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REVIEW ARTICLE

Measurement and interpretation of swarm parameters and their application in plasma modelling

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Abstract

In this review paper, we discuss the current status of the physics of charged particle swarms, mainly electrons, having plasma modelling in mind. The measurements of the swarm coefficients and the availability of the data are briefly discussed. We try to give a summary of the past ten years and cite the main reviews and databases, which store the majority of the earlier work. The need for reinitiating the swarm experiments and where and how those would be useful is pointed out. We also add some guidance on how to find information on ions and fast neutrals. Most space is devoted to interpretation of transport data, analysis of kinetic phenomena, and accuracy of calculation and proper use of transport data in plasma models. We have tried to show which aspects of kinetic theory developed for swarm physics and which segments of data would be important for further improvement of plasma models. Finally, several examples are given where actual models are mostly based on the physics of swarms and those include Townsend discharges, afterglows, breakdown and some atmospheric phenomena. Finally we stress that, while complex, some of the results from the kinetic theory of swarms and the related phenomenology must be used either to test the plasma models or even to bring in new physics or higher accuracy and reliability to the models.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The physics of swarms has always provided the foundation for non-equilibrium plasma modelling. To some degree that is illustrated by the fact that the whole field has continuously produced numerous data source listings or more importantly critical data reviews with recommendations either on its own (Dutton 1975, Gallagher *et al* 1983) or in combination with binary collision experiments data (Kieffer 1973, Christophorou and Hunter 1984, Hunter and Christophorou 1984, Sakai 2002). Recently, however, only several reviews have been published (Christophorou and Olthoff 1998a, 1998b) mainly based on recent binary collision data while swarm experiments have almost disappeared. At the same time swarm physics related theory has continued to develop new methods and concepts and to explain more and more complex phenomena. Nowadays the main interest of theorists is special situations when physical insight may be gained and some phenomena explained rather than cross section conversion from the transport data.

In our recent publication (Petrović *et al* 2007a) we have covered mainly our work, as dictated by the page limit for that special issue, while in this paper we extend the basic swarm studies to the results of other groups with some additions from our results when necessary. The basic idea behind the review will be to give guidance to the plasma modelling community on where to find the swarm data, how to implement swarm based transport theory and kinetic phenomena, how to apply experimental results and calculated data and how to take advantage of the developments in the kinetic theory of charged

particles in general plasma modelling. In a way, the paper consists of a number of tips on how to handle a wide range of phenomena where swarm studies could provide guidance or direct modelling in the context of gas discharges. This paper, therefore, represents to some degree an extension of the discussion of the application of transport coefficients from Robson *et al* (2005).

The maturity reached by the non-equilibrium plasma community has opened new levels of sophistication in the models that have made it necessary to include more of the relevant physics. It seems that the often posed dilemma on whether to do things according to the high rigour of the swarm physics since plasmas are so complex anyway is not being mentioned quite so often. Awareness has grown that if we can do something better we should and some examples have taught us that it was worthwhile in terms of new physics and better representation of experiments and numerous applications (Lieberman and Lichtenberg 2005, Makabe and Petrović 2006).

In the centre of the plasma modelling stage as viewed in this paper is the non-equilibrium nature of plasmas and charged particle distribution functions. From the low current limit and well-established application of Boltzmann's equation to the higher space charge densities when distribution will become closer to the Maxwellian (Hagelaar and Pitchford 2005) we have a wide range of possibilities that may lead to uncertainty in determining the rate coefficients and other basic data for plasma models. We have tried here to stay in the low current limit corner and to point out how to use such data and phenomenology in a broad range of non-equilibrium plasma phenomena including some examples when swarm based models may be used as almost exact representation. We also focus on the interpretation of transport coefficients, availability of the data and future needs. Development of a better database and kinetic representation of plasmas is one of the priorities for the next ten years in plasma physics in general, as non-equilibrium plasmas have taken one of the leading roles in bringing future technologies based on best science that we can do (Graves and Kushner 2008).

2. Current status of swarm experiments

The heydays of swarm experiments were described well in numerous reviews, in particular (Elford 1972, Huxley and Crompton 1974, Christophorou and Hunter 1984). The common characteristics of low energy swarm experiments (i.e. with mean electron energies of ($\leqslant$2 eV) was attention to accuracy that would eventually result in acceptable error margins for the derived cross section sets (Phelps 1968, 1991, Crompton 1994). In other words, those experiments were built to produce complete sets of cross sections in the energy range that was covered by the analysis. Having only two useful coefficients as the basis for cross sections, attempts were made to either expand the applicability of the technique by using mixtures or at simplifying systems by going to low temperatures or parahydrogen (Huxley and Crompton 1974, Haddad and Elford 1979, Haddad and Crompton 1980, Haddad 1984, Petrović 1985, Petrović and Crompton 1987).

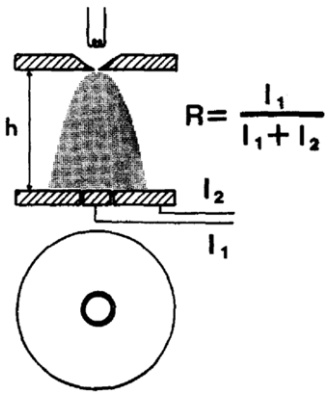

Figure 1. Electrons are released from a small hole in the cathode and as they cross the gap their radial profile develops under the influence of radial diffusion. The anode is divided into two parts, the central disc and the outer annulus. Transport theory provides relationship between the ratio of two currents R and the characteristic energy. Measuring the two very small currents while maintaining zero potential was part of the exceptional experimental technique implemented in swarm experiments in times when operational amplifiers of desirable characteristics were not available and is still difficult to achieve with the modern day electronics (Huxley and Crompton 1974). It was necessary to measure currents as low as 10^{-12} A with an uncertainty of less than 1% without perturbing the potential between the two segments in order not to disrupt the radial profile of the electron with very low energies.

Classical swarm experiments are the drift tubes with grids (Crompton *et al* 1967, Crompton *et al* 1970) or Tyndall Powell (Hegerberg *et al* 1982, Larsen and Elford 1986) which are used to measure drift velocities (and in principle may be used for longitudinal diffusion) and the so-called Townsend Huxley drift tubes for measuring characteristic energies (Crompton and Jory 1962, Crompton 1972) eD_T/μ. The principle of operation of the Townsend Huxley experiment may be understood from figure 1. Highest accuracy was achieved by the experimental systems developed at Australian National University (Elford 1972, Huxley and Crompton 1974).

Drift velocity experiments existed at a number of centres around the world: Westinghouse Laboratories (Phelps 1968, 1991), Oak Ridge (Christophorou and Hunter 1984), Hokkaido (Tagashira *et al* 1977), Gdansk (Roznerski 1996), Liverpool (Kucukarpaci and Lucas 1981), Heidelberg (Schmidt *et al* 1994), Keio University (Nakamura 1987) and many more. With some effort and reduced accuracy the grids could be brought to work at energies of several electronvolts (Roznerski *et al* 1994) but the limit of high accuracy data was between 1 and 2 eV (which, as far as the energy range goes, is not sufficient for modelling of non-equilibrium plasmas). Extension to moderate and higher energies could be more easily achieved by a different albeit slightly less accurate pulsed Townsend technique which was used at a number of laboratories around the world. The pulsed Townsend apparatus (as used by de Urquijo *et al* 1999) is shown schematically in figure 2.

In addition to drift velocities this technique may produce longitudinal diffusion coefficients (although selecting conditions to measure drift velocity accurately makes longitudinal diffusion coefficients more uncertain and vice

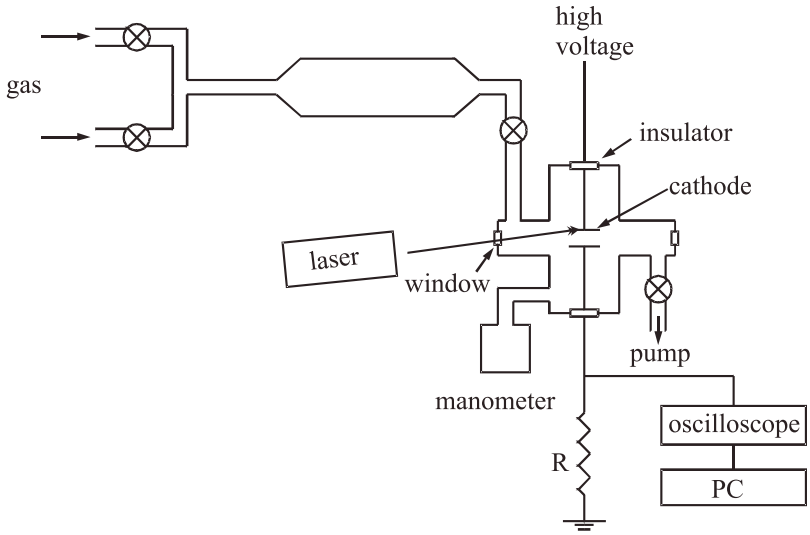

Figure 2. Schematic representation of a pulsed Townsend technique (Šašić *et al* 2005). Laser induced photoemission of electrons produces a brief pulse and the resulting current in the gap is detected or integrated on the resistor R.

versa), attachment and ionization rates. This technique has been the principal source for moderate and higher energies overlapping with the standard operating conditions in gas discharges. One word of caution is that pulsed Townsend data suffer from a degree of uncertainty due to the fact that it is not well understood how these data may be interpreted in transport theory (Sakai *et al* 1977, Tagashira *et al* 1977, Robson 1991).

Steady state Townsend (SST) discharges usually operating in self-sustained regimes (sometimes even the non-self-sustained regime was used—Urošević *et al* (1983)) have been used in order to obtain the excitation and ionization coefficients for a wide range of gases (Bulos and Phelps 1976, Lawton and Phelps 1978, Tachibana and Phelps 1981, 1987, Yamabe and Phelps 1983, Buckman and Phelps 1985, Malović *et al* 2003, Nikitović *et al* 2007). One should be warned that conversion of SST data to cross sections also involves a more sophisticated theoretical interpretation than the standard time of flight (TOF) data (Sakai *et al* 1977, Tagashira *et al* 1977, Boeuf and Marode 1984, Robson 1991).

At present very few experimental centres exist which is the primary reason for the reduced activity in swarm physics. For example one may claim that only two centres are active in measurements of drift velocities of electrons, that of de Urquijo and co-workers (de Urquijo *et al* 2001, Goyette *et al* 2001, Hernández-Ávila *et al* 2002, Šašić *et al* 2005, Jovanović *et al* 2009a) and at Keio University (Yamaji and Nakamura 2003). At the same time gathering such data is one of the principal activities deemed important in the next 10 years of plasma science (Graves and Kushner 2008). From the viewpoint of the need to establish a database for plasma modelling, rejuvenation of activities in measurements of transport coefficients would be necessary. In particular, there is a need for measurements in a series of reactive gases even with a somewhat reduced accuracy. Pulsed Townsend system would be the best suited for this purpose supplemented perhaps by a SST experiment.

It is also very important to find means to study time-resolved or rf transport to verify all the predictions. Reactivation of the Cavalleri diffusion experiment (CDE) (Rhymes *et al* 1975, Crompton and Haddad 1983, Petrović 1986) would open a possibility to study transport in rf fields which was originally initiated by Cavalleri (Cavalleri 1969) but was not supported by sufficiently sophisticated theory.

In addition, with recent theoretical advances in the modelling of positron transport and in the availability of the cross sections for low energy positrons (Marler *et al* 2009, Marler and Surko 2005), positron drift tube should be developed (Charlton and Humberston 2001, Charlton 2009) and implemented as a source of data and normalization of the cross section sets. That would allow us to extend some of the modelling capabilities developed for electrons to positron transport in gases and liquids even including the human tissue.

3. Availability of data for scattering cross sections and transport coefficients

3.1. Introduction

There is a large number of review papers giving tabulations of cross section sets for electron scattering and those may be categorized into three groups. The first would be compilations of binary collision data only (e.g. Kieffer (1973), Zecca *et al* (1996), Buckman and Brunger (1997), Karwasz *et al* (2001)). While very useful as sources of data, for comparison between different sources and for a degree of critical evaluation, sets from these compilations cannot be used directly in plasma modelling as those are usually not complete.

In the second group belong the reviews consisting of critical analysis of both binary collision data and swarm parameters that most importantly involve normalization of the sets based on swarm analysis. There is a number of reviews and papers covering individual atoms or molecules. We shall label those the swarm derived cross section sets. By far such sets are the most useful in plasma modelling as they satisfy two most important requirements—completeness (in a sense of complete energy, momentum and number balances) and the fact that the calculated EEDF should be

correct (if analysis was done properly). Such sources include compilations of the late Hayashi (which are being taken over by Nakamura) (Hayashi 1981), 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 Dr Phelps (Phelps ftp://jila.colorado.edu/collision data/electronneutral/electron.txt).

Recent reviews of Christophorou, Olthoff and co-workers (e.g. Christophorou *et al* (1996)) fall mainly into the category of compilations based on combination of the data from swarm analyses and binary collision data, and they make a further step to recommend best choices for plasma modelling and also to calculate some of the transport data. However, in some cases the sets were based mainly on the binary collision data and required further swarm based normalization (Bordage *et al* 1999, Kurihara *et al* 2000).

The third possible source of the cross section sets is the databases supplied with the generally available codes for solving the Boltzmann equation (Elendif—Morgan (2000), Morgan and Penetrante (1990), Morgan http://www.kinema.com/prod03.htm; Bolsig—developed by Pitchford and Boeuf http://www.laplace.univ-tlse.fr/-BOLSIG-Resolution-de-l-equation-de Boltzmann électronique, Magboltz 2—Biagi (1999)). While those sets are (presumably) complete, based on swarm analysis and directly applicable in modelling, they sometimes suffer from limited information on the sources and choices. Even when the required information exists for some of the molecules in some of the sets (Morgan 1992a, 1992b) the correlation to the source of information may be overlooked by users. For example it is essential to know the actual limits where the cross section set has been properly normalized and data should not be used outside those limits.

Classical references for compilations containing only the swarm transport data (including both measured and calculated) are still useful and have not been replaced by more recent updates. For general transport principal sources are those of Dutton (1975) and Gallagher *et al* (1983). For attachment rates and some of the transport data for mainly electronegative gases older reviews by Christophorou and co-workers are principal sources (Hunter and Christophorou 1984).

Collections representing just lists of bibliography related to either cross sections or transport data may also be very useful (e.g. Hayashi (2003a), Gallagher (1985)) as some original sources, especially those not covered by electronic publishing, are not easy to find and may be overlooked easily.

Finally, it must be emphasized that in general (for all types of data), the most useful (perhaps in this day of electronic publishing the only useful) are compilations which provide critical evaluation and give some recommendations. In principle, every swarm analysis must include that step, a fact which is often overlooked in recent times. Another neglected, albeit very important practice is to provide data in tabulated form (or simple analytic forms) in easily accessible publications or on the internet. Hiding presentation of the choice of sources, comparisons and the data from the scrutiny of colleagues into obscure publications and local reviews does not lead to a wide application.

3.2. Swarm procedure as applied to electrons

A detailed description of the procedure to obtain cross sections from electron transport coefficients has been given in a number of publications (Pack *et al* 1962, Crompton 1994, Huxley and Crompton 1974, Hunter and Christophorou 1984, Morgan 2000, Petrović *et al* 2007a). To summarize, we may say that a set of cross sections (as complete as possible) is compiled from all available sources, and applied to calculate the swarm parameters. If the calculated values agree with the compiled set of experimental data the set is consistent with the transport data, which means that a proper electron energy distribution function has been obtained which together with the cross sections gives accurate number, momentum and energy balance for electrons. If the calculated values disagree with the measured transport data the cross sections are adjusted and the cycle is repeated until agreement is achieved.

Limitations of the swarm technique (Petrović 1985, Crompton 1994, Petrović *et al* 2007a) include non-uniqueness, limited resolution, averaging over angular distribution, complexity and indirect nature of the procedure. These may be corrected by a number of techniques. The best strategy is to start with the information on the relative magnitudes and shapes of the cross sections from the binary collision techniques (both experimental and theoretical). Putting several processes into one effective cross section is particularly useful if one does not seek detailed reaction rates for all the channels. Using low temperature and mixture data increases the pool of information that gives more unique final results.

The advantages of the swarm technique (as compared with the binary collision experiments) include completeness (as discussed above in terms of number, momentum and energy balances of particles), good pressure calibration, accurate determination of the absolute cross sections and direct applicability of the swarm and transport data (distribution functions) in plasma modelling and analysis of diagnostics data. Binary collision experiments have made major improvements over the past 20 years and are able to give cross sections with a high accuracy. The results for individual cross sections compare well with the swarm data and even have advantage in giving detail and angular resolution (Buckman and Brunger 1997). Still, however, swarm analysis is necessary before the cross sections may be applied in plasma modelling as one experiment cannot give all the cross sections with the same accuracy and some processes may be missing thus spoiling the balances and the EEDF (Christophorou *et al* 1996, Bordage *et al* 1999). As a general rule, in the analysis at moderate and higher energies one may safely assume that ionization cross sections are known accurately and may focus on adjusting the dissociation cross section (into neutral fragments) which is usually not known accurately (see Kurihara *et al* (2000)).

Techniques to improve swarm results, including the role of benchmark calculations, have been covered on numerous occasions (e.g. Petrović *et al* (2007a)). Here we shall only discuss the often overlooked issue of the accuracy of the cross section data as a function of the E/N range that has been covered by the data (Petrović 1985). Starting from the cross sections for parahydrogen (one elastic process, one rotational and one vibrational, see figure 1 in Petrović *et al* (2007a))

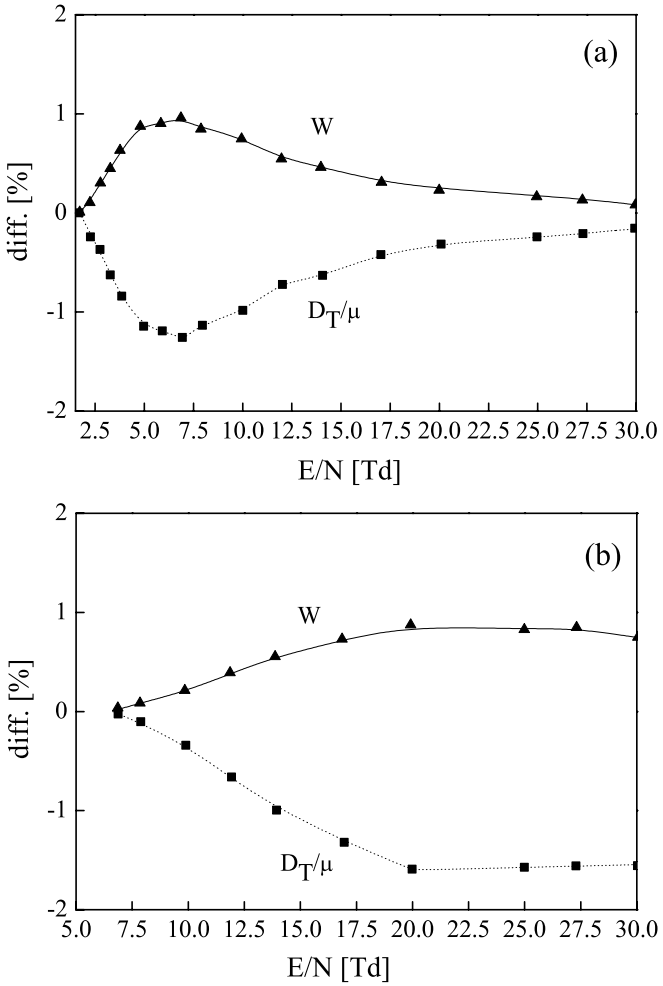

Figure 3. The effect of perturbation on drift velocity and normalized transverse diffusion (Petrović 1985)—the differences between perturbed and unperturbed calculations. The vibrational cross section was modified (reduced) (*a*) starting from 0.6 eV with the width of 0.25 eV and for (*b*) starting from 1.4 eV with the width of 0.5 eV. The depth was 25% of the local value in both cases.

