2nd Int. Workshop on Non-equilibrium Processes in Plasmas and Environmental Science IOP Publishing
Journal of Physics: Conference Series **162** (2009) 012004 doi:10.1088/1742-6596/162/1/012004

Cross sections and transport properties of negative ions in rare gases

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Abstract.
We have used a combination of a simple semi-analytic theory - Momentum Transfer Theory (MTT) and exact Monte Carlo (MC) simulations to develop momentum transfer cross sections of negative ions in collisions with noble gases based on the available data for reduced mobility at 300K as a function of E/N. At very low energies, we extrapolated obtained cross sections using Langevin's cross section and supplemented it by the total detachment cross section that was used from the threshold around 6 eV up to 100 eV. Other possible reactive processes have not been taken into account. A good agreement for the mean energy and diffusion coefficients is an independent proof of the validity of the cross sections that were derived for the negative ion mobility data.

1. Introduction

The purpose of this work is to provide plasma modelers with cross section data and transport coefficients that may be used in simulations of plasmas containing negative ions. The negative ions play an important role in laser and electrical discharges and in radiation chemistry in the atmosphere. They are present in numerous technological plasmas including plasma etching chemistries. Negative ions determine kinetics of electronegative plasmas [1] and their presence may change critically the nature of plasmas (examples of obvious changes can be seen in [2]). Ion-Ion plasmas [3] have very distinct characteristics. Numerous applications relay on electronegative reactive gases including plasma etching [4], atmospheric plasmas for biomedical application [5], and many more. Furthermore, negative ions may be used directly, for example to reduce the charging [6] of high aspect ratio structures or to be converted to fast neutrals with the aim to achieve fast neutral etching [7]. Modeling of such processes requires either cross sections or transport data or both.

The procedure used here to determine the cross sections is to apply first the momentum transfer theory (MTT) which is fast albeit with limited accuracy to fit the cross sections until the transport data fit the experimental results. In the next step further, but always slight adjustments are made to have a good agreement between experimental data and Monte Carlo (MC) calculations which provide exact results. Monte Carlo simulation code is based on the time integration technique [8, 9]. It was developed to include both isotropic and anisotropic scattering for all processes, non-conservative collisions with proper calculation of both bulk and flux transport coefficients [10], proper calculation of the collision frequency for thermal collisions and it was tested with exceptional results against all known benchmarks. Normally, the disagreement between MTT and MC (and thereby experimental) results was within 11% for all gases. We have extrapolated data to somewhat higher energies based on behavior of similar ions in similar gases and by the addition of reactive processes so a relatively complete set was derived which can be used in modeling of plasmas by both hybrid, particle in cell (PIC) and fluid codes [1, 11].

It is important to note that so far the data presented here and other similar results were interpreted by using interaction potentials [12] which while producing results of high accuracy is not directly applicable in plasma modeling. Plasma modeling requires data of a lesser accuracy (10%-30%), as compared to the derivation of accurate interaction potentials, and the data are required either as drift velocities and diffusion coefficients or as sets of cross sections. Thus we have set out to provide sets of data that may be used in modeling of reactive plasmas. As both hybrid and PIC models involve MC simulations for collisions and as applications to plasma etching devices requires control of negative ions in the afterglow or for neutralization [7, 13] the data for cross sections of negative ions found in argon-fluorocarbon mixtures are of great importance.

We have applied a simple form of MTT [14] based on elastic collisions as the first step in order to develop Br^-, F^-, Cl^-/He, Ne, Ar, Kr, Xe elastic momentum transfer cross section based on the available data for reduced mobility [15, 18]. The analytic equations allow quick calculations of the transport data and their comparisons with the experimental data. Having in mind the mean energy of ions and the overall energy range for any particular E/N and with some experience we modify the cross sections to obtain better and better agreement with experiment. The MTT is well developed to take into account reactive processes [19] but that extension is quite complex so we have applied a simple form of the theory based on elastic collisions since the influence of reactive processes starts at much higher energies for the chosen gases.

In the following sections we present details of determination of the elastic momentum transfer cross sections, transport data and discussion of the observed discrepancies between the results of MTT and MC.

