Theoretical Answers to Some Experimental Questions about Gaseous Ion Transport∗

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Abstract

It is shown that the diffusion coefficients parallel to the electric field in an ion swarm experiment are greater than the perpendicular diffusion coefficients at low values of \( \frac{E}{N} \), the ratio of the electric field strength to the gas number density, but that at high \( \frac{E}{N} \) the two are approximately equal or the inequality is reversed. For electron swarms the inequalities are the reverse of those for ion swarms, unless there is a significant Ramsauer minimum in the momentum-transfer cross section. A second point is that for many ion–atom systems the zero-field mobility is not close to its polarisation limit even when the gas temperature is 4.35 K. It is also shown that the unusual mobilities observed for Ar\(^+\) ions in He gas at 4.35 K are not due to quantum-mechanical (resonant scattering) effects as postulated by the experimenters. Finally, it is shown that it is possible to compute gaseous ion transport coefficients for molecular ions from a knowledge of the fundamental interaction potentials rather than from assumed models for the cross sections.

1. Diffusion Coefficients

As the scientific ‘grandson’ of J. Townsend and the scientific ‘son’ of L. G. H. Huxley, Robert W. Crompton was almost predestined to be intimately involved with the changes in our understanding of electron transport through gases that occurred in the early 1970s (Crompton 1972; Crompton and Huxley 1974). It was realised then that the diffusion coefficients parallel (\( D_L \)) and perpendicular (\( D_T \)) to the electric field are different, except in the limit of low values of \( \frac{E}{N} \), the ratio of the electric field strength to the gas number density. The question that arises is what are the relative magnitudes of the two diffusion coefficients. This question has been difficult to answer experimentally because the two diffusion coefficients cannot be measured using the same apparatus or technique.

For electron swarms, the relationship between \( D_L \) and \( D_T \) was established by theoretical means many years ago (Parker and Lowke 1969; Lowke and Parker 1969; Skullerud 1969). Consider first the situation where the collision frequency is increasing with increasing energy. An electron diffusing against the electric field will lose energy, and thus acquire a lower velocity, a lower collision frequency and an increased instantaneous drift velocity, which after some time ... will have reduced the distance which the electron lagged behind the average electron

∗ Dedicated to Professor Robert W. Crompton on the occasion of his seventieth birthday.
position’ (Skullerud 1969). An electron diffusing with the field will gain energy, acquire a higher velocity and collision frequency, a lower instantaneous drift velocity, and will eventually reduce the distance it led the average electron position. No similar effects will occur in perpendicular directions, so ‘the longitudinal spread of a group of electrons will ... be diminished compared with the lateral spread’ (Skullerud 1969). This means that $D_T$ will be greater than $D_L$ when the collision frequency is increasing with energy. Similar arguments show that $D_T$ will be less than $D_L$ when it is decreasing with increasing energy.

Fig. 8-3-5 in McDaniel et al. (1993) is an adaptation of the experimental data of Hunter and Christophorou (1984) that directly compares the ratios of $D_L$ and $D_T$ to the mobility. This figure clearly shows that for electrons in hydrogen $D_T > D_L$ at low values of $E/N$, while the inequality is reversed at high $E/N$. Similar results can be seen by careful examination of the results of Kucukarpaci et al. (1981), Kucukarpaci and Lucas (1981), Wedding et al. (1985), and others. The following seems to be a valid generalisation of the experimental results for electron swarms in situations where there is no significant Ramsauer minimum: $D_T = D_L$ in the limit $E/N = 0$, $D_T > D_L$ at low but non-zero values of $E/N$, and $D_T \approx D_L$ or $D_T < D_L$ at high $E/N$. This generalisation is consistent with what is known about the momentum-transfer collision frequencies for electron–neutral systems and with the theoretical arguments given above for how the energy dependence of the collision frequency produces spatial variations in the ion distribution function.

