The Effect of Inelastic Collisions on Diffusion Coefficients for Electron Swarms

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Abstract

The effect of inelastic collisions on the ratio of the longitudinal to lateral diffusion coefficients for electrons in electrostatic fields in gases is investigated for several different momentum transfer cross sections. The effect of varying both the strength of the inelastic effects and their energy dependence is examined and the results are used to discuss some of the D_L/μ data of Wagner *et al.* (1967).

Introduction

The calculation of anisotropic diffusion coefficients from the Parker–Francey solutions of the Boltzmann equation for the case of an elastic collision cross section has already been described in detail in two previous papers (Francey and Jones 1975, 1976; hereinafter referred to as Papers I and II). In the present paper we continue this work to include some inelastic collisions and investigate their effect on the ratio of the longitudinal to lateral diffusion coefficients D_L/D_T. The work is, to some extent, an extention of that of Francey and Stewart (1971), who investigated the effect of inelastic collisions on the mean energy and isotropic diffusion coefficient for a constant cross-section gas.

We consider a model which has a cross section for momentum transfer of the form

$$Q(\varepsilon) = Q_0(\varepsilon/\varepsilon_0)^{\frac{1}{2}l}$$

and which makes a series of weakly inelastic collisions with the background gas molecules. Each inelastic level within the molecule is labelled with the index h and has an excitation cross section Q_h which varies with energy as

$$Q_h(\varepsilon) = Q_{0h}(\varepsilon/\varepsilon_{0h})^s.$$

The equation we use is

$$\frac{\varepsilon}{3NQ}\nabla^2 f_0 + \frac{eE}{3}\frac{\partial}{\partial Z}\left\{\frac{\varepsilon}{NQ}\frac{\partial f_0}{\partial \varepsilon} + \frac{\partial}{\partial \varepsilon}\left(\frac{\varepsilon f_0}{NQ}\right)\right\} + \frac{(eE)^2}{3}\frac{\partial}{\partial \varepsilon}\left(\frac{\varepsilon}{NQ}\frac{\partial f_0}{\partial \varepsilon}\right) + \frac{2m}{M}\frac{\partial}{\partial \varepsilon}\left(\varepsilon^2 NQ f_0\right)$$

$$+ \sum_h \{(\varepsilon+\varepsilon_h) f_0(\varepsilon+\varepsilon_h) NQ_h(\varepsilon+\varepsilon_h) - \varepsilon f_0(\varepsilon) NQ_h(\varepsilon)\} = -(\tfrac{1}{2}m\varepsilon)^{\frac{1}{2}}S, \qquad (1)$$

which is the same as equation (5) in Paper II, except for the last term on the left-hand side, which accounts for the inelastic collisions. This equation describes a steady state electron stream which originates from a point source at the origin $\rho = 0, Z = 0$ of an axially symmetric cylindrical coordinate system and then drifts and diffuses

through the gas under the action of a uniform electrostatic field E which is directed along the axis of the cylinder; f_0 is the spherically symmetric part of the electron distribution function, ε the electron energy, m and M the mass of an electron and gas molecule respectively, N the gas number density and S the electron source term.

In the papers of Frost and Phelps (1962) and Hake and Phelps (1967) there is a further inelastic term of the form

$$\sum_h \{(\varepsilon - \varepsilon_h) f_0(\varepsilon - \varepsilon_h) NQ_{-h}(\varepsilon - \varepsilon_h) - \varepsilon f_0(\varepsilon) NQ_{-h}(\varepsilon)\}.$$

This accounts for collisions of the second kind, or superelastic collisions, which are collisions in which thermally excited molecules impart excitation energy to the electron. However, as we will be working in the large E/N limit, where the thermal motion of the gas molecules is negligible, this additional term will not be necessary.