2. Cross sections

The MTT consists of a specific simplification of the Boltzmann equation collision operator and a specific procedure to determine approximate distribution functions.

$$[\frac{\partial}{\partial t} + \vec{v}\frac{\partial}{\partial \vec{r}} + \frac{e}{m}\vec{E}(\vec{r},t)\frac{\partial}{\partial \vec{v}}]f^{mix}(\vec{r},\vec{v},t) = \Im^{mix}(f^{mix}, f_1^{mix}, ...f_\ell^{mix}) \tag{1}$$

Considering ions with number density n in neutral gas in equilibrium at temperature T_0 and assuming that density gradients are weak, we have the following simple approximate balance equations for mobility and mean energy of ions [15, 20, 21]:

$$K = \frac{q}{m\nu_m} = \frac{W}{E}, \tag{2}$$

$$\epsilon = \frac{1}{2}m_0W^2 + \frac{3}{2}k_BT_0, \tag{3}$$

where q and m are the swarm charge and negative ion mass, respectively, m_0 is the mass of neutral molecule, W is the drift velocity, E is the electric field, k_B is the Boltzmann constant and ν_m is the total momentum transfer collision frequency in the center of mass reference frame given by

$$\nu_m = N\sqrt{\frac{2\varepsilon}{\mu}}\sigma_m \tag{4}$$

where σ_m denotes total momentum transfer cross section, ε is mean energy of ions in the center of mass reference frame and μ is the reduced mass $\mu = \frac{mm_0}{m+m_0}$.

The most important scattering process in the low energy region (up to few eV) will be elastic scattering. Rare gas atoms do not form negative ions and in these cases the charge transfer is not possible so the main reactive process would be detachment. The equations (2-4) are easily solvable and the mobility data [15, 20] could provide cross sections up to 2−3 eV. Even the range where the detachment cross sections become significant was not covered by the earlier cross section data so extrapolation was used. The momentum transfer cross section is supplemented by detachment cross section [22, 23, 24] that was used from the threshold around 6 eV up to 100 eV.

In order to make proper calculations for thermal energies, we allowed the momentum transfer cross sections to converge towards Langevin's cross section [25],

$$Q_P = 2.21\pi\sqrt{\frac{e^2\alpha_D}{2\varepsilon}} \tag{5}$$

Values of α_D (dipole polarizability) [26] for gases used in this paper are given in Table 1 where ε is the relative energy and a_0 is the Bohr radius.

Table 1. Values of the dipole polarizability [26] for some gases of interest.

molecule	polarizability [a_0^3]
He	1.39
Ne	2.68
Ar	11.08
Kr	16.7
Xe	27.1

The cross section sets for Cl^-/He,Ne,Ar,Kr,Xe have been presented in our previous paper [8] so in this paper, in Figures 1 - 5 we presented sets of cross sections for Br^-, F^-/Ar, Kr, Xe. Figure 5 is just an example of the corrections that have been made. The major correction was made in thermal energy region. At higher energies the correction is mostly the consequence of the detachment which starts from the thresholds around 6 eV.

3. Transport data

We have done all the calculations with an assumption of isotropic scattering for elastic and detachment collisions. The MTT results were obtained in the same range of E/N as experimental results and therefore the influence of the detachment process was not included in MTT calculations.The MC calculations were performed over a range of E/N from 1 Td to 1000 Td (1Td=10^{-21}Vm^2), that is somewhat wider than that covered by the measurements.

3.1. Reduced mobility

Result for drift velocities and mean energies for Br^- in Xe is shown in Figure 6 but these results we have for all mentioned combination of gases. MC perfectly agrees with the experimental results, but there is a significant discrepancy with the MTT results.

The mean energy does not show a significant deviation from the thermal value up to 40 Td. Beyond that point the mean energy increases rapidly, reaching about 6eV at 1 kTd (in all cases).