There is an additional mechanism that comes into play for ion swarms: the average ion energy is no longer isotropic in the lab frame. Equivalently, the ion temperatures parallel and perpendicular to the electric field direction, $T_L$ and $T_T$, differ substantially. Theoretical calculations for atomic ions in atomic neutrals, many of which are accessible by electronic means (Viehland and Kirkpatrick 1995), have shown that $T_T = T_L$ in the limit $E/N = 0$, $T_T < T_L$ at low but non-zero values of $E/N$, and $T_T > T_L$ at high $E/N$. The anisotropy in energy has a much larger effect on ion diffusion than does the spatial variations due to small energy dependences of the collision frequencies. Therefore, for ion swarms, $D_T = D_L$ in the limit $E/N = 0$, $D_T < D_L$ at low but non-zero values of $E/N$, and $D_T \approx D_L$ or $D_T > D_L$ at high $E/N$. Monte Carlo simulations (Tan et al. 1993) also have given this result. Note that these inequalities are exactly the reverse of those for electron swarms.

Experimental verification of the theoretical prediction for ion swarms has been hard to achieve, primarily due to the limited measurements of $D_T$ at high $E/N$. However, verification is available for K$^+$ in Ar (Fig. 5-2-4 of Mason and McDaniel 1988) and for Li$^+$ in Ar at 295 K (using the data compiled by Viehland and Mason 1995). It is also significant that the data for the other alkali ion–rare gas systems show the same qualitative trend, even though they do not extend to high enough $E/N$ to verify the reversal of the inequality. Theoretical and experimental tests of the relationship between $D_T$ and $D_L$ when molecular ions or neutrals are involved remain to be performed.

2. Temperature Dependence of Zero-field Mobilities

Robert Crompton and others (Haddad and Elford 1980; Hegerberg et al. 1980) showed that the temperature dependence of thermal electrons is not as simple as
expected from consideration of asymptotic limits, e.g. that the momentum-transfer collision frequency is constant at low energy. The generality of this idea has not been appreciated by experimenters, some of whom have been ‘surprised’ recently by the fact that the mobilities of some gaseous ions are not close to their polarisation values when $E/N$ is almost zero and the gas temperature is 80 K, or even 4 K.

The general aspects of the temperature dependence of zero-field mobilities are thoroughly covered in Section 6.1.D of Mason and McDaniel (1988), but their choice of dimensionless variables for most of the graphs may have obscured the fact that the polarisation limit is not reached until very low temperature. The zero-field mobilities shown in Fig. 1 were calculated for Li$^+$ ions in He gas at various temperatures from the model potential of Koutselos et al. (1990), using the Gram–Charlier techniques described previously (Viehland 1994). Obviously, the low-field mobility for an ion–neutral system does not approach the polarisation (Langevin) limit until extremely low gas temperatures are reached! Similar results for many other ion–neutral combinations and for other interaction potentials are available upon request from the author (preferably by electronic mail from viehland@ions.slu.edu).

Fig. 1. Standard mobility $K_0$, in cm$^2$ V$^{-1}$ s$^{-1}$, for Li$^+$ ions in helium gas at various temperatures $T$, in K, in the limit of low electric field strengths. The points were calculated in the manner described in the text. The polarisation limit of the mobility (19.17 cm$^2$ V$^{-1}$ s$^{-1}$) is indicated by the horizontal line.
3. Mobility of Ar\(^+\) Ions in He at 4.35 K

Recent experiments at Tokyo Metropolitan University (Kojima et al. 1992; Sanderson et al. 1993, 1994, 1995; Saito et al. 1994) have found unusual mobilities of positive ions in helium gas at 4.35 K. Specifically, for values of \(E/N\) below about 10 Td (1 Td = \(10^{-21}\) V m\(^2\)) the mobilities of open-shell atomic ions and diatomic ions did not approach constant low-field values, much less the polarisation values discussed in Section 2. Instead, the mobilities dropped abruptly with decreasing \(E/N\). Many possible experimental errors were considered and rejected, and an argument was advanced that the unusual behaviour might be caused by quantum-mechanical (resonant scattering) effects. The calculations summarised here and discussed in detail by Viehland and Hurly (1996) test this argument for Ar\(^+\) ions in helium.