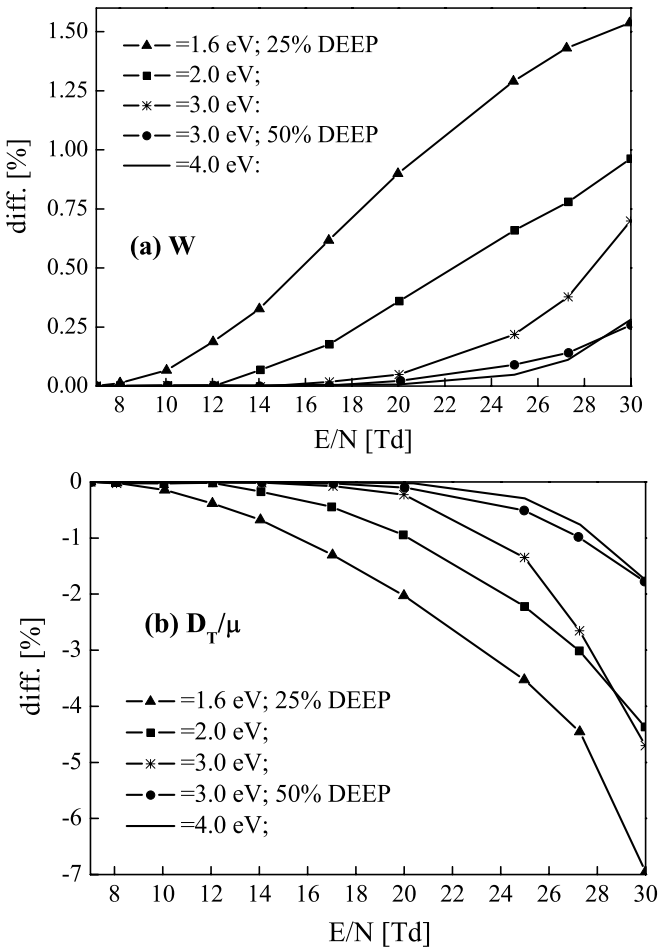

Figure 4. Differences between results for the original cross section for pH_2 and the cross section set where vibrational cross section is reduced above some threshold towards higher energies by a certain percentage of the local vibrational excitation cross section: (*a*) drift velocities and (*b*) diffusion coefficient normalized by mobility (Petrović 1985).

we have applied perturbations to the vibrational cross section varying the threshold, the depth and the width, while making adjustments to stay within the uncertainty of 1% for the drift velocity (W) and 1.5% for the normalized diffusion coefficient (D_T/μ). In figure 3 one can see that very large and broad indentations may still be acceptable for the swarm analysis even as deep as 25% and with a width of 0.5 eV.

One can see that a relatively large indentation in the cross section may pass as acceptable to the swarm analysis. If one were to use increased values of the cross section just before and just after the indentation there would be very little discrepancy but it would oscillate throughout the E/N range. In other words the swarm method is good at detecting an integral value and is not sensitive to narrow peaks or valleys in the shape. Also compensating a reduced value at one energy by an increased value at the nearby energy would require another reduction later on and the result would oscillate around experimental values. Sensitivity in the case of a gas like helium is much larger (Crompton 1994) than that in molecular gases and it may reach the level where the uncertainty in the transport data leads to the same uncertainty in the transport coefficients. However, for molecular gases having several processes in parallel, 1% of uncertainty in the transport data may lead to 10% uncertainty in the cross sections.

In figure 4 we show how reduction of the vibrational cross section of pH_2 beyond a threshold (T) affects the calculated transport data. The sensitivity is greater than in the previous case as the energy range is quite a bit broader effectively starting from the threshold and extending as long as the vibrational energy loss is significant compared with electronic excitations (Petrović 1985). The set of transport data that we had in mind here is that for pure parahydrogen (see Huxley and Crompton (1974), Petrović (1985)) extending from 0.002 to 30 Td. The figures show just a narrow range that is affected by the perturbations to the cross section.

We can see that any imposed variation (either an increase or a decrease) affects the transport data in a wide but still limited range of E/N (mean energies). One could find an energy above which any modification of the cross sections will not affect the transport data because only a very small number of electrons reach that energy. One could argue that setting cross sections to zero would be acceptable but that is not true. In that case the very few electrons crossing that limit would be

in runaway and gain extraordinarily high energies and in turn could affect the results. Thus something has to be included above the limit of sensitivity of transport data. However, when a cross section set is to be used one should be aware of the E/N range that was used to produce the set and should not rely on the cross sections beyond the limit of sensitivity of the transport data. For example, if the mean energy in parahydrogen at 30 Td (which is the highest point in the E/N range of the available transport data) is close to 1 eV the transport data are typically sensitive to perturbations that start at 4 times higher energies and lower. The integration range that would allow proper calculation is typically extended to 10 times the mean energy. So one could regard as the cross section of around 1–2 eV as the limit of the reliable data and also that some knowledge may be available up to 4 eV. Between 4 and 10 eV (or higher) the transport data cannot provide any information.

While all early discrepancies between swarm derived cross sections and those provided by either binary collision theory or experiments were resolved in favour of the data based on transport coefficients (Crompton *et al* 1967, Crompton *et al* 1969, Gibson *et al* 1973, Huxley and Crompton 1974), some recent disagreements are still open and require resolution. The most striking problem is the 50–60% difference between the vibrational excitation cross sections for molecular hydrogen. This problem was opened when adiabatic nucleii calculations of Morrison and Saha were tested in a swarm analysis and found to be in disagreement with DT/□ measurements for parahydrogen (Petrović 1985, Morrison *et al* 1987). It should be stressed that for all other cross sections covered by both analyses the agreement was excellent.

The first attempts to explain the difference focused on criticizing the formula for analysing the Townsend Huxley experiment but that led to no resolution although similar attempts are often repeated. One should be aware that similar tests were made using drift velocities in a He/H_2 mixture where interpretation does not depend on an uncertain theory and it was confirmed that the calculated data do not satisfy the energy balance of the electron swarm (Petrović and Crompton 1987). In the meantime the beam experiments were made with an improved accuracy (Buckman *et al* 1990) and appeared to confirm the theory in the range of energies where three sets of data overlapped, but the agreement of experiment with theory was not very good at higher energies. Thus one could claim that the discrepancy is still not very well understood (Crompton and Morrison 1993, Crompton 1994). The claim of Yoon *et al* (2008) that the discrepancy renders swarm results inappropriate seems premature as one cannot expect their data to satisfy the energy balance in the swarm and plasma which would make their set less than useful for plasma modelling. In conclusion, one should bear in mind that for vibrational excitation in nitrogen a similar discrepancy exists (Crompton 1994) albeit with a different combination of agreements and discrepancies. In both cases problems are yet to be resolved and are somehow related to a process that involves motion of nuclei in a molecule so one should keep an eye open for similar discrepancies for dissociative processes. Having said that, some recent examples of swarm analysis (rooted deeply in the knowledge of relative magnitudes and energy dependences provided by binary collision beam experiments) led to excellent agreement with new theory and experiments. One example is NO where a disagreement by a factor of 40 with some previously accepted binary collision data was corrected to a reasonably converged set of data (Josić *et al* 2001, Jelisavčić *et al* 2003, Allan 2005 Trevisan *et al* 2005). The resolution of this problem may require revisions of scattering theories, binary collision experiments and transport theory (White *et al* 2007).

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

General reviews of the basic binary collision cross section data cover a wide range of references and molecules (Kieffer 1973, Csanak *et al* 1984, Christophorou *et al* 1984, Maerk 1984, Trajmar and Cartwright 1984, Winstead and McKoy 1996, 2000, Zecca *et al* 1996, Karwasz *et al* 2001, Brunger and Buckman 2002, Brunger *et al* 2003a, 2003b, 2003c). General older reviews of the cross section sets that involved some level of analysis of the transport data are well known and still quite useful (Huxley and Crompton 1974, Hayashi 1981, Hunter and Christophorou 1984 and the continuously updated data of Phelps ftp://jila.colorado.edu/collision data/electronneutral/electron.txt). At this point one has to mention the reviews of transport data that may be either directly used or provide a basis for normalization of cross sections (Dutton 1975, Gallagher *et al* 1983) and bibliography collections (obtained in the times when journals did not have electronic publications and thus were not open to searches) for cross sections (Gallagher 1985) and transport data and swarm studies (Morgan 1990). We will mention some of the more recent work of the past decade that could be regarded as a worthy addition to previous studies. This is not a comprehensive survey.

A review of the cross section data obtained by the group at Hokkaido University was presented by Sakai (2002) covering He, Ne, Ar, Kr, Xe, N_2, O_2, CO, CO_2, CH_4, C_2H_4, CF_4, SiH_4, Si_2H_6, GeH_4 and Rb. In a similar way discussion of the available data for a large number of atoms and molecules including new developments was given by Morgan (2000) covering also data for recombination. A broad range of molecules has been covered in a review of cross section data and some of the transport coefficients (mainly attachment rates) by Christophorou and Olthoff (2000a, 2000b). A series of similar reviews of the available data with recommendations was presented for N_2, H_2, CO_2 and O_2 by Professor Itikawa and co-workers (e.g. Yoon *et al* (2008), Itikawa (2009)).

Particularly useful recent review of bibliography on cross sections have been published by Hayashi covering halogen molecules (F_2, Cl_2 and I_2) (Hayashi 2003a), Ar (Hayashi 2003b), Xe (Hayashi 2003c), H_2 (Hayashi 2004a), N_2 (Hayashi 2003d), CO_2 (Hayashi 2003e), H_2O (Hayashi 2003f), SF_6 (Hayashi 2003g) and NH_3 (Hayashi 2004b). These compilations often include the author's earlier papers or tabulations of data based on his swarm analyses. It is unfortunate that this series has not continued. A useful presentation of the ionization cross section for hydrocarbon molecules including radicals has been given

by Janev *et al* (2001). One should be warned that rate coefficients given here were obtained under the assumption of the Maxwellian EEDF.

A series of papers from the NIST group was published with electron beam cross section data and the data from swarm analyses for fluorocarbon gases (of interest for plasma etching) including CF_4 (Christophorou *et al* 1996, Christophorou and Olthoff 1999), C_2F_6 (Christophorou and Olthoff 1998a), C_3F_8 (Christophorou and Olthoff 1998b), CHF_3 (Christophorou *et al* 1997), CF_3I (Christophorou and Olthoff 2000a) and also SF_6 (Christophorou and Olthoff 2000b). While these papers present the calculated transport coefficients, it seems that the recommended sets were made by averaging several of the cross sections for each process that were regarded as acceptable by a set of standards. It appears that new swarm analysis was not performed for the newly formed sets and thus, for example, the CF_4 set had to be improved by adjusting the second vibrational excitation resonance (Bordage *et al* 1999) to fit the ionization rate. A different approach, as mentioned earlier was taken by Kurihara *et al* (2000) which was to fit the ionization rates by adjusting the dissociation cross section. While this paper was complete in terms of EEDF and transport data, it had to be augmented by processes with smaller cross sections (in terms of affecting the EEDF and total transport data) which are the only channels to produce some ions such as CF_3^- (Georgieva *et al* 2003).

Ionization and attachment coefficients in C_2F_4 and C_2F_4/Ar mixtures were measured and analysed by Goyette *et al* (2001). Other measurements on fluorocarbons (Yamaji and Nakamura 2003, Yamaji *et al* 2003) include data for drift velocities, ionization and attachment rates in 0.468% and 4.910% c-C_4F_8/Ar mixtures and pure c-C_4F_8. New data for thermal attachment for fluorocarbons (together with SF_6 which could be used as a benchmark for accuracy—see Petrović and Crompton (1984)) were presented by Merlino and Kim (2008) for C_7F_{14} and Mayhew *et al* (2005) for c-C_4F_8, $_2$-C_4F_8. Yoshida *et al* (2002) have made a comprehensive study of electron transport properties and collision cross sections in C_2F_4 which involved both measurements of the transport data, derivation of the cross section set and incorporation of the newly calculated cross sections.

Low temperature drift velocities were measured in He^3 showing a difference from the standard helium due to a difference in mass especially since in helium energy balance is dominated by recoil at electron energies below 19 eV (Kusano *et al* 2008). Cross sections for rare gases have been tested in the moderate and higher energy regions (Šašić *et al* 2005). The sets for Xe and Ar (Strinić *et al* 2004) were expanded by more detailed excitation cross sections and cross sections for excitations into ionic states. Those extensions were mainly based on excitation coefficients measured and the work on measurements and interpretation of excitation coefficients and secondary electron emission yields by the Belgrade group was summarized by Malović *et al* (2003).

In this century there were several improvements of the cross sections for atmospheric gases (Hernández-Ávila *et al* 2002, Itikawa 2002, 2006, 2009, Yousfi *et al* 2009), especially for the oxides of nitrogen NO_x (Zecca *et al* 2003). A major

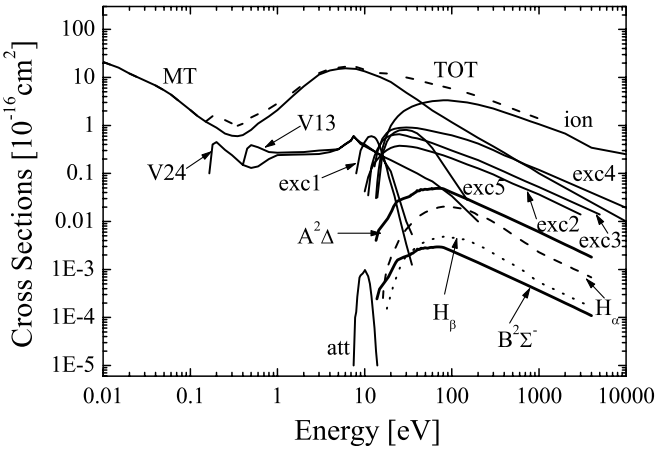

Figure 5. A set of cross sections for electrons in methane (Šašić *et al* 2004). Labels for the cross sections are MT—momentum transfer, TOT—total, V (24 and 13) are the two cross sections for vibrational excitation lumping together two different modes of excitation each, exc—different excitation cross sections, att—attachment, ion—ionization cross section, excitation cross sections to specific states that are subject to diagnostics are labelled by the states of the excited molecule or atom.

revision of the cross sections for NO was recently completed by using a combination of the shapes of expected vibrational resonances from simple theory or from experiments for the total cross section with normalization by swarm data (Josić *et al* 2001). Cross sections for vibrational excitation were supported by subsequent beam experiments and theory (Allan 2005, Trevisan *et al* 2005, Jelisavčić *et al* 2003). A set of cross sections was produced for N_2O based on combined input from beam experiments and swarm data (Mechlinska-Drewko *et al* 2003), which has been improved on the basis of new measurements of drift velocities and attachment and ionization rates (Dupljanin *et al* 2009). New data for water vapour were recently produced (Hasegawa *et al* 2007) though several groups are continuing to improve their water vapour cross sections (Ness 2009).

Cross sections for methane have been extended to somewhat higher energies and more detailed kinetics of excitation (Šašić *et al* 2004). To some degree, related to this is the recent progress on organic molecules more complex than basic hydrocarbons and one is perhaps to expect first swarm experiments in organic vapours. The set of cross sections for methane has been given in figure 5 as one example of a complete set for a molecule.

Due to the lack of experimental transport data a set of cross sections for HBr was constructed from the available experimental and theoretical binary collision data (Šašić and Petrović 2007). Studies of electrons were made in SF_6 and its mixtures (Banhenni *et al* 2005) and it may lead to improvement of the cross sections at higher energies. Measurements were also performed in trimethylsilane (Yoshida *et al* 2005).

3.4. Positive and negative ions—transport coefficients and cross sections

It is customary in physics of ion swarms to aim at establishing the interaction potentials, where, in the analysis the calculation

of the cross sections is either bypassed or not presented as the final result. It is possible to calculate the cross sections from the potentials but the techniques are by no means trivial and require specialization that is not usually available to plasma modellers. Thus we have decided to focus here on transport coefficients and on the available cross sections. It is important to note that the method used to calculate the transport coefficients from the cross sections is in principle, identical to that which is employed in plasma modelling (in kinetic modelling).

The classic sources of transport data have maintained their importance over the last 20 years probably, since the focus of the research has shifted to more complex molecular physics. The data for ions have been compiled in special reports (Ellis *et al* 1976, 1978, 1984, Viehland and Mason 1995) and in books of Mason and McDaniel (1988). The electronic database of Viehland is continuously updated and provides facilities to calculate interactively the data for the gases and ions of interest (Viehland—the electronic database can be accessed by contacting viehland@sassafrass.chatham.edu).

Rare gas ions were studied in their parent gases and in mixtures of rare gases and data were analysed to obtain the cross sections (Piscitelli *et al* 2003). Transverse diffusion was measured for argon ions in argon by Stefansson and Skullerud (1999). Transverse diffusion is not always measured for ions but such data proved to be useful in establishing separation between charge transfer and elastic scattering at low energies for argon and neon (Jovanović *et al* 2002).

Group of de Urquijo has studied mobilities of He^+, Ne^+, Ar^+, N_2^+, O_2^+ and CO_2^+ in their parent gases (Basurto *et al* 2000). Transport of SF_x^+ ($x = 1$–3,5) and ion conversion in SF_6–N_2 mixtures were covered in a paper by Basurto and de Urquijo (2001). Mobilities of interest for plasma modelling of etching (CF_3^+ in CF_4, CHF_2^+ in CHF_3, and C^+ in Ar) have been measured by Basurto and de Urquijo (2002) but this is just a small part of the data that are needed. In that paper a drift tube-double mass spectrometer technique has been used to measure transport and conversion of ions such as CF_3^+ in CF_4 and CHF_2^+ in CHF_3 between 30 and 750 Td. C^+ was produced through the reaction of CF_3^+ with Ar. Secondary species F^+, CF^+, CF_2^+ and ArH^+ were generated in collisions of positive ions and argon buffer gas. Ar^+ colliding with CF_4 were found to produce CF_3^+ with almost 100% efficiency at high $E/N > 100$ Td.

The same group has studied transport of negative ions such as the mobility of SF_6^- in tSF_6–Ar and SF_6–Xe mixtures for E/N in the range 1–180 Td (Banhenni *et al* 2005), and in mixtures of SF_6 with CF_4 and CH_4–Ar (de Urquijo and Yousif 2003). Negative ion formation and motion in mixtures of CCl_4 and Ar were studied by Yousif and Martinez (2004) and mostly CCl_4^- was formed in the range 1–50 Td.

A review of the transport and cross section data for negative ions in gases of interest for plasma processing in nanotechnologies was published by Petrović *et al* (2007b). Along similar lines Cl^- and F^- ions in rare gases were covered by brief papers by Jovanović *et al* (Petrović *et al* 2008a, Jovanović *et al* 2009a, 2009b).

A large range of data was measured by application (and analysis of observables) of the FAIMS (high-field asymmetric waveform ion mobility spectrometer) which may be used for both positive and negative ions (Barnett *et al* 2000, Guevremont *et al* 2001, Viehland *et al* 2001, Buchachenko *et al* 2005). This technique was one of the main sources of transport data in the recent years while potentially more accurate drift tubes with grids were not active.