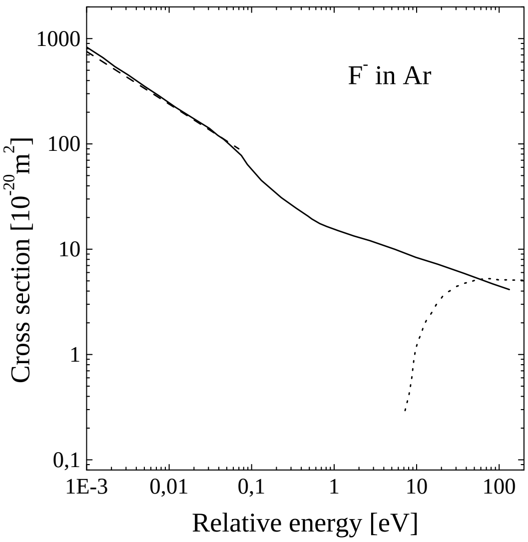

Figure 1. Cross sections for F^- in Ar. Solid line: momentum transfer cross section; dashed line: Langevin cross section; dotted line, detachment cross section from reference [22].

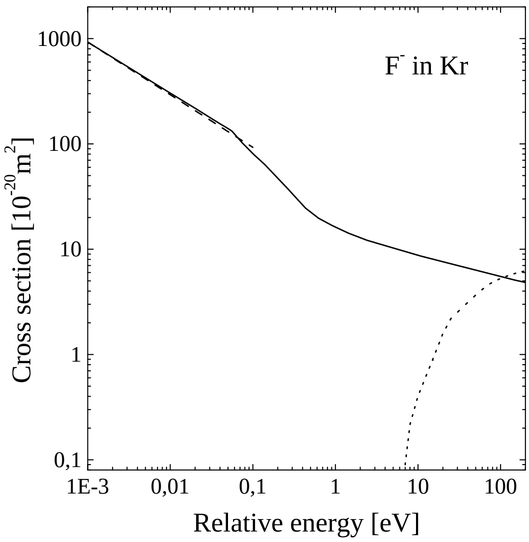

Figure 2. Cross sections for F^- in Kr. Solid line: momentum transfer cross section; dashed line: Langevin cross section; dotted line, detachment cross section from reference [22].

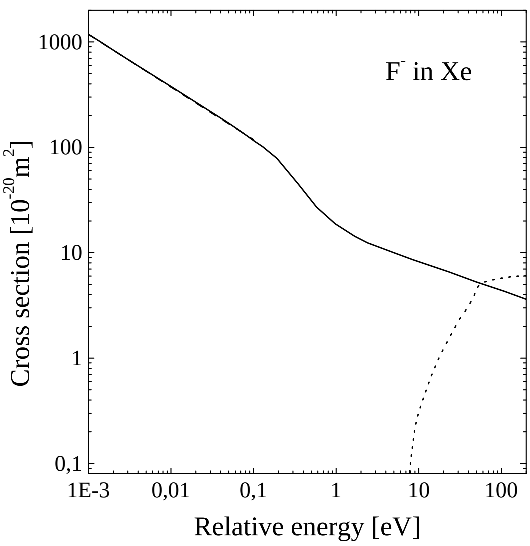

Figure 3. Cross sections for F^- in Xe. Solid line: momentum transfer cross section; dashed line: Langevin cross section; dotted line, detachment cross section from reference [23].

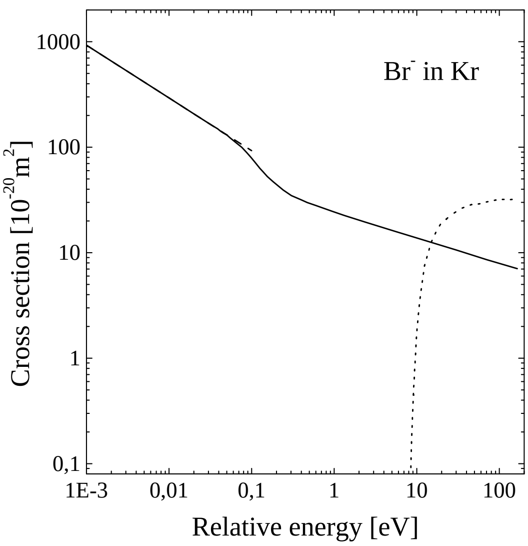

Figure 4. Cross sections for Br^- in Kr. Solid line: momentum transfer cross section; dashed line: Langevin cross section; dotted line, detachment cross section from reference [24].