When all of the Ar\(^+\) ions are in the \(2P_{3/2}\) ground state, collisions with helium atoms are equally likely to be governed by the X \(2\Sigma_{1/2}^+\) and the A \(2\Pi_{3/2}\) states of the molecular ion. The phrase ‘ground molecular state’ in the remainder of this section will refer to this situation, where the cross sections for these two molecular states are averaged. When a fraction \(x\) of the Ar\(^+\) ions is in the twofold degenerate \(2P_{1/2}\) excited state and a fraction \(1-x\) is in the fourfold degenerate \(2P_{3/2}\) ground state, the weighting is \((1-x)/2\), \((1-x)/2\) and \(x\) for the X \(2\Sigma_{1/2}^+\), A1 \(2\Pi_{3/2}\) and A2 \(2\Pi_{1/2}\) states, respectively. When the energy is sufficiently high that the ions have a statistical distribution, \(x = \frac{1}{3}\) and the weighting is \(\frac{1}{3}\) for each of the three molecular states. The phrase ‘statistical molecular state’ in the remainder of this section will refer to this situation, where the cross sections for all three molecular states are averaged.

In an earlier paper (Viehland et al. 1991), it was shown that the \textit{ab initio} interaction potentials available in 1991 for the HeAr\(^+\) ion are incapable of reproducing the experimental transport data for Ar\(^+\) ions in helium gas. A more accurate set of potential-energy curves for this system then was derived by combining spectroscopic potentials and the accurately known ion-induced dipole potential that describes the interactions at large separations. No new \textit{ab initio} potentials have been reported since 1991. However, Carrington et al. (1995) have recently determined a set of interaction potentials by least-squares fits of seven potential parameters to microwave transition frequencies, ultraviolet spectroscopy data, and \(g\) factors. The new (MALI) interaction potentials are expected to be much better than the previous ones, particularly at the large separations that are most important in swarm experiments at 4.35 K. Consequently, we used them in our calculations.

Using the program described previously (Hurly et al. 1992), we computed the quantum-mechanical phase shifts for each of the three MALI potentials up to angular momentum quantum numbers high enough that they gave an uncertainty in the cross sections of less than one part in a million. The phase shifts were used with the general expressions of Meeks et al. (1994) to obtain the transport cross sections \(Q^{(l)}(E)\) as a function of relative kinetic energy \(E\), for \(1 \leq l \leq 6\). The transport cross sections were also calculated by classical-mechanical techniques, using the program QVALUES (Viehland 1982, 1984).
Fig. 2 compares the classical- and quantum-mechanical values of the momentum-transfer cross section $Q_m = Q^{(1)}(E)$, for the ground molecular state with those for the statistical molecular state. The quantum- and classical-mechanical values are in excellent agreement at $E = 0.001$ hartree (1 hartree = 27.21 eV = 1 a.u.) and above. The complicated structure exhibited by the quantum-mechanical cross sections at low $E$ is a result of orbiting resonances.

Note from Fig. 2 that the cross section for the ground molecular state is substantially larger than that for the statistical molecular state near and just above the thermal energy at 4.35 K. Since in first approximation the mobility at low $E/N$ is inversely proportional to the energy average of $Q_m$, we expect the mobility of ground state Ar$^+$ ions in helium at 4.35 K to be smaller than when the ions are in a mixture of states. Moreover, we expect this difference to be much more evident when the mobilities are calculated from the quantum-mechanical cross sections than from the classical-mechanical cross sections, since the latter are virtually indistinguishable for the two molecular states. Both of these features are shown by our calculations.
Calculating the mobility and other transport coefficients that describe the motion of Ar\(^+\) ions through helium gas from the transport cross sections requires solving the Boltzmann equation. We have used a recent technique (Viehland 1994) that is based on a Gram–Charlier series. The calculations were iterated until convergence was reached to a predetermined level of accuracy, including 0.1\% for the ion mobility. We calculated the transport coefficients at numerous gas temperatures and $E/N$ values. The entire set of calculated transport coefficients is lengthy, so it has been added to the database that can be accessed electronically (Viehland and Kirkpatrick 1995).