4. Interpretation of transport data and their implementation in plasma modelling

In the good old days (of 1960s and 1970s) life was easy, drift velocity was the drift velocity, and diffusion coefficient was likewise the diffusion coefficient. It was easy to decide what and how to use. Well, in most cases a simplified view of the transport data is still taken by plasma modellers and it is justified by the complexity of the object that is being modelled. The fact that it often even works reasonably well does not allow us not to use the full capacity of the recently developed kinetic theory for charged particle swarms. Nowadays there are plenty of examples where failure to adhere to the newly developed concepts in kinetic theory may lead to overlooking some pertinent physics. One of the key issues is how to select simplifying assumptions for the transport coefficients without losing the important physics. For example one needs to decide whether transport coefficients may be assumed to be uniform and independent of time, whether additional coefficients should be included when both electric and magnetic fields are present and, for example, whether to use measured data or those calculated using the Boltzmann equation analysis or a Monte Carlo simulation (realizing of course that there could be some difference).

In this section we shall try to outline the basic phenomenology and hopefully to give some recommendations on the use of transport data and how to represent some aspects of plasma theory where these problems may be relevant. It is inevitable that this attempt, being limited in space (and time for preparation), is doomed to fail to explain everything. However, as Eugene Ionesco once stated 'it is not the answer that enlightens, but the question' so we hope that raising the issues will suffice and prompt the readers to look for more detailed answers.

4.1. The basic kinetic theory of charged particles

In our view the best introduction to kinetic theory of charged particles in gases is still the review of Kumar *et al* (1980) (see also Kumar (1984), Robson (2006)). Contemporary contributions have been reviewed by White *et al* (2002), Winkler *et al* (2004) and Makabe and Petrović (2006). It is normally assumed that the Boltzmann equation (BE) is an exact representation of charged particle transport (or the equivalent Monte Carlo simulation technique) provided that the cross section data that are used are correct. The BE may be written as

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \frac{q}{m}[\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}] \cdot \frac{\partial f}{\partial \boldsymbol{v}} = -J(f), \qquad (4.1)$$

where $f(\boldsymbol{r}, \boldsymbol{v}, t)$ is the phase-space distribution function, $\boldsymbol{r}$ and $\boldsymbol{v}$ denote the position and velocity coordinates, $\boldsymbol{E}$ and $\boldsymbol{B}$ are time-dependent electric and magnetic fields while q and

m are the charge and mass of the swarm particle and t is the time. The right-hand side of (4.1), $J(f)$, denotes the linear particle–neutral molecule collision operator, accounting for elastic, inelastic and non-conservative collisions. Though there are some disagreements over the exact form of the collision operator (Ness and Robson 1985, Ness and Robson 1986, Robson *et al* 2003b), it is essential that the collision operator should be standardized in the literature.

The hydrodynamic description for charged particle swarms is applicable far from boundaries, sources and sinks, and usually represents the first step in the development of the various approaches to solve the Boltzmann equation. According to this description, the phase-space distribution function can be expanded in terms of powers of the density gradients:

$$f(\boldsymbol{r}, \boldsymbol{v}, t) = \sum_{k=0}^{\infty} f^{(k)}(\boldsymbol{v}, t) \otimes (-\nabla)^k n(\boldsymbol{r}, t) \tag{4.2}$$

where $f(\boldsymbol{v}, t)$ are time-dependent tensors of rank k and $\otimes$ denotes a k-fold scalar product. Under hydrodynamic conditions and assuming the functional relationship (4.2), the flux $\boldsymbol{\Gamma}(r, t)$ and the source term $S(\boldsymbol{r}, t)$ in the equation of continuity (that is otherwise quite general),

$$\frac{\partial n}{\partial t} + \nabla \cdot \boldsymbol{\Gamma}(\boldsymbol{r}, t) = S(\boldsymbol{r}, t), \tag{4.3}$$

can also be expanded in terms of density gradients with time-dependent coefficients. By doing so, the following transport equation can be obtained:

$$\frac{\partial n(\boldsymbol{r}, t)}{\partial t} = \sum_{k=0}^{\infty} \boldsymbol{\omega}^{(k)}(t) \otimes (-\nabla)^k n(\boldsymbol{r}, t), \tag{4.4}$$

where $\boldsymbol{\omega}^{(k)}(t)$ are time-dependent tensorial transport coefficients of order k. This is the well-known generalized time-dependent diffusion equation. Its truncation at $k = 2$ yields the time-dependent diffusion equation which defines the *bulk* transport coefficients:

$$\begin{aligned} &\omega^{(0)}(t) = S^{(0)}(t) \qquad \text{(loss rate)},\\ &\boldsymbol{W}(t) = \boldsymbol{\omega}^{(1)}(t) = \boldsymbol{W}_{\mathrm{F}}(t) - \boldsymbol{S}^{(1)}(t) \quad \text{(bulk drift velocity)},\\ &\boldsymbol{D}(t) = \boldsymbol{\omega}^{(2)}(t) = \boldsymbol{D}_{\mathrm{F}}(t) - \boldsymbol{S}^{(2)}(t) \quad \text{(bulk diffusion tensor)}, \end{aligned} \tag{4.5}$$

where $\boldsymbol{W}_{\mathrm{F}}(t)$ and $\boldsymbol{D}_{\mathrm{F}}(t)$ are the flux drift velocity and flux diffusion tensor.

At this point it is important to note several important issues. First, while the diffusion equation (4.4) is valid under hydrodynamic conditions only, the equation of continuity (4.3) applies for either hydrodynamic or non-hydrodynamic conditions and as such it is quite general in its applications. Second, expanding the distribution function in terms of powers of density gradients, it is possible to separate the velocity distribution function $f(\boldsymbol{v}, t)$ from the spatial profile of the swarm $n(\boldsymbol{r}, t)$. As a consequence, the energy distribution is uniform in space and appropriate averaging could be performed throughout the entire volume of the swarm/discharge. Certainly this is something that cannot be taken as correct in all situations and will be discussed further.

Finally, as emphasized above, the flux of charged particles can also be expanded in terms of powers of density gradient

$$\boldsymbol{\Gamma}(\boldsymbol{r}, t) = \sum_{k=0}^{\infty} \boldsymbol{\Gamma}^{(k+1)}(t) \otimes (-\nabla)^k n(\boldsymbol{r}, t) \tag{4.6}$$

and truncation at $k = 1$ gives

$$\boldsymbol{\Gamma}(\boldsymbol{r}, t) = \boldsymbol{W}_{\mathrm{F}}(t) n - \boldsymbol{D}(t)_{\mathrm{F}} \cdot \nabla n. \tag{4.7}$$

This is the well-known flux-gradient relation which is often used to define the flux transport coefficients. Therefore, in order to calculate the flux of charged particles one needs the flux transport coefficients. It should be emphasized that the majority of the Boltzmann equation solvers provide only the flux transport coefficients.

The diffusion equation (4.4) joins in a logical manner terms due to the flux and due to the source of charged particles multiplying the same density gradient and thereby bulk coefficients are generated and have to be used in the diffusion relation. The bulk coefficients may be constructed from the solution of the Boltzmann equation but if one is able to generate the spatial profiles of the swarm those may be used to obtain bulk coefficients as these profiles would contain, just like experiments, effects of both the flux and of the source of charged particles. One has to pay attention to which data are produced in different types of experiments, or in other words how many terms in equation (4.6) are required to describe that experiment.

The explicit influence of non-conservative collisions on the bulk transport coefficients is described by the terms $\boldsymbol{S}^{(1)}(t)$ and $\boldsymbol{S}^{(2)}(t)$. We can, of course, also use even higher order transport coefficients, the term $\boldsymbol{\omega}^{(3)}(t)$ is, for example, known as skewness. That is often not necessary but one should be aware that different physical situations may require different numbers of gradient terms.

The basis for the classical theory of electron transport in gases through and prior to the 1970s was the so-called two-term theory (TTT) or the two-term approximation (TTA) for solving the Boltzmann equation. It was well understood that the effect of spatial gradients and external forces is to cause the swarm to acquire a directed velocity. That is, the velocity distribution function will become anisotropic since more electrons will be moving in one direction than another. For this case it was assumed that the distribution function can be written as a sum of two terms, f_0 and f_1, where f_0 is an isotropic distribution while f_1 is a small perturbation which causes f to be anisotropic. The angular dependence of f is quite complex in the velocity space and one needs to take advantage of some symmetry if any symmetry exists. For example, in the case when only the electric field drives the swarm and if the electric field and all spatial inhomogeneities in the swarm define some fixed space direction, say the z-axis, then the velocity distribution function is symmetrical around the electric field and the Legendre polynomial expansion can

be used in order to resolve the angular dependence of the phase-space distribution function in velocity space. This procedure is valid only for the so-called spatially homogeneous swarms driven by an electric field only. For swarms in electric and magnetic fields or for the so-called spatially inhomogeneous swarms in an electric field, transverse spatial gradients can destroy rotational symmetry in velocity space and Legendre polynomial expansion is thus invalid (except for the TTA used for swarms in parallel electric and magnetic fields) (Ness 1993, White *et al* 2002). In such a case the use of spherical harmonics is mandatory. It should be emphasized that within the contemporary kinetic studies of charged particle swarms in gases, it is normally assumed that the two-term approximation is a representation of the electron distribution by the first two terms of an expansion in spherical harmonics in velocity space (White *et al* 2003).

Whatever expansion is made, taking two terms in order to resolve the angular dependence of the velocity distribution function leads to two simple equations for the dependence of the velocity distribution function on the modulus of velocity that are easily converted to equations for the distribution of energies. The lowest order equation in spherical harmonics expansion is often also called the Boltzmann equation in the literature and then copied as the starting point in numerous papers. Within the conventional two-term theory for solving the Boltzmann equation, the isotropic component enters the expressions for the number density and mean energy of the swarm while the anisotropic component is required to calculate the particle and energy fluxes. However, during the 1970s and 1980s of the last century it became clear that if electrons undergo large energy exchange in collisions (e.g. when inelastic collisions are important) with background molecules then the distribution function in spherical harmonics will not be able to achieve the full convergence. In such a case the distribution function can substantially deviate from isotropy in velocity space and the only way out is to take more than two terms in spherical harmonics decomposition of the Boltzmann equation. The multi-term theory originally developed by Lin *et al* (1979) as expanded and implemented by Robson and co-workers will be regarded here as the 'standard' multi-term theory. A salient feature of their numerical method to treat the speed dependence in velocity space is a systematic use of Sonine polynomials. That is, the velocity distribution function is expanded in terms of Sonine polynomials about a variety of Maxwellian-weighted functions. The temperatures of these Maxwellian-weighted functions do not coincide with the temperature of the background gas. In the case of electrons the so-called two-temperature method was found to be, in general, sufficient. In addition to the polynomial expansion, many other methods are available for the treatment of speed dependences of the phase-space distribution function in velocity space. Some illustrative examples include the finite difference schemes (Maeda and Makabe 1994a, 1994b) and splines (Pitchford *et al* 1981, Pitchford and Phelps 1982).

Nevertheless, in all cases, if a sufficient number of terms are used the results should converge and therefore it is important to have different 'benchmark' tests in order to test theories. In earlier years it was customary to include such tests whenever a new multi-term theory or a Monte Carlo code was introduced.

In principle, it is not necessary to make hydrodynamic expansion which may lead to a theory may be applicable to 'non-local' (non-hydrodynamic) transport although it would necessarily be more numerically demanding.

Finally, we may say that it is possible to obtain the same results (though not at the same level of detail) by simulating charged particle transport. Monte Carlo simulations work particularly well for modelling of transport in gases, and although demanding as far as computer time is concerned the present day personal computers may handle the task with admirable accuracy. It is now customary to have simulations with 100 000 electrons each going through more than one million collisions (Raspopović *et al* 1999, Dujko *et al* 2005).

4.2. To 'two term' or not to 'two term'

The dilemma of the title is perhaps not as Hamletian as the title would have it; rather than being a matter of indecision it is more a matter of convenience and habit. The 'standard truths' about the applicability of the TTA, from the days when cross section studies abounded were the following:

(1) TTA breaks down if inelastic cross sections were not very small (a factor of 50 was safe) as compared with elastic cross section. This would eventually break down at very high energies (well above the threshold for ionization) but those energies were seldom visited by standard swarm experiments and it was unlikely that under such conditions a hydrodynamic expansion would be applicable. Thus a more critical issue was how elastic cross sections in the Ramsauer Townsend minimum compare with the inelastic cross sections (typical examples are gases like CF_4 and CH_4 and mixtures of molecular gases with argon).

(2) In most cases drift velocities could be calculated with high accuracy by the TTA while it broke down for D_T/μ at a level that was sufficient to induce serious discrepancies in the derived cross section (Petrović 1985, Ness and Robson 1986, Crompton 1994, Yousfi and Benabdessadok 1996). It was even assumed that this could be a universal rule, but as can be seen from figure 6 it is definitely not the case, e.g. for gases such as CF_4 even the drift velocity is suspect in the two-term theory. Of course, this is a severe case and in more standard gases errors are negligible (less than experimental uncertainty of 1%) for the drift velocity and are of the order of a few per cent for the diffusion (Haddad and Crompton 1980).

(3) Many cross section data were derived by using TTA and thus may lead to somewhat erroneous calculations if applied in exact calculations. Thus, if a TTA is used to generate the cross sections it is not a problem if it is used to obtain the basis for the plasma modelling as the EEDF would be calculated correctly.

(4) TTA is often used to make calculations on a large number of points to make a smooth graph and may be tested to show the degree of departure from the exact values. In a similar fashion TTA is often used to adjust the cross sections having in mind the difference between

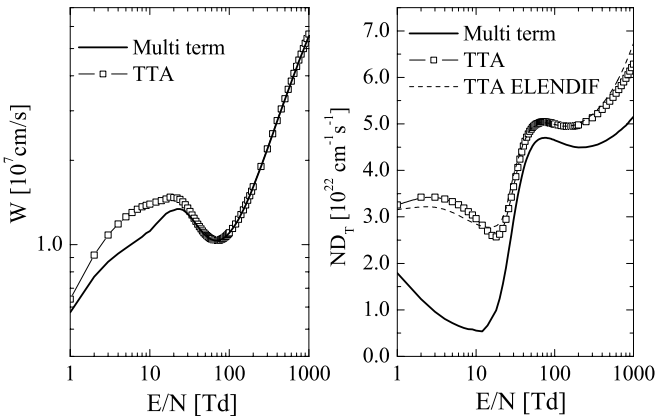

Figure 6. Drift velocity and transverse diffusion coefficient as a function of E/N for electrons in CF_4 (Dujko *et al* 2008a). Here TTA denotes results obtained by truncating the standard multi-term theory. The errors associated with the TTA for drift velocity are ∼30% while the errors associated with the TTA for transverse diffusion coefficients are ∼400%. The results for the transverse diffusion coefficients obtained by the public domain Boltzmann solver ELENDIF (Morgan and Penetrante 1990) are shown for comparison.

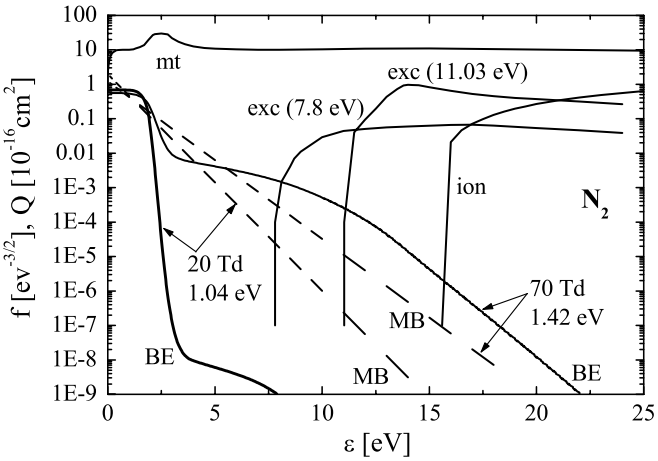

Figure 7. Distribution functions and cross sections for two values of E/N in nitrogen. Only some of the cross sections are plotted. Maxwellian EEDFs are plotted for the same mean energy as the non-equilibrium EEDF.

the TTA and the exact theory. Finally TTA may be useful to calculate some rate coefficients as extension to the Monte Carlo simulations, since processes with small cross sections may not occur frequently enough in simulation to easily achieve a good statistics. In a similar fashion the relative simplicity of the TTA may be an advantage if one wants to develop a time-dependent, spatially dependent (non-hydrodynamic) theory or apply automated techniques to obtain the cross sections (Taniguchi *et al* 1987, Morgan 1991, Bulatović *et al* 1998). Finally TTA may be used as a quick way to make tests of different assumptions when cross section sets are modified or extended.

(5) There are a number of TTT codes generally available which have been used extensively in plasma modelling.

(6) Partly a problem in comparison between Monte Carlo simulations (MCS), multi-term calculations and TTT is in the choice of angular dependence of the collisional processes. MCS uses total cross section and differential cross sections. In principle, it can also use momentum transfer cross section with the assumption of isotropic scattering and this approximation should work reasonably well unless particles are predominantly in a non-hydrodynamic regime (Stojanović and Petrović 1998). In principle, the common thing in comparisons dealing with different models of anisotropic scattering should be the momentum transfer cross section (as well as the summed inelastic cross section) (Haddad *et al* 1981, Petrović 1985). So, when angular distribution is changed if one keeps a constant total cross section the momentum transfer cross section will change very much and so will the drift velocities.

When it comes to using TTA the issue is really a degree of accuracy that one aims for. One could perhaps state that in most cases of plasma modelling the uncertainty of around 10% that could be taken as the upper limit is acceptable for transport coefficients. However, if one wants to do the analysis/normalization of the cross sections then accurate schemes should be employed such as MCS or multi-term codes.

4.3. Non-equilibrium nature of the EEDF

Petrović *et al* (2007a) have shown how differences between the Maxwell–Boltzmann distribution and the non-equilibrium EEDF may be large and may affect the calculated rates especially for the processes with thresholds above the mean energy. And no process is more important than ionization for plasma maintenance.

Here we show a similar figure (figure 7) to that in Petrović *et al* (2007a) but the idea is somewhat different. We can clearly see how large inelastic losses create a sudden fall of the high energy tail of the non-equilibrium EEDF. At 20 Td the Maxwellian distribution will have a much larger high energy overlap with high threshold processes and rates would differ by a large amount. By increasing the E/N the bulk of the distribution function almost stays the same while the high energy tail increases and at 70 Td the overlap of the high energy tail with the cross sections is greater than that for a Maxwellian of the same mean energy. The presence of the high energy electrons is something that may be adjusted by the choice of field and gas mixture and will definitely affect the charged particle balance in the discharge.

The EEDF in non-equilibrium plasmas (unlike the EEDF in thermalized plasmas) is strongly affected by collisional processes which give it its shape. If a sharp cross section exists such as the resonance in N_2, the distribution function may even have two peaks or one local minimum. When averaged, such strongly dependent shapes of EEDF may lead to effects on transport coefficients such as diffusion heating (or cooling). In the presence of non-conservative processes the hole drilling in the distribution function becomes more prominent and leads to a number of different kinetic phenomena that will be mentioned later (Petrović *et al* 2007a, Petrović *et al* 2002).

4.4. Moments of BE and fluid equations

It is possible to use a standard technique to create moment equations from the BE, each representing a balance over some physical property. A series of moment equations may on the one hand be solved in order to obtain transport coefficients (directly without first generating the velocity distribution functions, Lin *et al* (1979)). On the other hand, using moments of the BE is the best way to set up simple approximate, semi-analytical theories.