The data for reduced mobilities of F^- and Br^-ions in rare gases are shown in Figures8-9. The relation between the reduced mobility K_0 and the mobility K of ions is

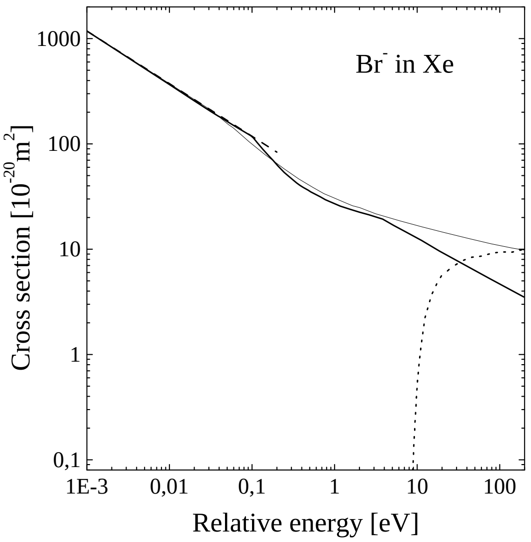

Figure 5. Cross sections for Br^- in Xe. Solid line: momentum transfer cross section; dashed line: Langevin cross section; dotted line, detachment cross section from reference [24]; thin solid line: originally obtained momentum transfer cross section.

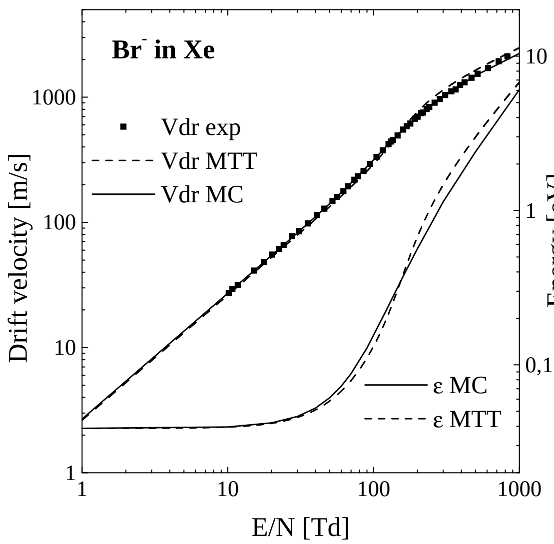

Figure 6. The drift velocity and mean energy for Br^- in Xe at T=300K. Squares are experimental results taken from Lamm et al. [17].

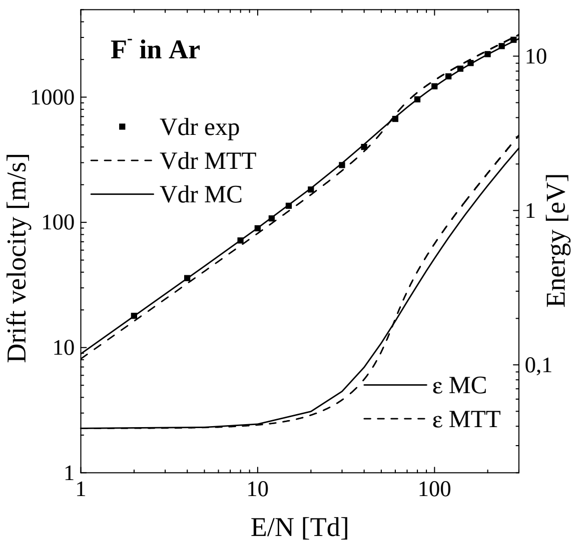

Figure 7. The drift velocity and mean energy for F^- in Ar at T=300K. Squares are experimental results taken from Ellis et al. [15].

$$K_O = \frac{NK}{N_0} \tag{6}$$

where $N_0 = 2.69 \times 10^{25}\mathtt{m}^{-3}$ is gas density at 300K and 760Torr.

MC results are in excellent agreement with the experimental results whose total experimental error does not exceed ±3%, but MTT results deviate between 10% for Br^- and F^- in Xe and 13% in the case of Br^- in Kr. These deviations cannot be related to the ratio ion-neutral gas masses or some systematic error. Thus it is only due to the limited accuracy of MTT that is exact only for the constant collision frequency model.