Fig. 3. Reduced mobility $K_0$, in cm\(^2\) V\(^{-1}\) s\(^{-1}\), of Ar\(^+\) ions in He gas at 4.35 K, as a function of the reduced field strength $E/N$, in Td. The upper and lower curves (alternately, sets of squares) are the quantum-mechanical (alternately, classical-mechanical) values calculated for the statistical molecular state and the ground molecular state respectively. The triangles with 2\% error bars are the experimental results of Saito et al. (1994).

Fig. 3 compares the classical- and quantum-mechanical mobilities calculated for the ground molecular state and the statistical molecular state with the experimental results (Saito et al. 1994) at 4.35 K and low $E/N$. The agreement above 2 Td is within the 2\% error bars estimated by the experimenters. Unlike the measured values, the classical- and quantum-mechanical values we have calculated do not show a precipitous drop in the mobility as $E/N$ decreases below 2 Td. The lack of a significant quantum-mechanical influence for this
system is consistent with the previous findings (Gatland et al. 1977) for \( \text{Li}^+ \) ions in helium. Whether this is true for the other systems studied at Tokyo Metropolitan University remains to be established.

4. Potential-energy Description of Molecular Ion Transport in Gases

Molecular electron–neutral and ion–neutral systems are often described entirely in terms of cross sections, the implicit assumption being that it is too complicated to try to base things on the more fundamental interaction potentials. This section is a brief description of recent work by Viehland et al. (1996) which reports the first calculations of transport coefficients for diatomic ions in atomic gases based on an \textit{ab initio} interaction potential energy surface.

For a description of the motion of NO\(^+\) ions in He, we must start with knowledge of the ground-state \((v = 0, \text{ or rigid-rotor})\) potential energy surface over wide ranges of the NO\(^+\)-He separation and as a function of the angle between the N–O and NO\(^+\)-He axes. Calculations on the \( \text{Li}^+-\text{N}_2 \) and \( \text{Li}^+-\text{CO} \) systems by Grice et al. (1992, 1993) demonstrated that it was necessary to use at least a MP4SDTQ/6-311+G(2df,p) level of theory to obtain values of structural, thermodynamic and transport properties in close agreement with experiment. This is a higher level of theory than was used in previous studies (Visser and Wormer 1985; Robbe et al. 1993). Therefore, we performed new \textit{ab initio} calculations of the NO\(^+\)-He potential energy surface using the GAUSSIAN 92 program at the MP4SDTQ/6-311+G(2df,p) level. Since our potential energy surface was calculated, a CCSD(T) potential in reasonable agreement with ours has appeared (Pogrebnya et al. 1995).

From the interaction potential energies we calculated, the appropriate transport cross sections must be calculated. Classical trajectory methods (Viehland and Dickinson 1995) have been shown (Liu and Dickinson 1996) to give diffusion and viscosity cross sections for a similar system, \( \text{N}_2\text{-He} \), that are in agreement with quantum calculations within 2\% for total energies above \( 2.3 \times 10^{-4} \) hartree. Therefore, we opted to use classical trajectories to calculate the cross sections we needed. The classical trajectory program we used was based on earlier programs for neutral diatom–atom collisions (Dickinson and Lee 1985) and for atomic ion–diatom collisions (Viehland and Dickinson 1995). It was, however, extensively revised to compute the type of cross section discussed below and to provide for automatic changes in the tolerance parameter governing the accuracy of a trajectory.

The transport cross sections of interest (Viehland and Dickinson 1995) are of two types, one completely real and the other entirely imaginary. They are functions of the pre- and post-collision values of the relative kinetic energy, \( E \) and \( E' \), the pre- and post-collision values of the ion rotational energy, \( E_r \) and \( E'_r \), the impact parameter, the angle between the pre-collision rotational angular momentum of the diatomic ion and the pre-collision orbital angular momentum of the relative motion, and the two angles conjugate to these angular momentum vectors. The relationships between these variables and the ion–atom separation and polar angle were given by Smith (1986) in action-angle variables.