One particularly successful theory based on moments of the BE is the so-called momentum transfer theory (MTT) (Robson 1986, Vrhovac and Petrović 1996, Jovanović *et al* 2004). The basis of this approach is to assume a monoenergetic distribution function and then develop simplified relationships between different swarm properties and rate coefficients. Although not very accurate, such relations are useful to analyse certain trends and physical foundation for processes. However, with careful implementation MTT typically gives results within 10% of the correct value while providing physical insight at the same time.

In a similar fashion beam equations were developed (Phelps *et al* 1987, Phelps and Petrović 1999) and applied as a set of differential equations that may be used to solve non-hydrodynamic transport at low pressures and high fields.

Fluid equations employed in the plasma models are often associated with sets of equations that originate from the literature but to our knowledge a detailed development is difficult to establish. Truncation of the otherwise infinite series of equations normally hinges on appropriate representation of the heat flux. Negative differential conductivity is a primary test for the appropriate solution to this problem. Robson *et al* (2005) (see also Nicoletopoulos and Robson 2008) have raised a number of issues about the equations that are currently in use for fluid models but are yet to produce definitive recipes that may replace the existing theoretical foundation. On the other hand, procedures to handle modelling of transport based on fluid equations have been developed and included in plasma models (Senega and Brinkmann 2007).

4.5. Non-conservative transport

The generalized diffusion equation (4.4) may be written in the following form:

$$\frac{\partial}{\partial t}n(\boldsymbol{r},t)+W_{\mathrm{F}}\cdot\nabla n(\boldsymbol{r},t)-D_{\mathrm{F}}:\nabla\nabla n(\boldsymbol{r},t)=S(\boldsymbol{r},t), \quad (4.8)$$

where the source term on the right-hand side can, just like the flux, be expanded in terms of powers of density gradients. The truncation at $k = 2$ yields

$$S(\boldsymbol{r},t)=S^{(0)}(t)-\boldsymbol{S}^{(1)}(t)\cdot\nabla n+\boldsymbol{S}^{(2)}(t):\nabla\nabla n. \quad (4.9)$$

If we group (as discussed in equations (4.4)–(4.6) the terms against the same order of density gradients, then we obtain effective transport coefficients that determine the spatial development of the swarm and therefore determine the spatial distribution in the experimental device. One may, in principle, use the flux coefficients in (4.6) but then one is left with the task of separately representing the source terms in the same equation. Thus one effectively should use the bulk transport coefficients for any comparisons with the transport coefficients measured in experiments. This fact is often overlooked which subsequently leads to neglecting explicit effects of non-conservative collisions and all the phenomena that those would introduce.

Within the momentum transfer theory, for example, the bulk drift velocity may be represented as

$$W=W_{\mathrm{F}}-\frac{\varepsilon}{e}\frac{2}{3}\frac{\mathrm{d}\nu^{\mathrm{loss}}(E)}{\mathrm{d}E}=W_{\mathrm{F}}+\Delta W \quad (4.10)$$

while the flux drift velocity on the other hand may be calculated in the lowest order of approximation from

$$W_{\mathrm{F}}=\frac{eE}{m\nu_{\mathrm{m}}},$$

where ε is the average energy of the swarm, ν^{loss} is the reaction rate (where attachment is taken as positive and ionization as negative) and ν_{m} is the total momentum transfer collision frequency.

As discussed by Robson (1991) and Ness and Robson (1986), the bulk transport coefficients enter equation (4.4). Thus we have two groups of transport coefficients, those that enter the diffusion equation that is otherwise used to analyse experiments that are known as 'bulk' transport coefficients, and those that enter the flux-gradient relation, which are known as the 'flux' transport coefficients. A convenient way to understand the origin and the difference between the two sets of transport data arises from the definition of the drift velocity used in MCS.

Starting from the definition that the drift velocity is the velocity of the centre of mass of a swarm of particles with positions $\boldsymbol{r}_k$ and velocities $\boldsymbol{v}_k$

$$\boldsymbol{W}=\frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{r}\rangle=\frac{1}{n_t}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{k=0}^{n_t}\boldsymbol{r}_k, \quad (4.11)$$

we observe that the differentiation operator may, in principle, be passed through summation leading to

$$\boldsymbol{W}_{\mathrm{F}}=\langle\boldsymbol{v}\rangle=\frac{1}{n_t}\sum_{k=0}^{n_t}\boldsymbol{v}_k=\frac{1}{n_t}\sum_{k=0}^{n_t}\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{r}_k, \quad (4.12)$$

where n is the total number of electrons at any time. This, however, is only correct if the number of particles does not change with time and in the non-conservative case it does, so the boundary of summation becomes a variable. The former drift velocity is the bulk drift velocity and the latter the flux drift velocity. In the Japanese literature those two types of transport coefficients are sometimes labelled the real space (bulk) and the velocity space transport coefficients (flux). Apparently, velocity space averaging is performed over the entire real space. Bulk transport coefficients may be produced in simulations following a similar kind of sampling as done in experiments.

The idea that non-conservative processes will affect the observables in experiments originated (Thomas 1969, Thomas

and Thomas 1969) at the same time as the idea of anisotropic diffusion which also required a real space analysis and spatial variation of the properties of the swarm (Parker and Lowke 1969, Skullerud 1969). The idea was consequently implemented in a large number of experiments by Tagashira and co-workers (Sakai *et al* 1977, Tagashira *et al* 1978). The debate about the meaning of the different transport coefficients that ensued and was often quite enthusiastic was mainly put to rest by the analysis of Robson (1991).

Most older codes for solving the Boltzmann equation calculated flux data while one needed bulk coefficients in the analysis of experiments. If analysis performed by an exact code was able to calculate both types of transport data, then the cross sections were properly normalized. As a matter of fact all experiments need a special analysis (Robson 1991) to interpret experimental observables in terms of cross sections and transport data. Introducing standardized flux and bulk transport data proved to simplify the situation in interpretation of transport data tremendously although all is still not clear. For example, the interpretation of the pulsed Townsend experiment still requires a careful analysis. The second remaining issue is how to deal with the steady state Townsend (SST) experiment which is the exact representation of the dark Townsend discharges. Under SST conditions at any particular point along the discharge there exist electrons originating from the cathode at different times. The correct implementation of the swarm data under the SST conditions when non-conservative collisions are operative was given in several papers each with a different degree of sophistication (Boeuf and Marode 1982, Stojanović and Petrović 1998). The most comprehensive analysis of the SST discharges is that of Dujko *et al* (2008).

As a recommendation for plasma specialists not wishing to dive into the plethora of different transport coefficients and interpretations it suffices that for the diffusion equation they have to apply the bulk properties while the flux properties should be used to calculate fluxes from (4.7).

The difference between the two sets of drift velocities is a good indication of the presence of non-conservative processes. For electrons, differences between the two sets are relatively small until the largest E/N where they could be up to 30%. In some special cases, the difference could be large even at lower E/N depending on the derivative of collision rates with E. However, for positrons the presence of positronium formation, which has a cross section sometimes exceeding the elastic cross section, non-conservative effects are huge and bring a completely different behaviour between the two sets of data (Šuvakov *et al* 2008, Marler *et al* 2009) and the difference between the bulk and flux properties may be as large as two orders of magnitude while Ps formation is able to induce negative differential conductivity (NDC) into the bulk component when no indication of the NDC exists for the flux component. These effects are mainly due to severe skewing and spatial separation of the swarm properties in real space. As an illustrative example of the effects of non-conservative collisions in figure 8 we show the percentage difference between the bulk and flux values for the drift velocity and the characteristic energy. In particular, for the drift velocity

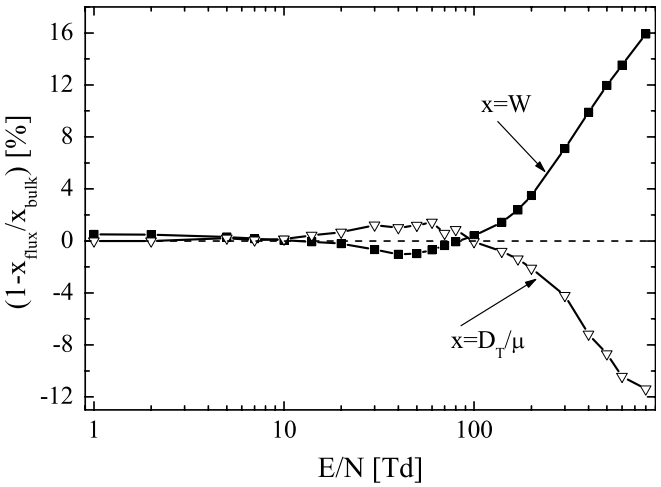

Figure 8. Differences between the flux and bulk properties for electrons in N_2O (Dupljanin *et al* 2009).

we note that for E/N less than 100 Td the flux value dominates the bulk value, while for E/N greater than 100 Td the opposite situation holds.

4.6. Transport in space and time-dependent fields

In real discharges, regions of high field are narrow and usually close to electrodes, where two effects combine, electrons relaxing from the initial conditions at the surface and electrons not being able to adjust to the local field before its value changes. Under such conditions the assumption that the EEDF is uniform in the entire volume of the discharge does not apply, the EEDF and all the properties change in space. In a similar fashion at low pressures even in uniform field properties of electrons will change from one point to another (see for example Stojanović and Petrović (1998)). Both of these situations are handled well by the hybrid codes and separation of electrons into two groups (Donko 2000, Bogaerts and Gijbels 2002, Donko *et al* 2006) or by relaxation continuum theory (Makabe *et al* 1992, Nakano *et al* 1994). There is simply no easy way to apply local field equilibrium to this physical situation. In figure 9 we show the spatial profile of the average velocity (Radmilović *et al* 2002) in a system where we have two different values of E/N. In the first half the electrons start from the initial Maxwellian with a mean energy of 1 eV and pass through a series of peaks indicating the Frank–Hertz experiment-like development while the mean energy increases to several electronvolts. Average velocity is almost completely relaxed by the time the middle of the discharge is reached (while energy is not fully relaxed) and then the E/N changes abruptly. One can see that although there is a need to change the energy again the average velocity relaxes very quickly to the new value passing through a small local maximum. At the same time the energy changes gradually throughout the rest of the gap. This situation is relevant to modelling of breakdown in inhomogeneous media such as liquid with bubbles (Babaeva and Kushner 2008).

It is evident why there are no experiments with non-uniform fields although one could perhaps envisage an

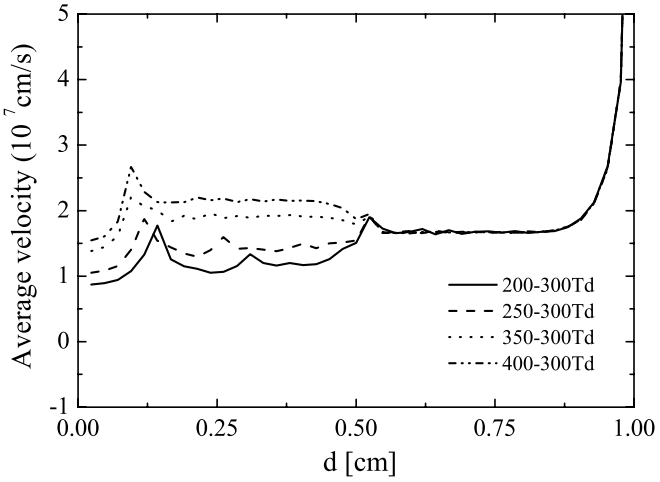

Figure 9. Spatial profile of average velocity in a system with an abrupt change in E/N between two halves of the gap (Radmilović *et al* 2002).

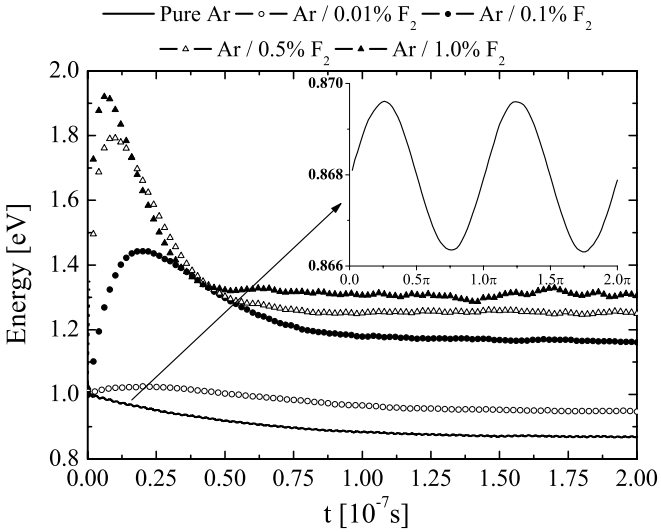

Figure 10. Temporal relaxation of the mean energy for different gas mixtures of a small amount of molecular fluorine mixed in argon buffer gas, $E/N = 0.141$ Td, $f = 200$ MHz, $p = 760$ Torr.

experiment in a cylindrical or spherical geometry. However, one may regard simulations (with swarm derived cross sections) as an exact representation of such transport and there seem to be plenty of such simulations for the relevant geometries such as cathode fall like field distribution (Boeuf and Marode 1982). Nevertheless, swarm experiments in non-uniform fields would be both important and fun to perform. One may, however, easily confirm that assuming transport coefficients to be constant in the region where electric field changes rapidly is an approximation that needs checking even when the system is separated into slow and fast particles and handled by a hybrid code. This is especially so, for low pressures when mean free paths are comparable to the characteristic length of the field variation.

Another important topic that is seldom tested experimentally (Cavalleri 1969) but has been an object of considerable interest in the past 10 years is the issue of transport in time-dependent fields. Even though it has not been analysed at a fundamental level, one may be safe to assume that the same definitions of transport coefficients may apply in rapidly varying fields. Time-dependent studies of swarms may be divided into two groups, the first being relaxation of properties following an abrupt change in E/N (in time) and the second transport properties in rf fields (periodic fields).

In figure 10 we show one example of temporal relaxation of the swarm mean energy in rf field (more complex examples may be found in Bzenić *et al* (1999b), Petrović *et al* (2002)). Apart from being an example for a very weakly undulated mean energy this figure also shows how addition of an electronegative gas may affect the EEDF significantly through a non-conservative process. Attachment in F_2 is very strong at zero energy and it decreases towards higher energies. Attachment is depleting low energy electrons and thus the distribution function shifts to higher energies leaving a higher mean energy and a local peak. After the maximum the mean energy drops, since electrons lose their energy towards the final value that they would achieve in that field, which is still higher in the presence of electronegative gas. It is also obvious that relaxation is faster when molecular gas is added because of its vibrational excitation.

Rf fields were singled out since they show a variation of properties while corresponding to technologically most interesting plasmas. For standard pressures (from 100 mTorr to 1 Torr) it is possible that either both energy and momentum or just one of those properties will fail to relax completely during the half period of the cycle, which may lead to a number of specific kinetic phenomena. In figures 11(*a*)–(*c*) we have plotted some examples of drift velocities calculated as a function of time during one rf cycle (phase).

In the first example we see how both bulk and flux drift velocities are identical (no non-conservative processes)—figure 11(*a*). Introduction of F_2 leads to depletion of low energy electrons and it results in a flux drift velocity that is considerably smaller than the bulk property. More importantly flux drift velocity is in the opposite direction to that determined by the electric field—a phenomenon known as negative absolute mobility (NAM) (Dyatko *et al* 2000, Robson *et al* 2003a). For dc fields bulk and flux properties are in the opposite directions in the case of NAM (a very unusual situation) while for rf field flux drift velocity (figure 11(*b*)) that is in the opposite direction to the expected follows the field without any delay, while the bulk drift velocity is delayed considerably. We have no room to explain the phenomenon here (for that we recommend the original papers (Dujko *et al* 2003, Dyatko *et al* 2000, Robson *et al* 2003a, Šuvakov *et al* 2005)). In figure 11(*c*) we see that as the abundance is varied, bulk drift velocity is, first, in phase with the field, and then the phase changes even for a very small amount of the molecular gas.

However, the sinusoidal shape of the transport coefficients, drift velocity in particular, is seldom preserved in rf fields. The most drastic example is of course that when we have a negative differential conductivity (NDC) where the dc dependence of the drift velocity is reflected into three peaked shapes for low frequencies (the lowest frequency shape is almost identical to that which one would get from the assumption of fully

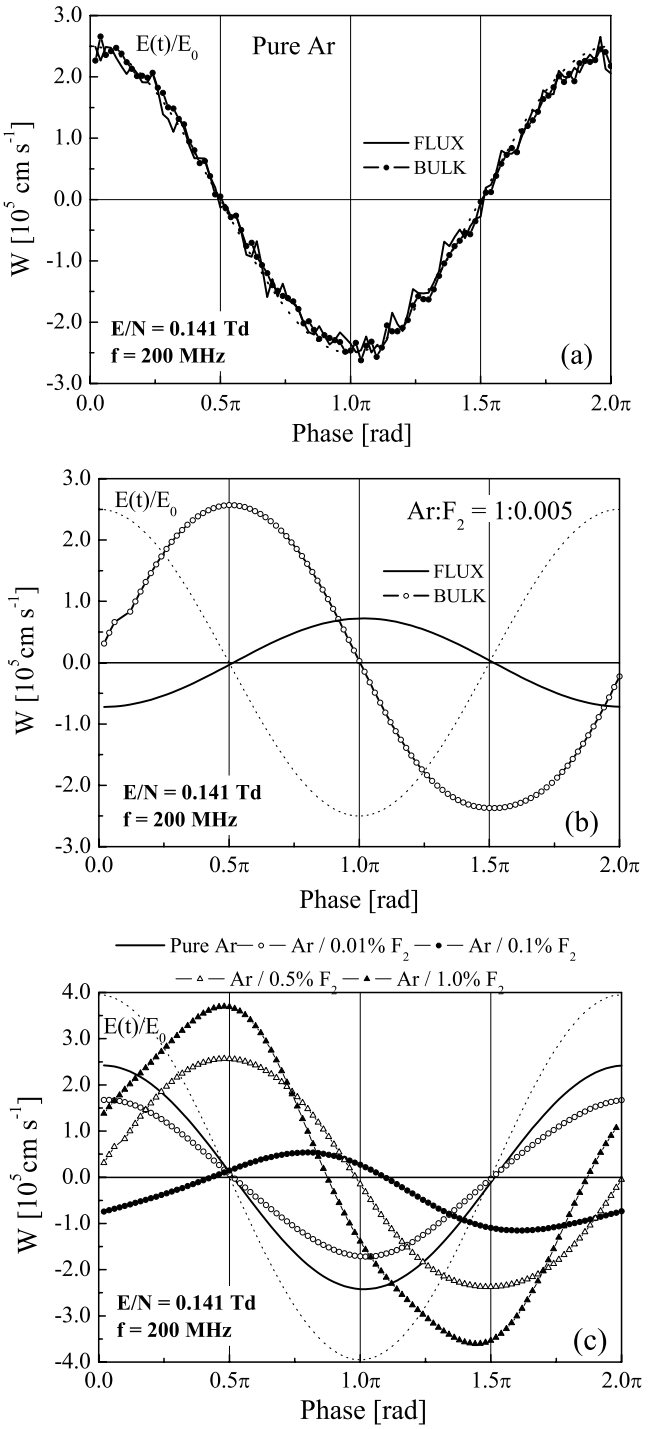

Figure 11. Temporal profiles of the bulk and flux drift velocity components for electrons in (*a*) pure argon and (*b*) in 0.5% F_2/Ar mixture. Finally, we show only bulk properties with variable abundance of F_2 ($p = 760$ Torr) (Dujko *et al* 2003).