It can be seen from the equation (2) that the mobility coefficient is proportional to the inverse of ν_m and there are three regions of field to be considered. At low fields mobility is approximately constant due to the influence of the attractive part of the long-range interaction potential arising from the polarization exerted by the ion upon the neutral. At high fields the mobility decreases rapidly due to the dominant repulsive part of the interaction potential arising from the short-range forces. At intermediate fields there is a peak in the mobility curve, corresponding to the enhanced transparency of the gas at intermediate energies, since attractive and repulsive forces cancel out to some extent. These three different regions of the mobility can be related to the corresponding three different portions of the elastic cross sections as displayed in Figures 1-5.

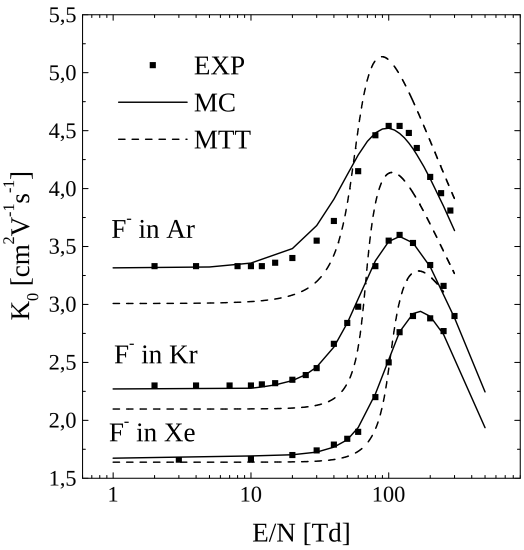

Figure 8. The reduced mobility K_0 for F^- at T=300K. Squares are experimental results taken from Ellis et al. [15].

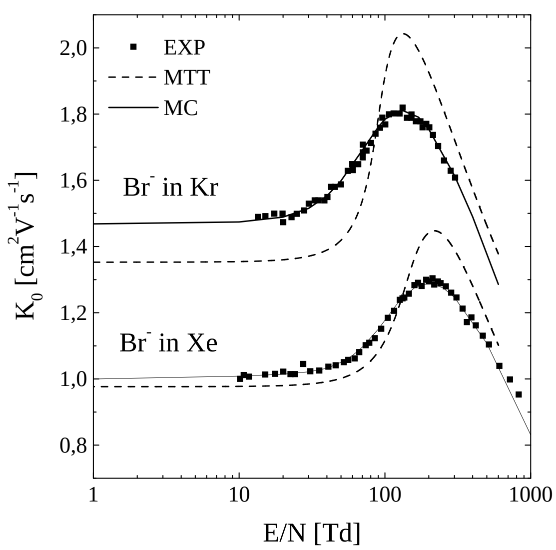

Figure 9. The reduced mobility K_0 for Br^- at T=300K. Squares are experimental results taken from Lamm et al. [17].

3.2. Diffusion coefficients

Diffusion coefficient is a tensor having components that refer to the directions parallel and perpendicular to the electric field named longitudinal and transverse diffusion coefficients respectively. In MTT equations anisotropy of temperature tensor was taken into account [27, 28, 29] and longitudinal D_L and transverse D_T diffusion coefficients were calculated from Generalized Einstein Relations obtained by Robson [27, 28].

$$D_L = \frac{k_B T_L}{q} K(1 + (1 + \Delta)\frac{\mathtt{dln}K}{\mathtt{dln}E}) \tag{7}$$

$$D_T = \frac{k_B T_T}{q} K, \qquad \Delta = \frac{Q}{2K_B T_L W} \tag{8}$$

In the case of constant mean free time where collision frequency ν_m is constant, the ion temperatures and heat conductivity Q are given exactly by the expressions [27, 28, 29]:

$$\begin{aligned} Q &= B m_0 W^3 \\ kT_T &= kT_0 + A_T m_0 W^2 \\ kT_L &= kT_0 + A_L m_0 W^2 \end{aligned} \tag{9}$$