To solve equation (1) we have to put the inelastic term into a more manageable form, and to do this we follow the method used by Francey and Stewart (1971). This essentially consists of noting that the inelastic part of the equation can be written as

$$N \sum_h \{\psi_h(\varepsilon + \varepsilon_h) - \psi_h(\varepsilon)\},$$

where $\psi_h(\varepsilon) = \varepsilon f_0(\varepsilon) Q_h(\varepsilon)$. The assumption that the collisions are weakly inelastic means that the energy lost by an electron in exciting an inelastic level in the molecule is very much less than the electron energy at that time, that is, $\varepsilon_h \ll \varepsilon$, and this allows us to expand $\psi_h(\varepsilon + \varepsilon_h)$ in a Taylor series about ε. The inelastic term then becomes

$$N \sum_h \varepsilon_h \cdot \partial \psi_h / \partial \varepsilon.$$

This type of approximation is very similar to the continuous approximation of Frost and Phelps (1962) for rotational excitation. If we were trying to model a particular real gas we would need to separate the various inelastic processes, i.e. rotational, vibrational, electronic etc., and assign different energy dependences for each. However, as this is only a model calculation we will simply use one energy dependence for all the inelastic levels. In terms of dimensionless variables x, y and z, defined by

$$x = B\varepsilon, \qquad y = eEBZ, \qquad z = eEB\rho,$$

with

$$B^{l+2} = \frac{1}{l+2} \frac{6m}{M} \left(\frac{NQ_0}{eE}\right)^2 \frac{1}{\varepsilon_0\, l},$$

the equation we wish to solve becomes

$$\nabla^2 f_0 + \frac{2 \,\partial^2 f_0}{\partial x \,\partial y} + \frac{2-l}{2} \frac{1}{x} \frac{\partial f_0}{\partial y} + \frac{\partial^2 f_0}{\partial x^2}$$

$$+ \left(\frac{2-l}{2} \frac{1}{x} + (l+2)x^{l+1} + (l+2)bx^{\frac{1}{2}(2s+l)}\right) \frac{\partial f_0}{\partial x}$$

$$+ \{\tfrac{1}{2}(l+2)(l+4)x^l + (l+2)b(s+1)x^{\frac{1}{2}(2s+l-2)}\} f_0$$

$$= -(l+2)x^{\frac{1}{2}l}\left(\frac{B}{2mx}\right)^{\frac{1}{2}} \frac{M}{NQ_0} \frac{x_0^{\frac{1}{2}l}}{2} S, \qquad (2)$$

where the inelastic parameter b is given by

$$b = \frac{M}{2m} \sum_h \frac{x_h}{x_{0h}^s} \frac{Q_{0h}}{Q_0}.$$

Solution of Boltzmann Equation and Formula for D_L

The Parker–Francey technique for the solution of the Boltzmann equation has already been described in detail elsewhere (Parker 1963; Francey 1969; Papers I and II). As the solution of equation (2) follows this method very closely there is no point in repeating it here, and so we simply state the result, which is

$$f_0(\varepsilon, Z, \rho) = \frac{C}{4\pi DZ} \exp\{-T(\varepsilon)\} \left(1 - \frac{\varepsilon}{eEZ}\right)^{-1} \exp\left\{-\frac{W\rho^2}{4DZ}\left(1 - \frac{\varepsilon}{eEZ}\right)^{-1}\right\}$$

$$\times \left(1 + \frac{g_1(B\varepsilon)}{eEB\beta_0^{(1)} Z} + \ldots\right). \tag{3}$$

In this equation D and W are the (isotropic) diffusion coefficient and drift velocity respectively and C is the normalization constant for the energy distribution function $\exp\{-T(B\varepsilon)\}$; g_1 is related to the lowest eigenfunction of the energy eigenvalue equation and $\beta_0^{(1)}$ to the lowest eigenvalue. Equation (3) is essentially the same as the corresponding expression for the elastic case (equation (17) of Paper II), except that the leading exponential is now $\exp\{-T(x)\}$, where

$$T(x) = x^{l+2} + \{2(l+2)b/(2s+l+2)\}x^{\frac{1}{2}(2s+l+2)},$$

instead of $\exp(-x^{l+2})$.