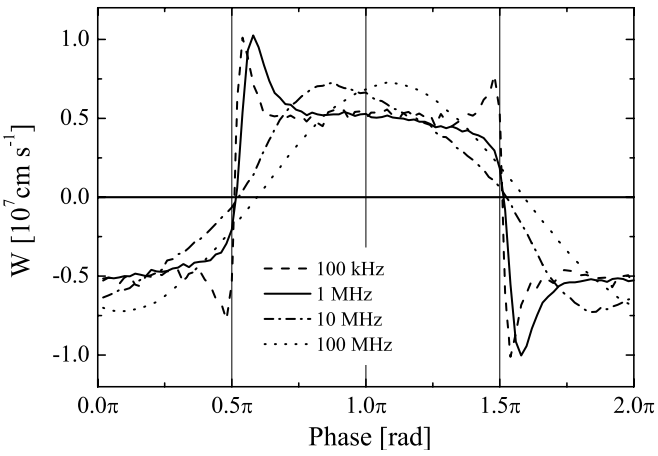

Figure 12. Temporal (phase) profile of the drift velocity for electrons in CH_4 under the influence of the electric field of the form $E(t) = 50\cos(2\pi f t)$ Td for various applied frequencies (Bzenić *et al* 1999a).

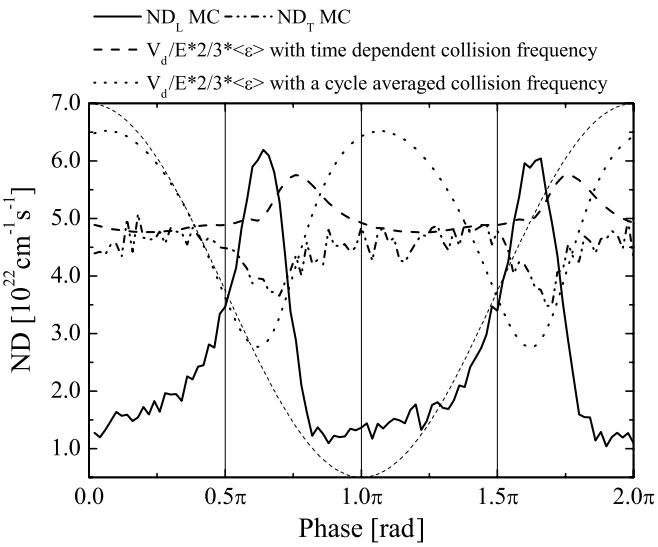

Figure 13. Temporal profiles of the diffusion coefficients for electrons in CF_4. The electric field has a form $E = 100\cos(2\pi f t)$ Td and the field frequency is $f = 10$ MHz while pressure was 1 Torr (Petrović *et al* 2006).

accomplished relaxation to the instantaneous field). However, as frequency progresses, the shape becomes asymmetric and eventually returns to a sinusoid at the highest frequencies. Nevertheless, we can see that assumptions that drift velocity is a constant, or even a sinusoid with the maximum equal to the effective dc value without any phase delay will all be wrong in the most interesting rf range. Thus agreement achieved under such assumptions in some cases of rf breakdown studies with the highly accurate experimental transport data is difficult to explain (Lisovskiy and Yegorenkov 1999) (figure 12).

Temporal dependences for diffusion coefficients are even more complex (Petrović *et al* 2006) (see figure 13). We can see an unexpected behaviour of the longitudinal diffusion coefficient which peaks as the field changes sign. At the same time the transverse diffusion, as expected, has a minimum indicating relaxation towards the thermal value which is never reached because of the rapidly changing field. Such anomalous diffusion was first predicted in the mid-1990s by swarm methods (White *et al* 1995, Maeda *et al* 1997). It is expected to be of considerable importance for maintenance of rf plasmas but to the present day we are not aware of whether anybody has included this effect in the model, and at the same time models that could perhaps reproduce this effect (such as particle in cell codes PIC) have not been tested for swarm-like situations.

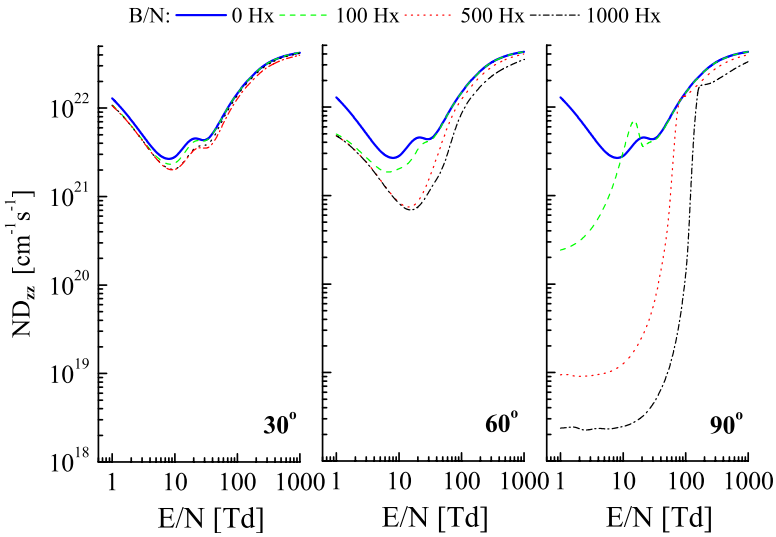

Figure 14. Variation of ND_{zz} as a function of E/N for various B/N and angles between the fields for electrons in CF_4.

4.7. Transport in combined electric and magnetic fields

One of the most critical issues in plasma modelling is correct treatment of the effects associated with the magnetic field on the charged particle transport. While the understanding of transport phenomena in combined dc electric and magnetic fields is on firm ground (Ness 1994, White *et al* 1999a, Dujko *et al* 2005, 2006b), their implementation in complex plasma models introduces many difficulties. Recent attempts to include the $\boldsymbol{E} \times \boldsymbol{B}$ transport data into plasma models accurately have led to a better understanding of the plasma heating issues associated with magnetically enhanced/assisted plasma reactors (Kinder and Kushner 2001, Sankaran and Kushner 2002). It was shown that inclusion of the $\boldsymbol{E} \times \boldsymbol{B}$ drift may lead to additional heating of ICPs (Tadokoro *et al* 1998, Vasenkov and Kushner 2003). These illustrative examples are very welcome steps in the right direction but in most models (with the exception of some PIC models) the effects of magnetic field are neglected when it comes to transport of charged particles even when it appears that in general the magnetic fields are included in the model. However, a number of physically relevant components of the model may be lost by not including the magnetic field in the transport. First, in the case of crossed magnetic and electric fields new transport coefficients are generated, such as the drift velocity along the $\boldsymbol{E} \times \boldsymbol{B}$ axis. Not only does it affect the outcome of modelling or phenomenology (Tadokoro *et al* 1998, Vasenkov and Kushner 2003) but also the anisotropy of diffusion changes and along the $\boldsymbol{E} \times \boldsymbol{B}$ axis a similar effect for diffusion occurs as for the E axis (Raspopović *et al* 2000). In general, the temporal profiles of transport coefficients become skewed, oscillatory, even chaotic (Petrović *et al* 2002) with more complex phase delays.

Additional calculations may be required with plasma models that would include more fundamental aspects of the effects of magnetic fields on charged particle transport properties, particularly when non-conservative collisions are operative. In the following we will demonstrate the applicability of our Monte Carlo simulation code under conditions when the electron transport properties are greatly affected by the magnetic field.

In figures 14–16 we demonstrate the effects of magnetic field on the diagonal elements of the diffusion tensor for electrons in CF_4. We employ a coordinate system where $\boldsymbol{E}$ defines the z-axis, while $\boldsymbol{B}$ lies in the y–z plane, making an angle ψ with respect to the $\boldsymbol{E}$. The explanation of anisotropic diffusion for electrons in an electric field only in the late 1960s (Parker and Lowke 1969) was a significant turning point in the development of both theoretical and experimental swarm studies. For the magnetic field free case ($B/N = 0$ Hx), the anisotropic nature of the diffusion tensor is clearly reflected in the profiles of the diffusion coefficients. The ratio between the transverse and longitudinal diffusion coefficients is considerable at low and intermediate values of E/N and it is therefore of some concern that it is a common practice for plasma modellers to assume that diffusion is isotropic (Sommerer and Kushner 1992, Boeuf and Pitchford 1995). When magnetic field is applied, the anisotropic nature of the diffusion tensor becomes even more evident. We observe that the longitudinal and transverse diffusion coefficient along the $\boldsymbol{E} \times \boldsymbol{B}$ direction may vary over several orders of magnitude with E/N and B/N while the diffusion along the y-direction shows a remarkable sensitivity with respect to the angle between the fields. Perhaps the most distinct property of D_{yy} is a high sensitivity to the energy dependence of the cross section which has been observed previously for argon (Ness and Makabe 2000). Clearly, care must be taken when the magnetic field is present since magnetic and electric anisotropies are coupled producing different fluxes along different directions. Although such fluxes have not been taken into account in fluid modelling of magnetized plasma discharges or in particle models as well, it is evident that contemporary plasma modelling requires their implementation. The first steps in this direction have been made recently (Kamimura *et al* 1999, Shidoji *et al* 2001).

All processes become more complex in magnetic fields. In figure 17 we show all the complexity that ensues with a

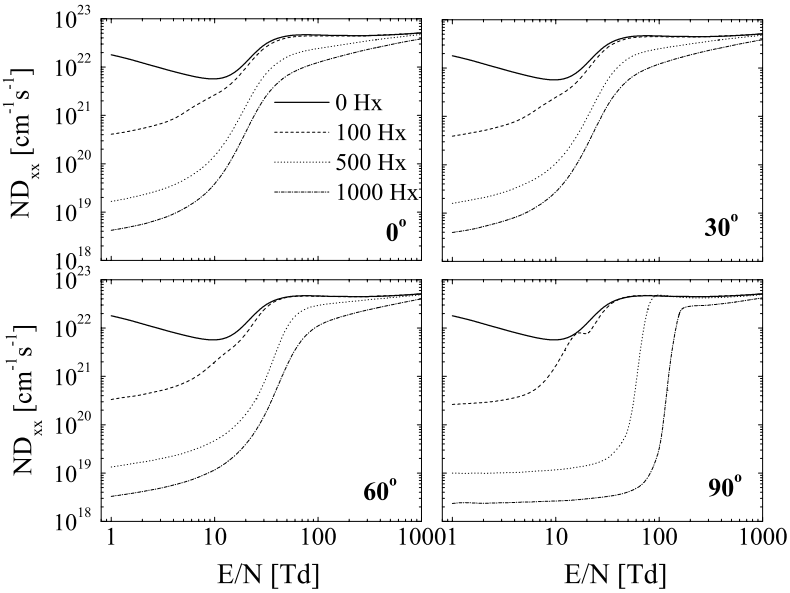

Figure 15. Variation of ND_{xx} as a function of E/N for various B/N and angles between the fields for electrons in CF_4.

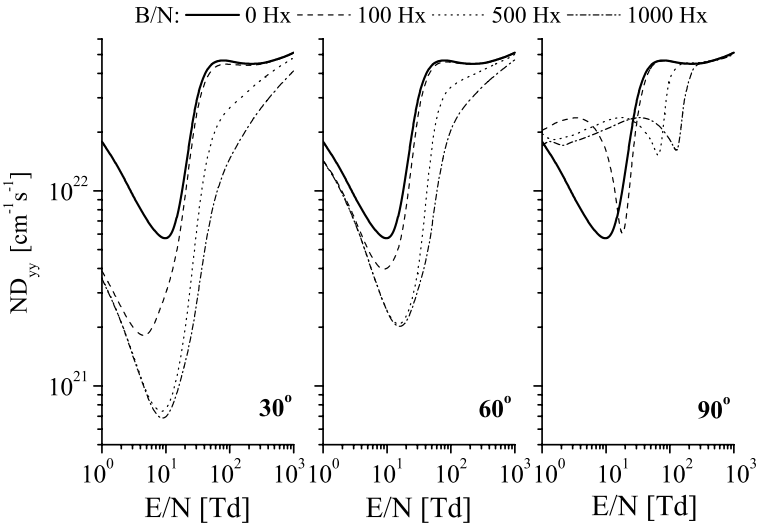

Figure 16. Variation of ND_{yy} as a function of E/N for various B/N and angles between the fields for electrons in CF_4.

combination of the effect of rapidly changing electric fields, additional rf magnetic fields and non-conservative processes. Certainly, simplified assumptions of a sinusoidal drift velocity with the maximum equal to the dc drift velocity cannot be applied here. On the other hand, such a degree of complexity is prohibitive for meaningful plasma modelling and a reasonable level of minimum requirements and benchmarks for testing codes should be developed. In any case, including the $\boldsymbol{E} \times \boldsymbol{B}$ component of the drift velocity (and the corresponding diffusion coefficients) is necessary for all magnetized plasmas and it should be coupled with a better understanding on how to calculate such data in the presence of non-conservative collisions.

4.8. Kinetic phenomena in charged particle transport

There are a number of phenomena that occur in swarm physics at the level of ensemble which cannot be easily explained by trajectories of individual particles or based on the transport in simpler conditions. These often complex phenomena make modelling of plasmas more difficult but sometimes open new possibilities. Here, we shall only list some as there are several review papers that were recently updated (Petrović *et al* 2007a, Petrović *et al* 2002, White *et al* 2002).

–*Diffusion cooling/heating* is caused by the shape of the momentum transfer cross section (Robson 2000). This effect may affect the transport in gases with strongly variable cross sections when position of the minimum or a high peak in the total cross section may lead to a situation when the mean free path for electrons in a certain energy range is comparable to the size of the vessel and thus groups may be lost preferentially to the walls. However, due to sheath fields it is perhaps interesting to focus on this effect only in low current discharges and modelling of breakdown and afterglow.

–*Attachment cooling/heating* consists of hole drilling in the EEDF that is caused by a sharp resonant attachment cross

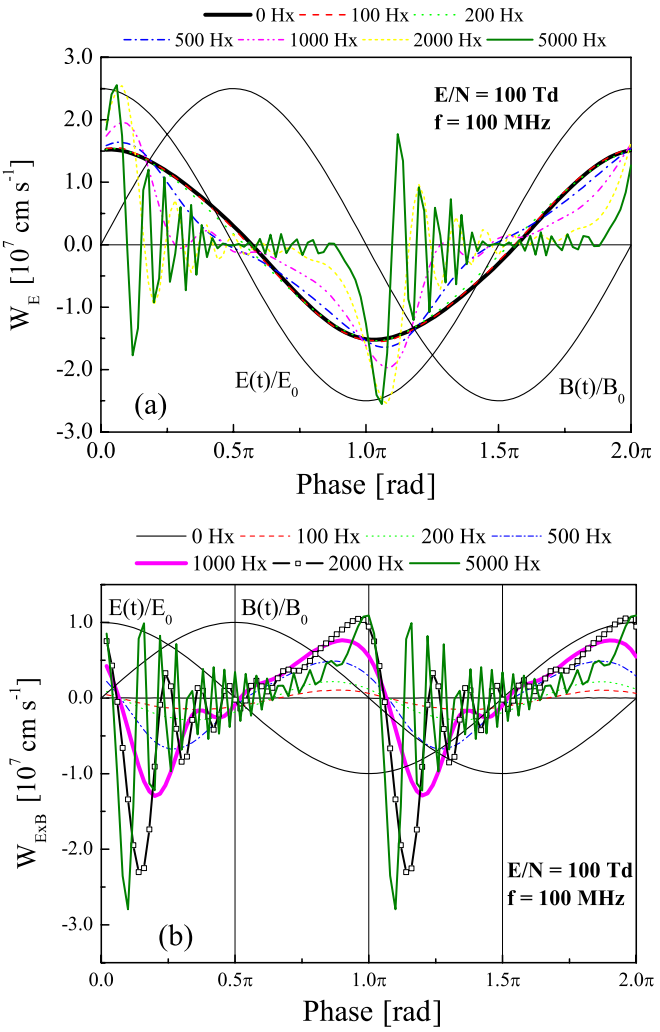

Figure 17. Temporal profiles of the longitudinal (*a*) and transverse (*b*) drift velocity component as a function of B/N (Dujko *et al* 2009).

section which can 'drill a hole' in the EEDF (McMahon and Crompton 1983). This effect may be significant at lower pressures for gases with strong, narrowly peaked attachment when the distribution function may be depleted in the relevant energy range and replenishment through other collisional processes may be lacking.

–*Anisotropic diffusion* is the effect of electric field on the spatial profile of the swarm when the field stops and accelerates electrons going against the field. As a result, longitudinal diffusion is typically reduced (Parker and Lowke 1969, Skullerud 1969). Certainly, assuming a spatially uniform and energy independent diffusion is inappropriate and it is made even worse if it is also assumed to be isotropic. This is a universal effect and will affect any model that assumes transverse and longitudinal diffusion to be identical. The ratio between the two is usually 2 but it may be as large as 10 (Kurihara *et al* 2000) for gases with strongly increasing momentum transfer cross section (e.g. Ar, CF_4, SiH_4 and many more). Typically transverse diffusion is measured and calculated but often it is used in modelling instead of the longitudinal coefficient.

–*Anomalous longitudinal diffusion* occurs in rf fields as mentioned above (see figure 13) (White *et al* 1995, Maeda *et al* 1997) and consists of a sharp peak in longitudinal diffusion when it should actually have a minimum (thermal value) as the field goes through zero and changes sign. At the same time the transverse diffusion behaves in a regular, expected fashion. Another aspect of anomalous diffusion is that the longitudinal component may become larger than the transverse even when in dc and in the larger part of the period transverse diffusion is larger by a large factor (typically 2). Anomalous diffusion is only observed when field changes sign and not when it goes to zero and back. It is associated with the momentum and energy balance of spatially separated groups of electrons where one predominantly moves against the field and the other in the direction dictated by the field. Changing sign combined with different relaxation times for losing and gaining energy and distributing directions of motion lead to this effect. This effect is universal to all cases studied so far where the direction of the electric field changes. It is important to note that not only is diffusion not constant in time (and space) but it is anisotropic and according to this effect one of the components may have local peaks instead of the expected minimum. This effect could affect the calculation of the electron fluxes in the region where heating by collisions with the moving sheath boundary is of importance.

–*Difference between the bulk and flux properties* stems from the effect of sources of new electrons (or losses) on spatial distributions of particles (Robson 1991). The origin is clear and the degree of the effect may turn standard E/N dependences of transport coefficients into surprising and hard to explain profiles. Certainly one should be able to distinguish which data go to which equation. The differentiation of the two processes should be made for conditions where ionization and attachment are important and one should be aware of the difference when selecting the data from the literature. It is not expected that in most gases making the distinction will make large quantitative changes in plasmas. To our knowledge cases when such effects have been included in plasma models have not been reported yet.

–*Enhanced electron conductivity* is a counterintuitive effect that the drift velocity is increased in a system with inelastic process as compared with the system that would have the same elastic cross section (Garscadden *et al* 1980). Simply speaking, the inelastic losses reduce the mean energy (as compared with the same E/N without inelastic processes) and consequently, the rate of momentum transfer collisions is reduced. Thus the directed velocity gained from the field is less likely to be distributed in all directions and the drift velocity increases. This effect is universal and affects the E/N dependence of drift velocities for all molecular gases. However, it is implicitly included in models through the drift velocity data.