where

$$\begin{aligned} A_T &= \frac{(1+\frac{m}{m_0})\frac{\nu_v}{3\nu_m}}{\frac{2m}{m_0}+\frac{\nu_v}{\nu_m}}, A_L = \frac{\frac{2m}{m_0}(1-\frac{\nu_v}{3\nu_m})+\frac{\nu_v}{3\nu_m}}{\frac{2m}{m_0}+\frac{\nu_v}{\nu_m}}, \\ B &= \frac{(1+\frac{m}{m_0})^2(A_L+\frac{1}{2}+\frac{3m}{2m_0})}{1+\frac{3m^2}{m_0^2}+\frac{4m\nu_v}{3m_0\nu_m}} - (A_L + \frac{1}{2} + \frac{m}{2m_0}) \end{aligned} \tag{10}$$

and ν_v is the collision frequency for viscosity.

Longitudinal and transverse diffusion coefficients are shown in Figures 10-13. The only available experimental results are the experimental data of Ellis et al. [30] for longitudinal diffusion of F^-,Br^-/Kr,Xe. There are no experimental data for the longitudinal diffusion available for F- ions in Ar. The agreement of the results for longitudinal diffusion is an independent proof of the validity of obtained cross sections sets since MC gives an excellent agreement with the experimental results whose uncertainty is 8% at low E/N increasing to 20% at the higher values, but MTT results are again of poor quality. There are two main candidates for the explanation of the discrepancies between the experimental data and MTT results: the approximate nature of the theory and the assumption of isotropic scattering. The differences at high fields are mostly the consequence of the detachment which is not adequately represented in the theory. Additional sources of information such as differential cross sections or transverse diffusion coefficients could be used to improve further the set by adding anisotropies [31] which may be important at higher mean energies where scattering is more likely to occur in forward direction. Nevertheless, we may still claim that a simple form of MTT may provide a reasonable first approximation for diffusion coefficients and further improvement by other but more demanding techniques.

The transverse diffusion coefficients are not available from experimental papers and the obtained MC results may be a useful source of data but one should be aware that further information on anisotropy of scattering may affect the results though much less than in the case of resonant charge exchange dominated transport [31].

3.3. Rate coefficients

In addition to transport coefficients in fluid plasma models one needs the rate coefficients for all relevant processes. The net rate coefficients of elastic scattering and detachment are shown in Figure 14-16. It is obvious that a large rate of detachment as a non-conservative process above 300 Td will affect the real space (bulk) and the velocity space (flux) definitions of transport coefficients. This is shown for Cl^-/Ar in Figure 17. Similar results are found for all other ions in other gases.

4. Summary

We have determined a set of cross sections for F- ion in Ar, Kr and Xe based on the available experimental transport data in a wide range of reduced electric field E/N of 1 Td - 1000 Td

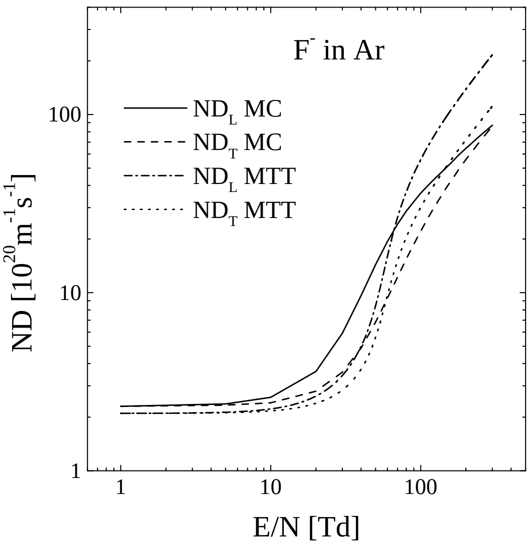

Figure 10. The diffusion coefficients for F^- in Ar at T=300K.