The energy eigenvalue equation results from a separation of variables in equation (2) and has the form

$$\frac{d^2A}{dx^2} + \left(\frac{2-l}{2}\frac{1}{x} + (l+2)x^{l+1} + (l+2)bx^{\frac{1}{2}(2s+l)}\right)\frac{dA}{dx}$$

$$+ \{\tfrac{1}{2}(l+2)(l+4)x^l + (l+2)b(s+1)x^{\frac{1}{2}(2s+l-2)}\}A - K^2A$$

$$+ \{(l+2)x^{l+1} + (l+2)bx^{\frac{1}{2}(2s+l)}\}\beta A = 0. \tag{4}$$

Here K is a separation constant from a zero-order Bessel equation and $A(x, K^2)$ and $\beta(K^2)$ are the eigenfunction and eigenvalue of equation (4). The dependences of the lowest eigenfunction A_0 and eigenvalue β_0 on K are assumed to have the forms

$$A_0(x, K^2) = C_0 \exp\{-T(x)\}\{1 + K^2A_0^{(1)}(x) + O(K^4)\},$$

$$\beta_0(K^2) = \beta_0^{(0)} + K^2\beta_0^{(1)} + O(K^4).$$

The lowest eigenvalue β_0 is found by writing equation (4) as

$$\beta_0^{(0)} = 0, \qquad \beta_0^{(1)} = I^{(1)}/I^{(0)},$$

where

$$I^{(0)} = \int_0^\infty (l+2)\exp\{-T(x)\}(x^{\frac{1}{2}(l+4)}+bx^{s+1})\,dx,$$

$$I^{(1)} = \int_0^\infty x^{\frac{1}{2}(2-l)}\exp\{-T(x)\}\,dx.$$

The quantity $g_1(x)$ is related to the lowest eigenvalue $A_0(x, K^2)$ by

$$g_1(x) = A_0^{(1)}(x) + A_0^{(1)}(0) + \text{const.}$$

When only elastic collisions are considered, equation (4) is considerably easier to handle, as the terms containing the inelastic parameter b are absent. The equation can then be solved analytically by expanding in associated Laguerre polynomials, and this was the method employed in Paper II. The addition of the inelastic terms makes the equation far too difficult for analytic solution though, and it must now be solved numerically.

The calculation of the longitudinal diffusion coefficient D_L from equation (3) is straightforward and follows the method outlined in Paper II. The longitudinal flux Γ_L is calculated from equation (3) using

$$\Gamma_L = -\frac{8\pi}{3(mB)^2}\frac{1}{N}\int_0^\infty \frac{x}{Q}\left(\frac{\partial f_0}{\partial y}+eEB\frac{\partial f_0}{\partial x}\right)dx$$

and the number density N from

$$N = \frac{4\pi}{m}\left(\frac{2}{m}\right)^{\frac{1}{2}}\int_0^\infty \varepsilon^{\frac{1}{2}}f_0(\varepsilon, Z, \rho)\,d\varepsilon.$$

We then require that

$$\Gamma_L \equiv WN - D_L\,\partial N/\partial Z.$$

By equating coefficients of powers of Z on both sides of the resulting equation we can find expressions for both W and D_L. The result is that W remains unchanged, while D_L becomes

$$\frac{D_L}{D_T} = \frac{4-l}{2} - \frac{I^{(0)}\,I^{(3/2)}}{I^{(1)}\,I^{(1/2)}} + \frac{I^{(0)}}{I^{(1)}}\left(\frac{2-l}{2}\frac{M^{(1)}}{I^{(1)}} - \frac{I^{(0)}}{I^{(1)}}\frac{H^{(1)}}{I^{(1/2)}}\right), \tag{5}$$

where

$$M^{(1)} = \int_0^\infty x^{-\frac{1}{2}l}g_1\exp(-T)\,dx, \qquad H^{(1)} = \int_0^\infty x^{\frac{1}{2}}g_1\exp(-T)\,dx,$$

$$I^{(\sigma/2)} = \int_0^\infty x^{\sigma/2}\exp(-T)\,dx, \qquad\qquad \sigma = 1, 3,$$

and D_T is the lateral diffusion coefficient which is equal to the isotropic diffusion coefficient D.

