical shortage is in the availability of the dissociation cross sections for the ground state fragments. Thus, the best strategy is to adjust the dissociation cross section to achieve a fit to the available transport data assuming that the ionization cross section is known quite accurately (Kurihara et al 2000). The set of cross sections verified by a swarm procedure against the transport data will give good distribution functions even if it does not have all the details as some of the processes may be grouped into effective cross sections. Separation of the effective cross sections into individual excitation cross sections is required if one wants to model the kinetics of excitation of the individual lines (Strinić et al 2004). Recently, revised and improved sets of cross sections have become available for gases such as CH$_4$, CF$_4$ (Kurihara 2000, Bordage et al 1999), HBr, NO (Josić et al 2001) and even for well covered gases such as Ar, H$_2$ and N$_2$ some improvements are sought. The set for NO has already been used to explain and predict new phenomena in atmospheric discharges (Campbell et al 2004).

In recent years it has become one of the primary targets of basic swarm physics to attempt to describe kinetic phenomena that may be associated with non-hydrodynamic behaviour but may also occur in generally hydrodynamic circumstances. One such example is the negative differential conductivity which proved to be a very good test case for transport theory and may be a good benchmark for plasma modelling. Even more interesting was the absolute negative mobility which occurs under special circumstances and which has received its detailed explanation based on different phenomenologies (Robson et al 2003, Suvakov et al 2005). The studies of kinetic phenomena and explanation of observed transport coefficients in terms of such phenomena provide a deeper physical insight into the kinetics of electrons and possible effects in non-equilibrium plasmas. Such studies add excitement to standard swarm studies that may be regarded merely as mundane data collecting and also provide phenomenology of the field that is a bridge between collisions and plasma physics.

In this review we have not been able to cover the field of elementary particle detectors where the largest number of swarm experiments persists, albeit with little communication with the mainstream swarm physics as it is developed in the present day. In addition, swarm experiments with ions and their analysis are strongly bound to chemical physics where they provide some of the key data for understanding interactions between different atoms and molecules. All these applications are worthy of special scrutiny from the swarm physics community that has mostly focused on plasma modelling.

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