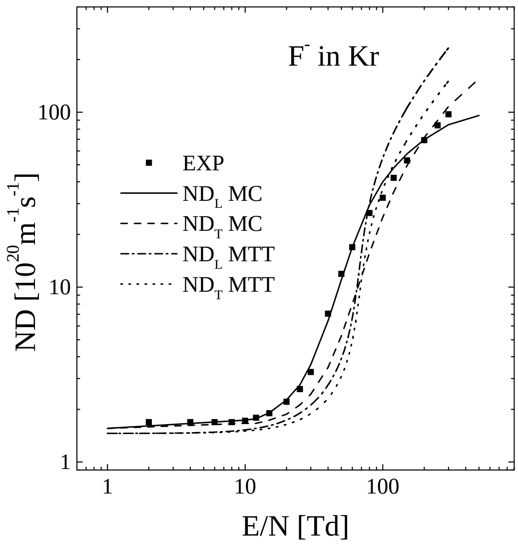

Figure 11. The diffusion coefficients for F^- in Kr at T=300K. Squares are experimental results of Ellis et al. [30].

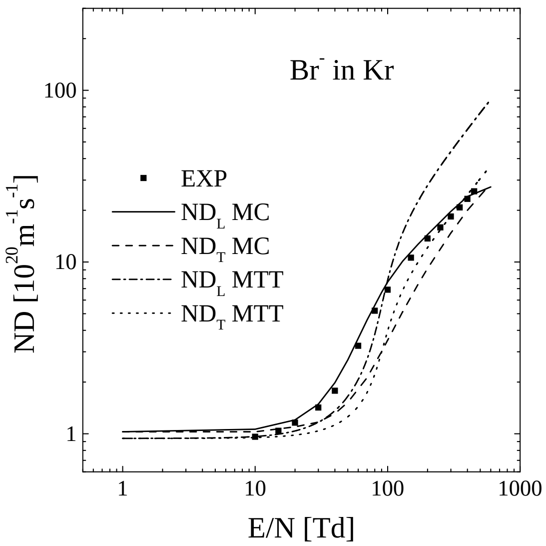

Figure 12. The diffusion coefficients for Br^- in Kr at T=300K. Squares are experimental results of Ellis et al. [30].

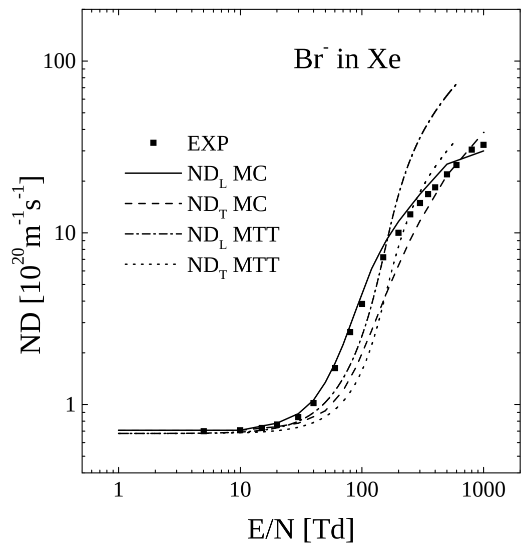

Figure 13. The diffusion coefficients for Br^- in Xe at T=300K. Squares are experimental results of Ellis et al. [30].

by employing a standard swarm technique. The procedure used here to determine the cross sections is to apply first the MTT which is fast albeit with limited accuracy to fit the cross sections until the transport data fit the experimental results. In the next step further, but always slight, adjustments are made to have a good agreement between experimental data and MC calculations which provide exact results. Normally, the disagreement between MTT and MC (and thereby experimental) results was within 13% for all gases.

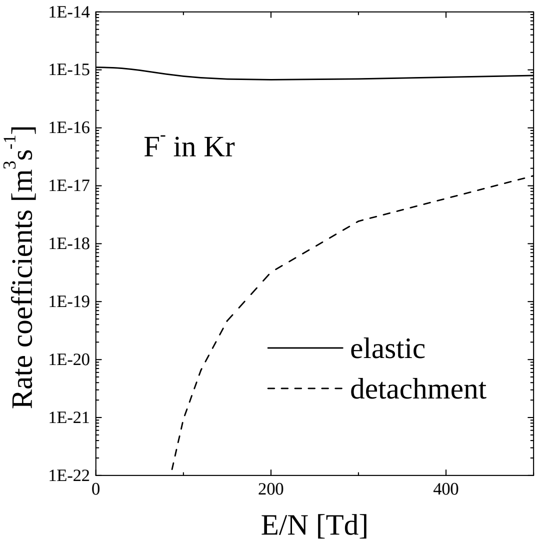

Figure 14. Net rates for elastic scattering and detachment for F^- ions in Kr at T=300K.