–*Negative differential conductivity* (Petrović *et al* 1984, Robson 1984, Vrhovac and Petrović 1996) is the opposite effect when an increase in the E/N leads to a decreasing drift velocity. NDC was found to be favoured by increasing momentum transfer and decreasing inelastic cross sections and the balance of different processes affecting it can be

put into a condition which is relatively accurate. NDC may occur in mixtures of two atomic gases where energy controlling processes are elastic collisions with the lighter molecule and also by the non-conservative nature of collisions. Exceptionally large NDC for bulk velocity only exists for positrons (Marler *et al* 2009). In rf fields NDC leads to complex behaviour of the drift velocity that may put the maximum of the drift velocity out of phase with the field (Bzenić *et al* 1999a).

NDC is observed in specific gases, mixtures of argon with molecular gases, methane, CF_4, SiH_4 and many more. It is present in typical gas mixtures used in plasma processing in microelectronics. It is important to note the time/phase dependence of the drift velocity which, when NDC is present, will have a three peaked structure and will change significantly the overlap of current with the voltage and consequently power transfer.

–*Absolute negative mobility* is another counterintuitive mechanism. In its transient form it occurs when the momentum transfer cross section increases rapidly and therefore electrons that are accelerated by the field have a large chance of collisions and changing direction, while electrons going against the field have a very low chance of colliding (McMahon and Shizgal 1985, Warman *et al* 1985). Eventually, the majority of electrons will move against the field and the drift velocity will be negative (which has been observed experimentally). When all the electrons slow down, the field will accelerate them and the drift velocity will become positive again. If we add a small amount of gas with thermal attachment the electrons that slow down will disappear and drift velocity will remain negative at the expense of a decreasing number of particles (Dyatko *et al* 2000). The fact is that the majority of electrons move in the wrong direction but also due to a wave of attachment the centre of mass moves in the thermodynamically acceptable direction. In other words, the flux drift velocity really is negative while the bulk drift velocity is positive, thereby helping preserve the second law of thermodynamics (Robson *et al* 2003a). It seems that the distinction between the flux and the bulk properties has a deeper meaning stretching all the way to the laws of thermodynamics. NAM was also explained from the viewpoint of spatial modelling of swarm development and segregation to two groups moving mainly in different directions is obvious there as much as a large shift in the mean position due to attachment which proves to be larger than the change in position due to drift, thus rendering the bulk drift velocity positive while the flux property is negative (Šuvakov *et al* 2005). NAM in rf fields has been discussed above and the spatial segregation leading to positive bulk drift velocity takes appreciable time to achieve, thus bulk velocity is delayed well behind the flux velocity and field (Dujko *et al* 2003). The effect of NAM has been observed in two gas mixtures so far (without the additional excitation by external beams or lasers), Ar–F_2 and Ar–NF_3, but it is possible that several more examples could be found. While it is not really significant for plasma processing, it could become the basis for some energy conversion technologies.

–*Transient negative diffusion* has been observed (Raspopović *et al* 2000) in a number of situations and has recently been a subject of a more careful study (White *et al* 2008). Transient negative diffusion will be important for brief periods of time in crossed magnetic and electric fields. Perhaps one could use it to improve gas detectors of elementary particles, but in non-equilibrium plasmas it is hard to see that it will have a major quantitative effect.

All kinetic phenomena have a special form in the presence of magnetic fields and new complex phenomena develop. In addition, in steady state Townsend discharges all these phenomena have a special manifestation. It is, however, important to state that kinetic phenomena described here strongly affect the temporal spatial and energy dependences of transport coefficients and swarms and need to be considered in plasma modelling. In any case it should be required for plasma models to be able to predict such phenomena as a test of the code and inclusion of all the necessary physics since some of it may even lead to new mechanisms of energy transfer and some may affect the functionality of rf plasma processing equipment.

4.9. Empirical and simplified relations for electron transport in electric and magnetic fields

Various approximations for the calculation of the charged particle transport properties in neutral gases in electric and magnetic fields have been employed in plasma modelling (Dujko *et al* 2006a). While the interpretation of swarm experiments and contemporary plasma modelling techniques require a rigorous kinetic theory, there remains a great need for approximate analytical formulae, particularly when the mathematical complexity associated with the solutions of Boltzmann's equation and/or computation and memory costs due to the statistical nature of the Monte Carlo methods, limit their efficient use. In this section, using a Monte Carlo simulation technique, we investigate the accuracy and range of applicability of some frequently employed analytical formulae, often employed in the plasma modelling community.

Sometimes in plasma modelling, Monte Carlo simulations are used to calculate the drift velocity from the following formula:

$$W = \frac{eE}{m\nu}, \tag{4.13}$$

where ν is the total collision rate sampled from simulation, E is the electric field and e and m are the electron charge and mass, respectively. In earlier years, before numerical solutions to the BE became possible, this formula was used a lot to estimate the cross sections, but empirically it was found that it is more accurate to use a modifying factor F multiplying the right-hand side. F was found to be around 0.8 and to be weakly dependent on the mean energy (Huxley and Crompton 1974). It seems that in recent practice a less accurate form (effectively with $F = 1$) is used. In plasma modelling collisional rate is sampled and from that drift velocity is established. Sometimes the rate is averaged over the period, sometimes it is left to be time dependent. The drift velocity produced from this approach may be applied to establish the diffusion coefficient based on the Nernst–Townsend–Einstein relation:

$$D = \frac{Wk_BT}{E} = \frac{2}{3}\frac{W\langle\varepsilon\rangle}{E}, \tag{4.14}$$

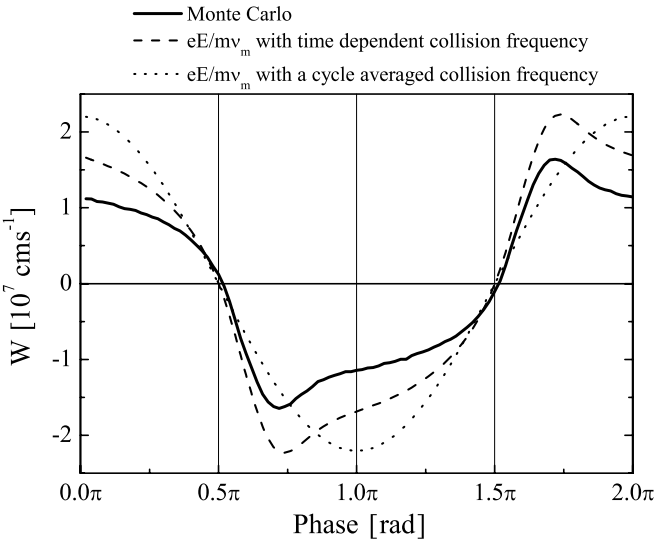

Figure 18. Temporal profiles of the drift velocity for electrons in CF_4 obtained with our exact Monte Carlo simulation and approximate formulae. The electric field has a form $E = 100\cos(2\pi ft)$ Td and the field frequency is $f = 10$ MHz (Petrović *et al* 2006).

where k_B is the Boltzmann constant and ε is the mean electron energy. Note that both formulae are only approximate and need verification. The former follows from the momentum balance equation where the critical step is the approximation of the momentum lost in collisions. The latter holds for a Maxwellian distribution of electron velocities and does not distinguish between the longitudinal and transverse diffusion. These formulae are tested for electrons in CF_4 in a time-dependent electric field, as shown in figures 13 and 18. The following strategy was applied: first, the drift velocity and the diffusion tensor were calculated using a time-dependent collision frequency and second, the same quantities were examined employing a cycle-averaged collision frequency. It would be easy to find but difficult to cite many papers in the plasma modelling community which employ these assumptions in transport modules for electrons and/or ions. The comparison between the exact Monte Carlo calculations and the approximate formulae has revealed some interesting properties. The use of cycle-averaged collision frequency produces purely sinusoidal profiles in both the drift velocity and diffusion coefficients and hence it is of limited accuracy (and use). On the other hand, the use of a time-dependent collision frequency predicts the existence of the time-resolved negative differential conductivity for the drift velocity and the only errors are associated with the magnitude of the drift velocity over certain phases of the field. When considering the diffusion, the use of a time-dependent collision frequency yields the isotopic diffusion while the exact Monte Carlo calculations have revealed a strong anomalous behaviour of the longitudinal diffusion coefficient. The temporal behaviour of the transport coefficients can definitely not be understood from the corresponding approximate formulae. Of course, if the drift velocity is assumed to be constant (either related to the maximum E/N or that value divided by the square root of 2) the predictions do not even stand a chance of representing temporal development of the drift velocities and diffusion coefficients.

Corrected forms of (4.14) exist often known as generalized Einstein's relations (GER) (Robson 1986). While such terminology implies that somebody is correcting Einstein, it is actually the correction that allows application beyond the conditions where Einstein's formula was intended to be used, i.e. GER are to be used with the electric field present. Just how large departure from the equilibrium may be covered by such formulae is not certain. A pair of GER developed for gases with both inelastic and non-conservative collisions was developed in Vrhovac and Petrović (1996):

$$D_T = \frac{1}{e}\frac{2}{3}\varepsilon\left[\mu - \frac{1}{2E}\Delta W\right], \tag{4.15}$$

$$D_L = \frac{1}{e}\frac{2}{3}\varepsilon\left[\mu\left(1 + \frac{\mathrm{d}\ln\mu}{\mathrm{d}\ln E}\right) - \frac{1}{2}\varepsilon\frac{\mathrm{d}}{\mathrm{d}E}\left(\frac{\Delta W}{\varepsilon}\right)\right], \tag{4.16}$$

where

$$\Delta W = -\frac{1}{e}\frac{2}{3}\varepsilon\frac{\mathrm{d}\nu^{\mathrm{loss}}(E)}{\mathrm{d}E} \tag{4.17}$$

is the difference between the bulk and flux drift velocities (see equation (4.7)).

The second set of approximate formulae concerns the electron transport in combined dc electric and magnetic fields. Tonks's theorem falls into this category and it assumes that the average energy and drift speed are, respectively, given by (Robson 1994, White *et al* 1999b)

$$\varepsilon(E, B, \psi) = \varepsilon(E_{\mathrm{eff}}, 0, 0), \tag{4.18}$$

$$W(E, B, \psi) = W(E_{\mathrm{eff}}, 0, 0), \tag{4.19}$$

where E_{eff} is an effective field whose magnitude is given by

$$E_{\mathrm{eff}} = E\sqrt{\frac{1 + (\Omega/\nu_{\mathrm{m}})^2\cos^2\psi}{1 + (\Omega/\nu_{\mathrm{m}})^2}}. \tag{4.20}$$

Here Ω denotes the cyclotron frequency of the electrons while ν_{m} is the momentum transfer collision frequency evaluated at E and Ψ is the angle between the electric and magnetic fields. Equations (4.18)–(4.20) represent a system of non-linear equations which has been solved iteratively.

In figure 19 we show a comparison between mean energies for electrons in CF_4 obtained by Tonks's theorem and the accurate Monte Carlo method. We chose an applied magnetic field of 1000 Hx and an orthogonal field configuration to ensure the relatively strong effect of a magnetic field on the momentum transfer collision frequency. Tonks's theorem is surprisingly accurate for non-orthogonal field configurations (Dujko *et al* 2006a). This suggests a weak sensitivity of the momentum transfer collision frequency with respect to the angle between the fields. For the perpendicular field configuration, the agreement between the empirical and accurate data is good only in the collision dominated regime and only when full convergence is reached. All in all, Tonks's

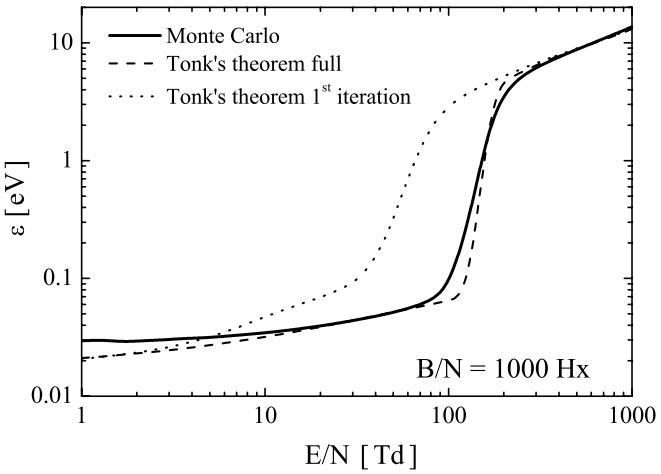

Figure 19. Comparison between the electron mean energies in CF_4 obtained by the Tonks's theorem and our exact Monte Carlo simulation technique (Dujko *et al* 2006a).

theorem is very convenient in the sense that one may attempt to use data for electric field only and apply it to the more general case involving both electric and magnetic fields crossed at an arbitrary angle. In applying the approximation the key parameter is the sensitivity of the momentum transfer collision frequency with respect to the magnetic field strength and/or the angle between the fields.

Another effective field theorem is the one used to represent transport in high frequency fields. The effective field in this case is given by

$$E_{\text{eff}} = \frac{E_0}{\sqrt{2}} \frac{1}{\sqrt{1 + (\omega/\nu_{\text{m}})}}, \tag{4.21}$$

where ω is the field frequency while ν_{m} denotes the frequency for momentum relaxation. Within the two-term theory for solving the Boltzmann equation, this approximation is exact for the isotropic component of the distribution function *if the total momentum transfer collision frequency is independent of the energy* (McDonald and Brown 1949a, 1949b). The effective field approximation was used in investigations of helium and hydrogen discharges where collision frequencies are essentially constant over the range of energies for the development of the breakdown in these gases at high field frequencies. The formula was tested further for CF_4 (Bzenić *et al* 1995) and it was found that the formula works reasonably well for microwave frequencies and very low frequencies while major departures could be expected for rf frequencies. The biggest problem is that the EEDF has a complex temporal dependence and due to poor relaxation at high frequencies the high energy tail may not be able to reach the threshold for some inelastic processes, most notably ionization. At low frequencies excursions of the high energy tail are larger and overlap with the cross sections with high thresholds may increase considerably. Thus it appears that as the frequency changes (see Petrović *et al* 2002) the rates for the high threshold processes such as dissociation and ionization fall tremendously by a factor as large as 10 as compared with the low frequencies and dc. Thus, when someone tests the effective field theorem, one should actually test whether the frequency dependence describes well the fall in the effective ionization as that is the critical process. In general and particularly for molecular gases, the effective field approximation is not valid due to the complex energy dependence of the momentum transfer collision frequency and inelastic collisions especially at frequencies and pressures of interest for most rf plasma applications.

Table 1. Constants A and B from equation (1) for different gases, and range of E/N where the formula is valid (Lieberman and Lichtenberg 2005, Marić *et al* 2005).

Gas	A ($\times 10^{-21}$ m^2)	B ($\times 10^{-21}$ V m^2)	Range E/N ($\times 10^{-21}$ V m^2)
He	8.5	234	100–750
Ne	13.3	337	300–1200
Ar	34.9	534	300–1800
Kr	47.3	667	300–3000
Xe	72.8	1000	600–2400
H_2	15.0	413	45–900
N_2	35.8	986	300–1800
CH_4	51.6	910	450–3000
C_2H_2	82.4	1440	850–8500
O_2	19.7	576	150–400
CF_4	32.8	646	80–600

One often used analytical expression is a simple form describing the spatial ionization coefficient with some degree of physical foundation albeit very approximate. It was proposed by Townsend (Townsend 1900, 1903) as

$$\frac{\alpha}{N} = A \exp\left[-\frac{B}{E/N}\right], \tag{4.22}$$

where the constants A and B are tabulated (usually in the form pertaining to normalization by pressure p, rather than by the number density even today). One should be warned about two things. It appears that the tabulations of A and B available in most books and used in most papers are copies of early tabulations made in Von Engel's book (Von Engel 1965) which although last published in 1965 has data mainly from the 1940s and before through its 1955 edition. While some of those data are still reasonably good, most of the recent generally accepted measurements were not available and purity of gases has not been established as an issue. The notable exception to that rule is the 2nd edition to the book by Lieberman and Lichtenberg (2005) where data have been updated based on Marić *et al* (2005). Nevertheless a critical analysis of the ionization data is lacking.

The other point is that one should be warned about the E/N (E/p) region where the experimental data were available and used to obtain parameters A and B. It is simply unscientific to use the formula outside that range without testing it (and showing that test in publication) . On the other hand Marić *et al* (2005) have adopted the use of the extended Townsend's formula, proposed by Phelps and Petrović for argon (Petrović and Phelps 1997, Phelps and Petrović 1999):

$$\frac{\alpha}{N} = \sum_i A_i \exp\left[-\frac{B_i}{E/N}\right]. \tag{4.23}$$

Here we show both the single term (table 1) and the extended form parameters (table 2) and again warn possible users not to

Table 2. Constants A_i and B_i from extended Townsend's formula for different gases, and range of E/N where the formula is valid (Marić *et al* 2005).

Gas	A_1 (10^{-21} m^2)	B_1 (10^{-21} V m^2)	A_2 (10^{-21} m^2)	B_2 (10^{-21} V m^2)	A_3 (10^{-21} m^2)	B_3 (10^{-21} V m^2)	A_4 (10^{-21} m^2)	B_4 (10^{-21} V m^2)	Range E/N (10^{-21} V m^2)
He	1.7	75	8	350	/	/	/	/	10–900
Ne	0.6	45	4	150	10	560	−36	23000	10–9000
Ar	0.11	72	5.5	187	32	700	−15	10000	15–6000
Kr	0.8	115	13	300	43	1200	/	/	15–6000
Xe	6	250	30	700	57	2250	/	/	40–7000
H_2	15	413	/	/	/	/	/	/	45–900
N_2	20	800	26	1800	−70	10000	/	/	90–4000
CH_4	27	600	30	1780	/	/	/	/	70–4000
C_2H_2	37	900	50	2400	/	/	/	/	160–8500
O_2	9	490	9	630	100	10000	/	/	70–400
CF_4	33	646	/	/	/	/	/	/	80–600

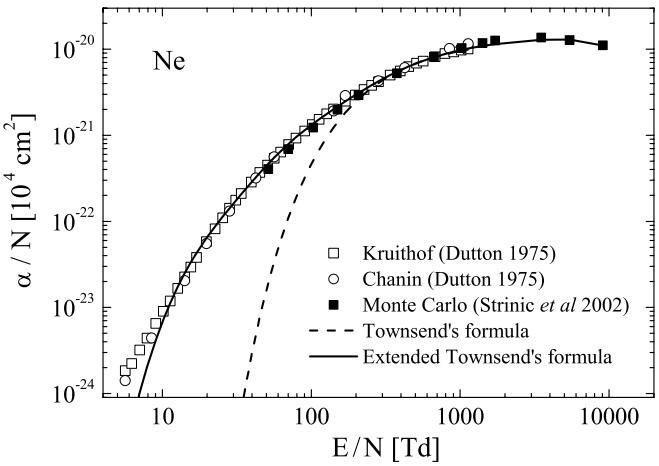

Figure 20. Electron ionization coefficient α/N dependence on reduced electric field E/N for neon. The symbols show the experimental data, the dashed lines are obtained by fitting the experimental results with Townsend's formula and the solid line represents fit by extended Townsend's formula. Original references for data from compilation (Dutton 1975) may be found there and will not be cited here.

use the fits outside the specified range of E/N. Other analytical forms have been used in many different gases and while being an accurate numerical representation of the data those have little physical foundation and again should be used only in the same range as the original experimental data.

In figure 20 we show two sets of older experimental data from the compilation of Dutton (1975) and the results of Monte Carlo simulation with the current set of cross sections (Strinić *et al* 2002) compared with the single term formula (with parameters close to those from Von Engel's book–Von Engel 1965) and with the extended formula (with parameters given in the present table). One can see that the physical meaning of the negative fourth term is to take care of the reduction of the ionization coefficient at very high E/N which has been observed both for argon and neon. The single term Townsend's formula has the advantage that it may be used to obtain the analytical form of the breakdown voltage but again, the resulting Paschen law in analytical form should be limited only to the range of E/N that used to the fit the ionization coefficient.