In order to obtain accurate cross sections, we repeatedly calculated the momentum-transfer cross section \( Q_m \), using different numbers of impact parameters, angles, etc. We established at high \( E \) and \( E_r \) that \( Q_m \) is accurate within a few tenths of a percent when we sampled ten impact parameters below 7.0 bohr, three
larger impact parameters, and ten values for each of the three angular variables. At values of the translational energy below 0.001 hartree, we increased both the division point and the number of large impact parameters, to ensure that the contribution of the long-range tail was included. As a check, eleven cross sections were successfully compared with values calculated using the independent atom–molecule code of Dickinson and Lee (1985).

Fig. 4. Momentum-transfer cross section $Q_m$ as a function of the rotational energy $E_r$ in atomic units. The delta symbols indicate the computed values, while the straight lines connecting the symbols are used only as a guide for the eye. From top to bottom, the curves correspond to $E$ values of 0.0001000, 0.0001778, 0.0003162, 0.0005623, 0.0010000, 0.0017780, 0.0031620, 0.0056230 and 0.0100000 hartree.

Fig. 4 shows how $Q_m$ varies with $E_r$ at low values of $E$. The accuracy of $Q_m$ when both $E$ and $E_r$ are low is clearly not very high, indicating that even more trajectories should have been sampled in this situation. However, such inaccuracies should have no importance for the calculations reported below, since the presence of an electric field will cause the average collision energy to increase from a value no lower than the thermal energy at 300 K, $9.5 \times 10^{-4}$ hartree.

Note from Fig. 4 that at $E = 5.623 \times 10^{-4}$ hartree the cross section shows two peaks, one near $E_r = 0.001$ hartree and a second, larger peak near 0.02 hartree. The small peak shifts to smaller $E_r$ and disappears as $E$ decreases, but
the large peak remains near 0.02 hartree for all $E$ values below about 0.0025 hartree. Unusual behaviour at 0.02 hartree is a general feature of all the transport cross sections we have examined.

According to the truncation scheme of Viehland and Dickinson (1995), 179 cross sections are needed to determine the first two approximations to the transport coefficients, but 1056 are needed for the first three. Therefore, we limited our considerations to second approximation. This is equivalent to the second approximation in the kinetic theory of transport of atomic ions in atomic gases; the cross sections we retained correspond to retaining only the $Q^{(1)}(E)$ and $Q^{(2)}(E)$ cross sections of that theory.

To calculate the transport coefficients from the cross sections we solved a hierarchy of kinetic equations (Viehland and Dickinson 1995) by a three-dimensional method of weighted residuals (Finlayson 1972; Robson et al. 1991) in which the zero-order distribution function is the bi-Maxwellian distribution. A fraction $g$ of the ions is characterised by a lower kinetic temperature $T_1$, and the remainder by a higher kinetic temperature $T_2$. This method of weighted residuals converges rapidly when $T_1$ is approximately the temperature that characterises the average energy of the ion-neutral interactions under the conditions of the experiment, and when the values of $g$ and $T_2$ are empirically adjusted to overcome the effects of partial ion runaway.

The trial and weighting functions we used are modeled after the basis functions of Curtiss (1981), but they were modified in the manner of Kumar (1980a, 1980b) so as to allow the ions to have kinetic and internal temperatures different from the gas temperature, and in the manner of Ness and Viehland (1990) to take into account the use of two ion kinetic temperatures. An important point about these basis functions is that they are complex, not real quantities, so the expansion of the ion velocity distribution function in terms of them must provide for the possibility of both real and imaginary expansion coefficients, in order to end up calculating real quantities from the real and imaginary cross sections. Further details in how a truncated set of the expansion coefficients (and hence approximations to the transport coefficients and the ion distribution function) can be computed from the cross sections by matrix methods are given by Viehland and Dickinson (1995).