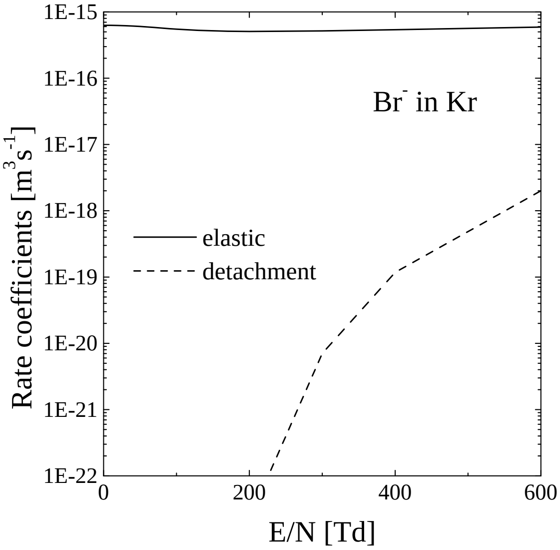

Figure 15. Net rates for elastic scattering and detachment for Br^- ions in Kr at T=300K.

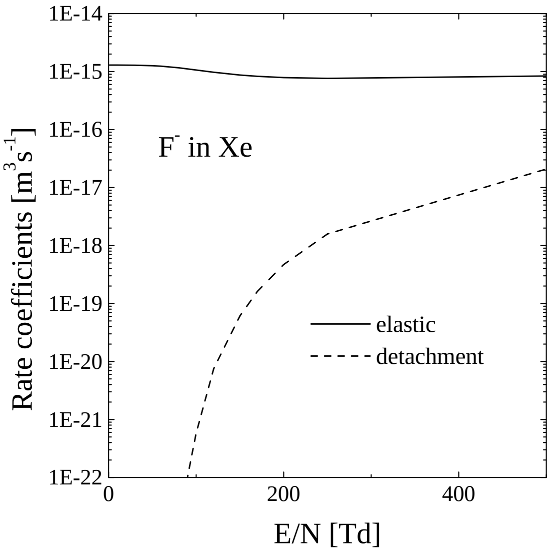

Figure 16. Net rates for elastic scattering and detachment for F^- ions in Xe at T=300K.

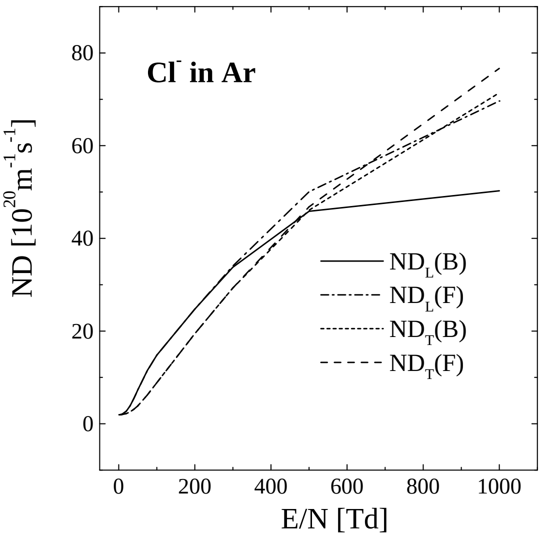

Figure 17. The effect of detachment as non-conservative process on the components of the diffusion tensor of Cl^- ions in Ar. The real space components are denoted by B (bulk) and the velocity space components by F (flux).

The issue of the transport data that may be used in plasma models has been pursued recently [9] as the basis to produce comprehensive plasma models [32]. Fundamental interest in the nature of kinetic phenomena still leads to new insights [33] and in many cases application of inadequate transport data in plasma models may lead to inaccuracies [10] and even failure to represent all relevant physics [34]. In case of negative ions it is important to represent properly the effect of detachment on the transport coefficients as detachment is a nonconservative process.

The cross sections provided here should be employed with the assumption of isotropic scattering and are very accurate in the region covered by the experiments.

5. Acknowledgments

This work has been supported by MNTRS 141025 project and FP6 INCO project 026328.

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