4.10. Transport in gas mixtures

More often than not, practical non-equilibrium plasmas are realized in mixtures. Using mixtures allows us to control different aspects of the kinetics, for example rare gas used as a buffer allows mean energies of electrons to become high, while some molecular gas present in a small abundance is the source of radicals, negative ions or target for ionizing collisions. In physics of swarms mixtures were used successfully to extend the range of available transport data and to separate momentum controlling from energy controlling collisions or to isolate rates of production of negative ions from the overall kinetics required to model swarms in pure electronegative gas (Haddad and Crompton 1980, Christophorou and Hunter 1984, Haddad 1984, Hunter *et al* 1989, Petrović *et al* 2007a).

It is relatively easy to use two or more sets of cross sections for kinetic modelling (Boltzmann's equation or Monte Carlo) but what is one to do when a fluid model is used. For practical reasons all possible mixtures have not been covered by measurements for all possible conditions. In fact, very little has been covered by measurements for mixtures or even by calculations that were published. A simple approach could be to use mixture laws, for drift velocities the law combining the data for pure gases to obtain the value for the mixture is known as Blanc's law (Blanc 1908). It is given as

$$\frac{1}{W^{\mathrm{mix}}} = \sum_{\alpha \in I_\ell} x_\alpha \frac{1}{W_\alpha}, \tag{4.24}$$

where data are taken for the same E/N and W^{mix} is the drift velocity in the gas mixture, W_α is the drift velocity of the αth component of the gas mixture and x_α is the fractional concentration of the αth gas component.

By definition, Blanc's law is incorrect but it may be useful when distribution functions are similar in shape and mean energies for the constituents and for the mixture for the given E/N. This is the case for ions throughout most of the region of E/N covered by gas discharges (with the exception of sheaths) but it is adequate for electrons only at very small E/N (i.e. when mean energies are close to thermal).

The reasons for the failure of Blanc's law are obvious from figures 21 and 22 where we show distribution functions for pure gases and for a mixture at a given E/N and mean energies as

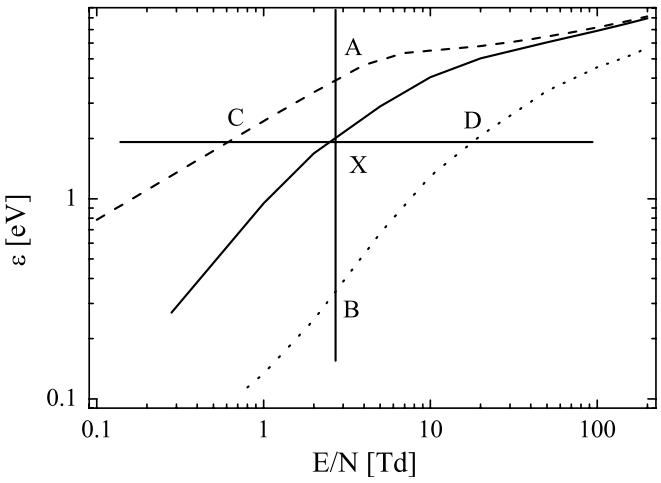

Figure 21. Comparison of calculated electron mean energies versus E/N in Ar (dashed curve), CH_4 (dotted curve) and 3% CH_4–97% Ar mixture (solid line).

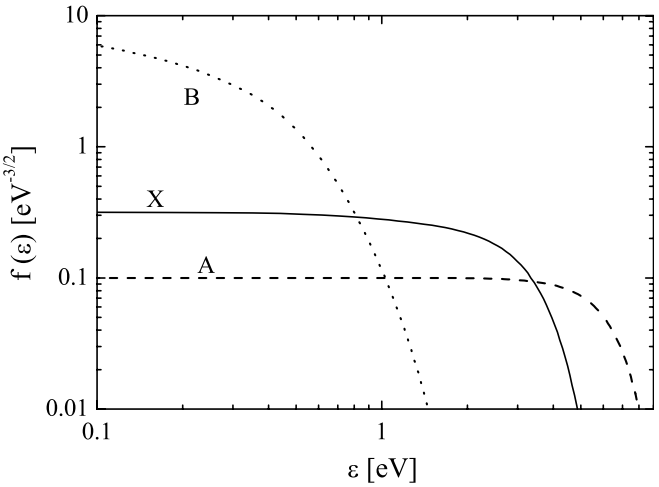

Figure 22. Comparison of EEDF at $E/N = 2.7$ Td in Ar (dashed curve), CH_4 (dotted curve) and 3% CH_4–97% Ar (solid line).

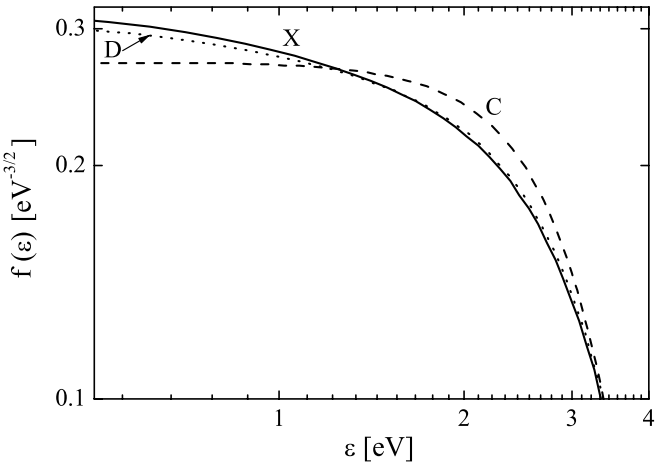

Figure 23. Comparison of EEDF in Ar at $E/N = 0.7$ Td (dashed curve), CH_4 at $E/N = 20$ Td (dotted curve) and 3% CH_4–97% Ar mixture at $E/N = 2.7$ Td (solid line).

a function of E/N and from the discussion that follows. The mean energies for the two gases (A and B) are different by a factor of 10 and correspondingly the shapes of the distribution functions are quite different. Thus the mean energy in the mixture will change significantly as the composition changes and also the EEDF will scan different energy ranges of the cross sections. The situation is improved considerably by using a common mean energy formulation of Blanc's law (Chiflikyan (1995), (2000), Jovanović *et al* (2004)—see points C and D):

$$\sum_{\alpha\in I_\ell} x_\alpha \frac{E_\alpha/N}{E/N}\left(\frac{W_\alpha(E_\alpha/N)}{W^{\mathrm{mix}}(E/N)}\right)^{\pm 1} = 1 \qquad (4.25)$$

where E_α/N and W_α are the reduced electric field and the drift velocity of electrons in the αth component and E/N and W^{mix} are the analogous parameters in a mixture. The positive and negative signs of the exponent ± 1 refer to the electron energy and momentum balance equations, respectively.

Even with a common mean energy Blanc's law may not be correct when the shapes of the distribution functions differ considerably even with the same mean energy.

The standard procedure of Blanc's law (4.24) involves combination of drift velocities at the same value of E/N (point A for Ar and point B for CH_4), to get data for the gas mixture (point X). The values of mean energies (points A and B) are about 3.9 eV and 0.34 eV, respectively, at 2.7 Td and the electron energy distribution functions (EEDF) are quite different (figure 21). If we consider the same value of the mean energy, at point X that is about 2 eV, the corresponding value of E/N in Ar is 0.7 Td (point C), while in CH_4 the corresponding value is as high as 20 Td (point D). The EEDF for these very different values of E/N shows similar behaviour for both pure gases and for the mixture (figure 23).

It is also possible to correct Blanc's law by a correction term δ_B that should include inelastic energy losses in order to predict the variation of the mean energy with the addition of a molecular gas to atomic in a mixture (Vrhovac and Petrović 1996, Jovanović *et al* 2004).

$$\frac{1}{W^{\mathrm{mix}}} = \sum_{\alpha\in I_\ell} x_\alpha \frac{1}{W_\alpha} + \delta_B, \qquad (4.26)$$

where

$$\delta_B = \sum_\alpha \frac{1 + \frac{m_\alpha}{2e}\frac{W_\alpha}{E/N}\frac{\mathrm{d}\Xi_\alpha^{(\mathrm{in})}}{\mathrm{d}\varepsilon_\alpha}}{\frac{m_\alpha}{2e}\frac{W_\alpha}{E/N}\Xi_\alpha^{(\mathrm{in})}(\varepsilon_\alpha) + m_\alpha (W_\alpha)^2 \frac{\mathrm{d}\ln W_\alpha}{\mathrm{d}\ln E}\left(1 - \frac{\mathrm{d}\ln W_\alpha}{\mathrm{d}\ln E}\right)^{-1}}$$
$$\times \frac{1}{2}\mu_\alpha \left\{ \frac{1 - \sum_\alpha \frac{x_\alpha}{W_\alpha}\sum_\alpha x_\alpha \frac{\Xi_\alpha^{(\mathrm{in})}(\varepsilon_\alpha)}{e(E/N)}}{\sum_\alpha \frac{x_\alpha}{W_\alpha}\sum_\alpha M_\alpha \frac{x_\alpha}{W_\alpha}} \right.$$
$$\left. - \frac{1}{M_\alpha}\left[(W_\alpha)^2 + \frac{\Xi_\alpha^{(\mathrm{in})}(\varepsilon_\alpha)}{e(E/N)} W_\alpha\right]\right\}\frac{x_\alpha}{W_\alpha}. \qquad (4.27)$$

Here $\Xi_\alpha^{(\mathrm{in})} = \sum_\alpha \Delta E_\alpha^s \tilde{\eta}_{s\alpha}(\varepsilon'_\alpha)$, $\tilde{\eta}_{s\alpha}$ is the normalized collision frequency for the inelastic process (s), ΔE_α^s denotes the threshold for these inelastic collisions; m_α is the mass of the αth neutral gas, $M_\alpha = m/(m + m_\alpha)$, m is the mass of swarm constituents of charge e and ε_α is the mean kinetic energy in pure gas α.

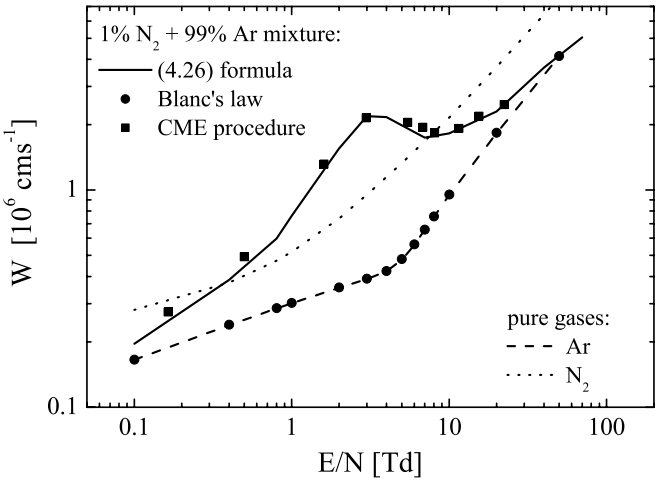

Figure 24. Calculated drift velocities versus E/N for 1% N_2–99% Ar mixture and for pure gases. Dashed curve—calculated values for Ar; dotted curve—for N_2 obtained by using the Boltzmann code; (■) calculated values from CME procedure; (●) is from standard Blanc's law calculations and it is practically identical to the line for pure argon because of the composition of the mixture; the solid line represents the values obtained by using formula (4.26) for the mixture.

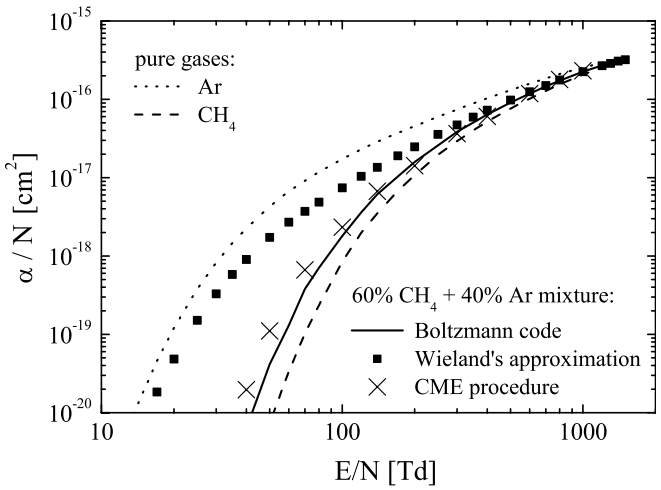

Figure 25. Ionization coefficients versus E/N calculated for pure gases and for the mixture of gases. The lines show the results calculated by the Boltzmann code (Morgan and Penetrante 1990, Morgan 1993, Morgan ELENDIF 93). Squares represent the data for the given mixture calculated by Wieland's approximation and crosses represent data calculated by the proposed common mean energy (CME) approach.

Application of the correction is more complex than using the common mean energy (CME) approach while both require additional information either for mean energy or rates for most important inelastic processes (as a function of E/N). One should, nevertheless, point out that the corrected version of Blanc's law is able to predict even the negative differential conductivity (NDC) in mixtures of two gases that in the pure state do not show NDC (e.g. N_2 and Ar) (figure 24).

The rates of inelastic processes with high thresholds are particularly sensitive to the shape of the EEDF and this includes ionization. There has been an attempt to define a mixture law for ionization coefficients—the so-called Wieland approximation (Wieland 1973) which is a simple combination of ionization rates normalized by abundances. Wieland's approximation is in general not applicable (Chantry and Wootton 1981, Hunter and Christophorou 1985, Van Brunt 1987, Marić *et al* 2005, Marić *et al* 2007) except for the very special circumstances. On the other hand, one could also apply the common mean energy approach. This proved to be worth doing even for ionization coefficients (Marić *et al* 2005, 2007) except at low E/N, where small changes in the tail of the EEDF for mixture and for pure gases may lead to large variations of the ionization rate (figure 25).

Mixture laws are sometimes used in plasma modelling but to our knowledge never in any of its corrected forms. Some corrections, however, offer sufficient accuracy for modelling of situations when compositions of the mixture are changing and it is not practical to employ kinetic schemes integrated into the plasma model.

5. Application of swarm data and models to describe ionized gases

Normally application of swarm data in plasma modelling is indirect. Transport coefficients enter readout tables that are used by fluid codes according to the local electric field. Even in hybrid and PIC codes the cross sections are applied that should be, without exception, tested against available transport data (if any data are available). This on its own makes swarm studies valuable for analysis of the available cross section sets, for analysis and insight into kinetic theory and kinetic phenomena and especially for measurements of the new data.

In the early days of gas discharge physics there were numerous studies where swarm data and models were applied directly to describe plasmas. Among the most successful models, even directly applied by the industry of integrated circuits, were zero dimensional plasma kinetics (plasma chemistry) models which involved solution of the Boltzmann equation to produce the rates that were used to calculate the densities of excited species (Capitelli and Bardsley 1990, Gordiets *et al* 1995). Of course, some effective E/N needs to be assumed corresponding to the expected mean energy. Nowadays in global models (Lieberman and Lichtenberg 1994, Gudmundsson 2002) energy balance is solved to establish the effective field/mean energy as the basis for calculating overall kinetics. Such calculations may still be useful in many systems.

It appears that the positive column is one example where local field may be used to predict some of the electron properties especially if coupled with the non-local approximation (Kortshagen *et al* 1996). Another example where one could describe the ionized gas by the local E/N or EEDF is atmospheric plasmas (ionosphere, etc). Rather than solving the kinetics of the entire plasma to establish mean energy and if possible EEDF it is sometimes advisable to directly employ measured EEDF (Campbell and Brunger 2007). Associated with this are all applications of thermalization of electrons where direct application of the swarm methods is also possible. One case of thermalization in the atmosphere from the very high energies will be illustrated later in this section.

Recently it has become possible to apply the swarm technique to model positron transport in gases (Marler *et al* 2009) and perhaps even use the same technique to model transport in dense matter such as liquids or human tissue. Swarm data and technique are the foundation for modelling and optimizing a number of detectors of elementary particles including drift tubes (Kirchner *et al* 2001), scintillation counters (Garg *et al* 1995), spark and streamer chambers (Charpak *et al* 1987), different types of calorimeters including gas phase ionization calorimeters (Denisov *et al* 1998), proportional counters (Grey *et al* 2004), gas phase electron multipliers (Bondar *et al* 2004). There is very little connection between the practice of developing particle detectors in gaseous media and gaseous electronics (Biagi 1989, Schmidt *et al* 1994, Robson *et al* 1997).

Studies of afterglows (provided that initial conditions are available) require only swarm related tools and some of the data (Sadeghi *et al* 2001, Osiac *et al* 2007). Direct application of swarm techniques is by definition applicable to modelling of the breakdown itself (Phelps and Petrović 1999) although late stages of the formative time may be affected by the accumulated charge. As long as there is no significant space charge the swarm technique will be valid (and even small space charge may be added by a perturbation procedure—Phelps *et al* 1993). Another system where the swarm method is directly applicable (albeit with a possible iterative correction at the high current end) is the so-called Townsend dark discharges. In higher current discharges increasing the charge density will lead to Maxwellianization of the distribution function due to a stronger coupling of electron energy balance with that of ions and subsequently of neutrals. In most applications of interest to us such coupling is what we want to avoid. Swarm is the low space charge limit of the non-equilibrium transport but when exactly the EEDF will start departing from the non-equilibrium EEDF is not easily predictable although the main mechanisms are well understood. It appears that the space charge will more directly affect the transport by shielding the electric field and raising the necessity to make self-consistent calculations of the field rather than directly through Coulomb collisions although that will eventually take place.

In this section we shall present a few examples when swarm like modelling could provide a full description of the phenomena although that, by far, is not a complete list.

5.1. Electron transport at very low pressures and high fields and thermalization of electrons

Low pressures bring out several physical phenomena that need to be included in plasma modelling. The distance required to have electrons starting from the cathode reach equilibrium with the local electric field (so that hydrodynamic approximation may become valid, and for example, we may observe exponential growth of electrons if energies are sufficient) may become quite long, even comparable to the gap between the electrodes, sometimes it may even extend beyond the length of the discharge. In a similar fashion, for pulsed discharges, the temporal duration of equilibration becomes significant and non-hydrodynamic development of

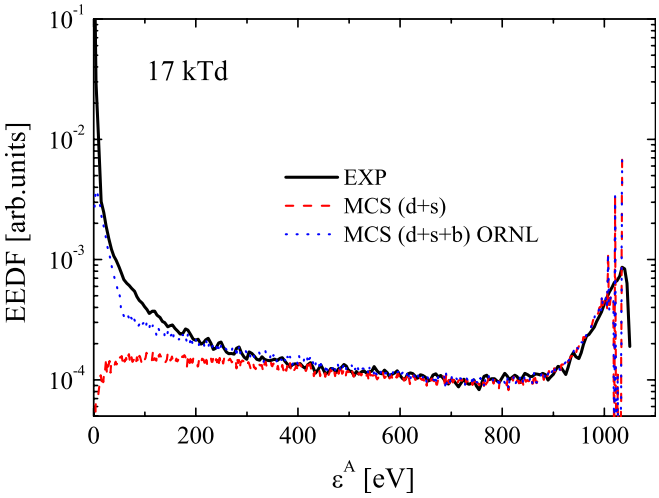

Figure 26. Electron energy distribution function as measured at $E/N = 17$ kTd ($E = 558\,\mathrm{V\,cm^{-1}}$, $N = 0.3293 \times 10^{16}\,\mathrm{cm^3}$) (Vrhovac *et al* 2001). Measured values are shown as the solid line while calculated values are represented as the dashed line (without reflection) and the dotted line (with reflection). MCS data are normalized to the experimental data at the energy of 700 eV. Energy distribution of secondary electrons is according to the Maxwellian distribution with a peak at 10 eV.

the discharge may last for a considerable period. In addition to representing non-hydrodynamic phenomena (or to use a different nomenclature a non-local approach) in the modelling of such electrons we also need to include the analysis of electron scattering at the surface where it may lose some energy before being reflected, may release secondary electrons and may perform ionization after reflection.