Table 1 contains the reduced mobilities for NO$^+$ ions in helium gas at 300 K that we have calculated as a function of $E/N$ below 20 Td. The calculations with $g = 1.00$ correspond to the use of a two-temperature approach to the solution of the Boltzmann equation (Viehland and Mason 1975, 1978), except that here it is used for diatomic rather than atomic ions. Therefore, columns A1 and B1 should be the same, as should columns A2 and B2. They are, except for small disagreements that result from round-off and other numerical artifacts.

Columns A1 (or B1) and D1 in Table 1 agree within 0.1%, which exceeds the accuracy expected for the cross sections used in the computations. Similar agreement is found between columns A2 (or B2) and D2. These values are therefore viewed as the ‘correct’ values obtained in the first and second approximations. However, the C mobilities are significantly different, both in first and second approximations. Why? The answer lies in the fact that the ion temperature $T_1$ corresponding to the largest $E/N$ value in Table 1 is 1600 K, corresponding to an energy of 0.0050 hartree. Therefore, the unusual behaviour of the cross
Table 1. Reduced mobilities $K_0$ in cm$^2$ V$^{-1}$ s$^{-1}$, calculated as a function of the ratio $E/N$, in Td, of the electric field strength to the gas number density.

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<th>A2</th>
<th>B1</th>
<th>B2</th>
<th>C1</th>
<th>C2</th>
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Fig. 5. Reduced mobility $K_0$ in cm$^2$ V$^{-1}$ s$^{-1}$, as a function of the ratio $E/N$, in Td, of the electric field strength to the gas number density. The squares surrounded by error bars are the smoothed experimental values with the 7% accuracy estimated by Ellis et al. (1976). The triangles are the present results in first approximation. The circles and small dots are the present results in second approximation using $T_2$ equal to 5 $T_1$ and 1.5 $T_1$, respectively.
sections for energies near 0.02 hartree, is probed by having a small fraction of
the ions at 5 \( T_1 \) but not when they are at only 1.5 \( T_1 \). The C calculations place
too much emphasis on energies above those relevant for mobilities below 20 Td,
and hence the C mobilities are not further considered in this work.

Fig. 5 shows a comparison of the calculated and measured mobilities. The
agreement is very good, although the error estimates for the experimental values
are large since these data were obtained (Lindinger and Albritton 1975) incidental
to the measurement of ion–molecule reaction rate coefficients. Note that the
first-approximation mobilities appear to be heading toward values at higher \( E/N \)
that lie below the experimental values and outside their error bars, but that no
similar tendency is shown by the second-approximation mobilities. However, the
difference between the first and second approximations becomes larger as \( E/N \)
increases, indicating that above 20 Td we need to calculate third-approximation
mobilities in order to achieve values converged within about 1%. Such calculations
are not possible with the cross sections that we have computed.

The calculations summarized here were the first in which gaseous ion transport
coefficients were calculated for diatomic ions moving through atomic gases from
an \textit{ab initio} interaction potential that depends both upon the ion–atom separation
and polar angle. The calculations were computationally intensive, particularly the
classical-trajectory calculations of the transport cross sections from the interaction
potential. For this reason, and because the experimental mobilities have rather
large uncertainties, we stopped at the second approximation of the kinetic theory.
The calculated mobilities converged at \( E/N \) values up to 28 Td, while the other
transport properties converged up to 8 Td. The good agreement shown in Fig. 5
between the calculated and measured mobilities below 20 Td indicates that the
\( \text{NO}^+–\text{He} \) interaction potential we calculated is at least moderately accurate in
the region probed by these data, i.e. for all polar angles but only for separations
ranging from approximately 2.5 to 3.5 Å.

\textbf{References}


Data Nucl. Data Tables} \textbf{17}, 177.


Gatland, I. R., Morrison, W. F., Ellis, H. W., Thackston, M. G., McDaniel, E. W., Alexander,


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