Including reflection of electrons proved to be necessary in the modelling of obstructed dc discharges (where high energy electrons from the cathode fall may fly through the cathode fall and negative glow and hit surfaces at high energies) (Phelps *et al* 1987, Donko *et al* 1994, Donko 1998, Belenguer and Pitchford 1999, Bano *et al* 2007).

A very direct observation of the effect of reflections requiring a more detailed representation was made in the modelling of Townsend regime discharges at high E/N where a sharp peak near the anode was observed (Jelenković and Phelps 1987, Phelps *et al* 1987, Petrović *et al* 1997). Even more importantly measurements of the energy distribution function in such discharges (Radovanov *et al* 1995, Vrhovac *et al* 2001) could not be interpreted properly at the low energy end of the distribution function without including reflection of electrons and subsequent ionization since under those conditions electrons reaching the anode may have energies above those that correspond to the maximum of ionization. One example of modelling of EEDF as measured through a hole in the anode is shown in figure 26. Overall it was possible to achieve a good agreement with the experiment for both spatial emission profiles and EEDF by including realistic data from the literature although such data are always subject to uncertainty due to varying surface conditions.

In the modelling of interaction of high energy electrons with surfaces one needs to represent the dependence of all parameters on the incoming angle (even though in most cases

the electrons at high energies fall at the 90°), one needs to include energy dependence of reflection and secondary electron production and also one needs to represent correctly the energy distribution of electrons (both primary reflected and secondary) from the surface (Gergely *et al* 1980, Rosler *et al* 1991, Radmilović *et al* 2009).

The presence of electrodes, as mentioned above, is felt more directly and through a larger extent of the discharge at low pressures. Close to the cathode there would be a region where electrons would have energy changing from the initial conditions to the mean value determined by the electric field. All processes with high thresholds (excitations and ionization) will commence at some distance from the electrode. At moderately high E/N it is possible to separate the gap into a part that is not (delay distance) and a part that is in equilibrium with the local electric field (Phelps and Petrović 1999, Malović *et al* 2003, Nikitović *et al* 2006). In addition to the delay distance several Frank–Hertz like peaks in emission may be observed in experiments (Phelps and Jelenković 1988, Holst and Oosterhuis 1921) which are also known as Holst–Oosterhuis layers (Kelly and Blevin 1989, Kelly *et al* 1989, Hayashi 1982) which is in agreement with recent studies of non-hydrodynamic transport in the Frank–Hertz experiment (Robson 2000, Sigeneger 2003).

While back diffusion (return of electrons after one or several collisions with gas molecules to the surface of the cathode where they are absorbed) is not very large at low pressures the estimates of the back diffusion coefficient will be affected by the finite geometry at lengths much larger than the delay distance (Radmilović and Petrović 2000).

In the proximity of the anode the electrons returning against the field and thus contributing to the low energy part of the EEDF would be missing and thus mean energy would increase while the density of electrons would decrease towards the anode in the region of few mean free paths (Stojanović and Petrović 1998, Petrović *et al* 2009a). Somehow for a wide range of conditions the flux is not affected as loss of electrons and increased mean velocity close to the anode compensate each other. Thus, exponential growth to the anode is maintained all the way to the very high E/N. where local equilibrium is not achieved anywhere in the discharge.

Spatial profiles of emission at high E/N where local equilibrium is not achieved (Petrović *et al* 1992, Malović *et al* 1999) are very specific and reveal integral of the cross section and energy distribution function so those data obtained in Townsend conditions (with uniform field) should be used as benchmarks for testing how well the non-local effects are represented in a plasma model. For that purpose it is essential to find more transitions that are not excited by heavy particles such as the first negative band of nitrogen (Stojanović *et al* 1990).

A review was recently written on how spatial and temporal relaxation of high energy electrons, originating from the cosmic rays, may be modelled while using the same techniques that were benchmarked in the modelling of high E/N low-pressure discharges (Petrović *et al* 2009a).

High energy, low-pressure effects as discussed here will be important to a different degree in almost all discharges as sheaths represent a region of high E/N. In particular, sputtering, some magnetron discharges and low pressure systems (below 100 mTorr) would be affected by the processes discussed here from surface interaction of electrons to the non-local transport. Some will depend predominately on one of the processes, for example multipacting discharges (Kishek and Lau 1995, 1998) need to be modelled with a detailed representation of electron surface interaction.

5.2. Modelling of fast ion and neutral transport in low-pressure discharges

One could argue that plasma modelling requires only low energy data for ions as for the typical effective E/N ions are close to the thermal equilibrium. It is nevertheless important to remember that the effective treatment of surfaces is based on the acceleration of ions in the sheaths and sometimes ions energies at electrodes may be as large as 1 keV or more. For that purpose we need cross sections for ions up to 1 keV, sometimes even 2 keV. One of the best ways to test and obtain the cross sections for ions up to such large energies, is to employ low-pressure swarm experiments at very high E/N.

Since the initiation by Phelps of the modern experiments (Jelenković and Phelps 1987, Phelps *et al* 1987, Petrović *et al* 1992) dealing with high E/N low-pressure discharges, the role of fast ions and, in particular, fast neutrals, has been addressed on numerous occasions. In this paper we shall summarize some of the work on fast ion and neutral transport in low-pressure discharges with focus on neutrals and modelling of such discharges.

At low pressures mean free paths of ions become large enough to gain high energies in spite of a large energy transfer in elastic collisions with the gas molecules. This is especially true for ions that are not in their parent gas, i.e. that may run away, i.e. reach very high energies (Mason and McDaniel 1988) even equal to that defined by the total available voltage. Very fast ions may produce fast neutrals in charge transfer collisions and it turned out that fast neutrals are more efficient in excitation and presumably ionization at the lower end of high energies. Thus it was shown experimentally that the emission close to the cathode, which was shown to be an indication of the heavy particle excitation, is generated predominantly by the fast neutrals (Petrović *et al* 1992, Petrović and Stojanović 1998, Scott and Phelps 1991). In figure 27 we show the spatial profile of emission in H_2 discharge at 145 mTorr (Petrović *et al* 2009b) calculated by the Monte Carlo simulation (Stojanović and Petrović 1998).

The effect of fast neutrals was shown to be important both in dc and rf discharges strongly affecting the kinetics of the sheath and production of secondary electrons (Radovanov *et al* 1995, Bogaerts and Gijbels 1999, 2002, Marić *et al* 2003). Nevertheless, the role of fast neutrals may be observed and modelled best in the simplest discharges, those that operate in Townsend's regime because of the effectively uniform electric field (Scott and Phelps 1991, Petrović *et al* 1992, Petrović and Stojanović 1998). Under these circumstances it is possible to develop simple transport based models without the complexities of self-consistent field calculation.

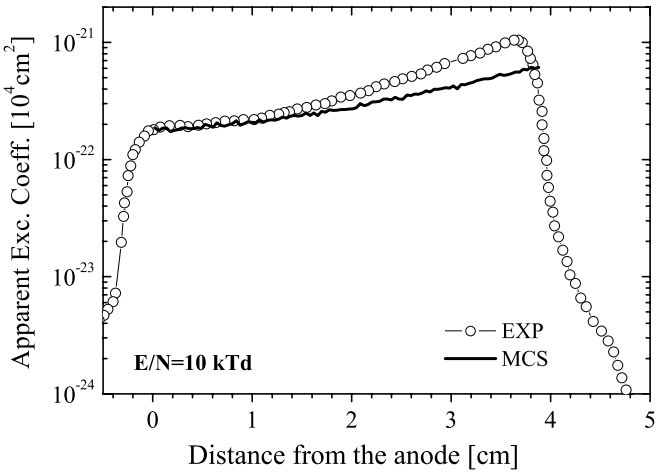

Figure 27. Spatial profile of emission in H_2 discharge at 10 kTd ($E = 477.6\,\mathrm{V\,cm^{-1}}$, $N = 0.4776 \times 10^{22}\,\mathrm{m^{-3}}$, $p = 145$ mTorr, $d = 4$ cm). Experimental data (EXP) (Petrović and Phelps 2009a) and Monte Carlo simulations (MCS) (Petrović *et al* 2008b) are compared for H_α emission normalized to the excitation coefficient.

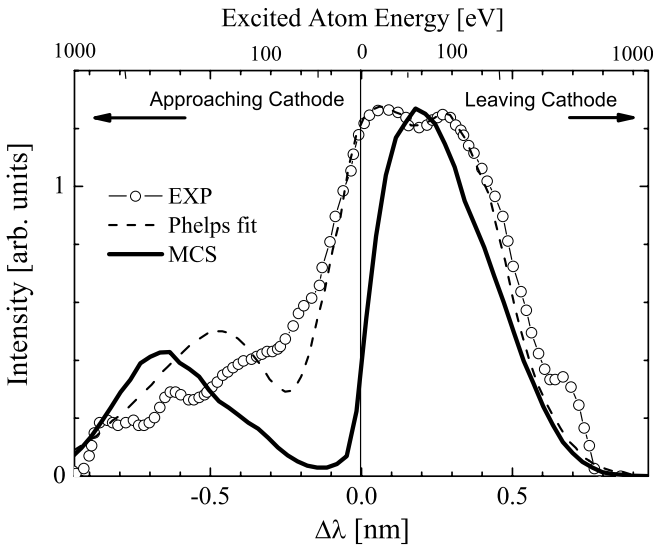

Figure 28. Doppler profile (Petrović *et al* 1991, 2008b) for $E/N = 10$ kTd—comparison of MCS results (Petrović *et al* 2008b) and results in figure 1 of Petrović *et al* (1992). Unlike experiments, calculated profiles do not contain the central line induced by electrons.

Molecules that contain hydrogen atom(s) open a possibility to use Doppler profiles to detect the velocity distribution of fast neutrals (even helium is sometimes used in higher energy fusion devices) (Petrović *et al* 1992, Phelps 2009, Petrović and Phelps 2009b, Petrović *et al* 2008b). The studies of Doppler broadened lines of atomic hydrogen have shown that neutralization and reflection from the cathode may create a wing that is consistent with fast heavy particles moving in the opposite direction to that imposed by the electric field on positive ions (Petrović *et al* 1992, Petrović and Phelps 2009b). All processes relevant to Doppler profile development have been successfully included into models and a very good qualitative and quantitative agreement has been achieved (Petrović and Phelps 2009b, Petrović *et al* 2009a). In figure 28 we show the predicted profile of red and blue wings in H_2 discharge at 145 mTorr (Petrović *et al* 1992, Petrović *et al* 2008b). The use of Doppler broadened fast neutral excited lines proved to be relevant for studies of the regimes of operation in dusty plasmas (Stefanović *et al* 2003) and in numerous rf and dc discharges (Vender and Boswell 1990, Konjević and Kuraica 1992).

Scattering cross sections and relevant transport data for ions at high energies and fast neutrals have been presented by Phelps for H_2 (Phelps 1992, Phelps 2006), Ar (Phelps 1991, 1992, 1994), N_2 (Phelps 1991), CH_4 (Petrović and Phelps 2006) and rare gases (Phelps *et al* 2000, Strinić *et al* 2004, Nikitović 2006, Nikitović *et al* 2007, Petrović *et al* 2009a). A particularly strong effect of fast neutrals is observed in mixtures of rare gases and hydrogen (or methane) since the threshold for heavy particle excitation of hydrogen atoms is very low (Petrović and Phelps 1991). The contribution of fast neutrals to secondary electron emission has been considered by Phelps and Petrović (1999). On the other hand, it is to be expected that fast neutrals may become relevant in modelling of micro discharges operating to the left of the Paschen minimum (Mariotti *et al* 2004, Wang *et al* 2005, Belostotskiy *et al* 2008, Petrović *et al* 2008c).

Finally it is worth noting that studies of fast neutrals (neutrals with energies in excess of 50–100 eV sometimes even more than 1000 eV—as opposed to hyper thermal neutrals (Giapis 1995) that may extend up to several electronvolts) have led to an idea to first include fast neutrals in modelling of plasma etching and also to use them for charging free etching of dielectrics (which is necessary for high resolution sub 100 nm nano-structuring of surfaces) (Petrović and Stojanović 1998, Panda and Economou 2001, Samukawa 2001).

5.3. Beyond the low current limit

As the current in discharges increases the space charge effects become more important and the role of charges and their spatial distribution is handled well by most plasma codes. In addition, the increased current also implies the increased density of the products of collisions (which were neglected under the basic definition of the swarm limit). Therefore densities of radicals and new molecules increase even to the level of several per cent thereby possibly changing even the kinetics of electron–molecule collisions both through a different distribution and through the specific properties of species that were not present in the original mixture.

It has been discussed for a long time that mixtures of radicals with the parent gas molecules may have different properties from the pristine mixture and that electron radical cross sections are desirable. Recently, after a major effort to produce both experimental (Field *et al* 2005, Graupner and Field 2007, Maddern *et al* 2008) and theoretical (Khakoo 2008, Munro and Tennyson 2008) cross sections it has become possible to make such calculations. A review has been published for CF_x radicals (Rozum *et al* 2006). Similar sets of data for F radical (Gudmundsson 2002) and F_2 molecule, which are common products in fluorocarbon plasmas (Morgan 1992a), are also available. It turned out that, as far as analysis

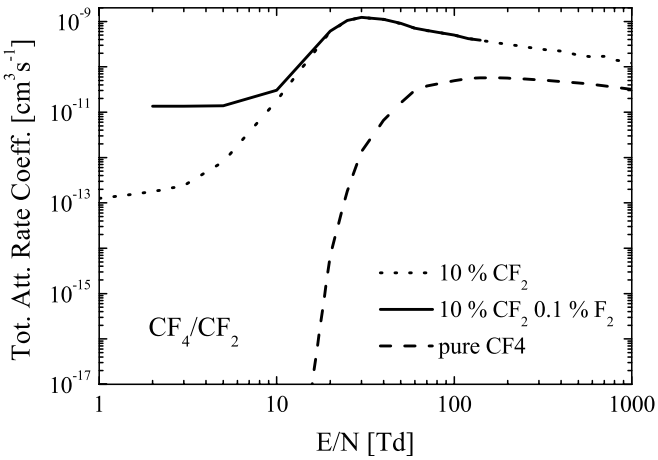

Figure 29. Effective attachment rate ion mixtures of CF_4 with CF_2 (10%) and F_2 (0.1%) (Nikitović *et al* 2009a, 2009b).

of transport data and distribution functions is concerned that the effect of some of these radicals is significant for CF_4 (Nikitović *et al* 2009a) and Ar–CF_4 mixtures (Nikitović *et al* 2009b) only through a different energy dependence of attachment and momentum transfer cross sections (as compared with the pure CF_4). CF_4 itself has a high threshold for attachment, and the discharge in its mixtures may not show all the properties pertinent to electronegative gases. Both F_2 and CF_2 have attachment that is very strong at low electron energies. Even at the abundance of few per cent for CF_2 and 100 times lower for F_2 the effective attachment rate for the perturbed gas is several orders of magnitude larger than that for pristine mixtures. In figure 29 we show attachment rates in pure CF_4 containing 10% of CF_2 and independently 0.1% of F_2.

Lack of vibrational and many electronic excitation cross sections for those radicals is not a major issue in modelling as those radicals are present at most at a few per cent (Nikitović *et al* 2009a). These processes are thus in competition with similar processes for CF_4 that is more abundant by a large factor. The only exception is for elastic or momentum transfer cross section as both Ar and CF_4 have a Ramsauer–Townsend minimum, which is not the case for CF_2 and as a result even at those small abundances there is a strong effect on negative differential conductivity (NDC).

In addition to collisions with products of dissociation of parent gas molecules, collisions with excited molecules may be equally significant. Perhaps the best covered related issue in the literature is that of the dependence of attachment (and dissociation) rates on the internal energy of molecules (Christophorou and Olthoff 2001a, Christophorou and Olthoff 2001b). We shall not cover this problem here but we shall mention and give some examples of how stepwise excitation/ionization and vibrationally excited molecules may affect the EEDF.

Stepwise excitation and ionization dominate kinetics of some dense non-equilibrium plasmas (e.g. inductively coupled plasmas, ICP (Sato and Makabe 2005, 2008). Approximate cross sections for electron excited state collisions could recently be replaced by new directly measured (Phelps and Lin 1981, Boffard *et al* 2006, Jung *et al* 2005, Jung *et al* 2007) or calculated (Bray 1994, Fursa and Bray 1995, Winsted and McKoy 2002, 2005) cross sections. While several attempts to include stepwise processes in plasma modelling exist (Bohle and Kortshagen 1994, Tochikubo *et al* 1994, Ventzek *et al* 1994, Petrović *et al* 1995, 1997, Hebner 1996, Okigawa *et al* 1996, Sato and Makabe 2008) a more systematic review of data and test of how these processes affect transport data and distribution functions is clearly needed.

Vibrationally excited states have their complex kinetics that may be coupled to the EEDF and a number of papers dealing with this set of circumstances exist in the literature primarily aimed at atmospheric molecules and hydrogen (Capitelli and Bardsley 1990, De Benedictis and Dilecce 1996, Capitelli *et al* 2000, Guerra *et al* 2004). Recently a complete albeit simplified (resonant scattering only) set of cross sections for electron induced transitions between vibrationally excited states has been developed (Mihajlov *et al* 1999). In addition to electron induced transitions there are collisional transitions between vibrationally excited states. Data and relevant processes have been summarized in a number of publications with a focus on applications such as atmospheric discharges (De Benedictis *et al* 1982, Loureiro and Ferreira 1986, Pintassilgo *et al* 2007), plasma sterilization (Kutasi *et al* 2006), sources of fast neutrals and magnetically confined ion sources (Bacal 1967, Lee *et al* 1997a, 1997b 1998, 1999), atmospheric reentry (Capitelli *et al* 2000) and many more.

6. Conclusion

In a brief attempt to summarize the current status of swarm physics and its relevance to plasma modelling we could claim that the burning issues are the following:

(1) Lack of new experiments, lack of experiments with reactive species, lack of experiments in time-resolved and spatially inhomogeneous fields.
(2) Consequently a large body of cross section data needs further verification (normalization) by the swarm technique.
(3) The need to push experiments and theory to lower densities and higher energies and very high densities with a more complex scattering theory stems from the frontiers of application and should be pursued rigorously.
(4) A possible growth can be expected in studies of ionospheric and astrophysical plasmas, positron plasma traps and motion in gases, living tissue and in complex systems where surface to volume ratio is very high.

Having achieved a large degree of sophistication, albeit with a narrow focus on the simplest possible system, swarm physics is able to provide theoretical and phenomenological guidance to plasma modelling dealing with non-equilibrium low temperature plasmas. Most importantly, benchmark models and results should be developed and broadly applied to test the codes in representing certain aspects of physics such as non-conservative phenomena, runaway particles, reflection from the surface, $\boldsymbol{E}\times\boldsymbol{B}$ transport and many more. Only a small number of benchmark calculations have been made by plasma

modelling codes and seldom in the most relevant systems. At the same time one should stress that plasma modelling codes should be able to give high accuracy results for all swarm benchmark (Robson *et al* 2005).

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