The expression (5) for D_L/D_T involves integration over the g_1 function, and this in turn requires the solution of equation (4). To do this we define a new function $u(x, K^2)$ by
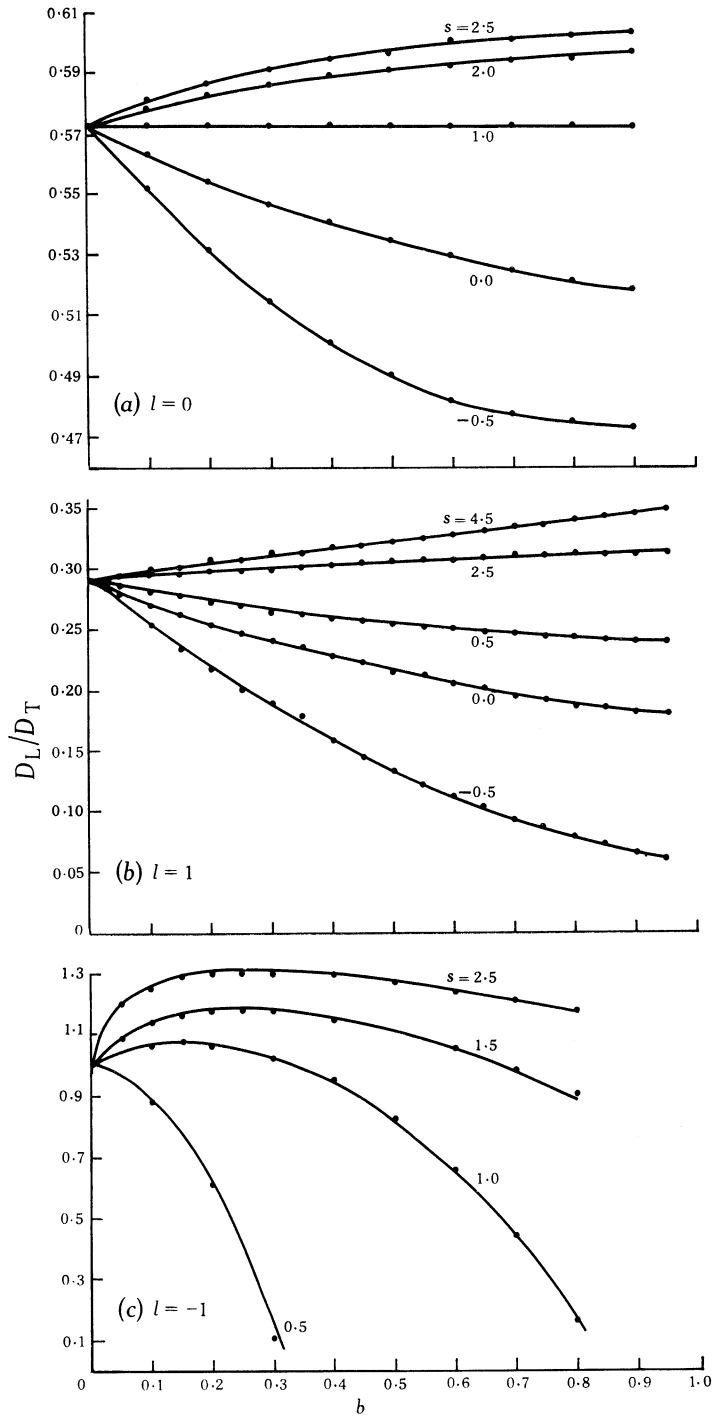
$$A(x, K^2) = \exp\{-T(x)\}\,u(x, K^2).$$

Fig. 1. Variation of the ratio D_L/D_T as a function of the inelastic parameter b for the indicated values of s and (a) $l = 0$, (b) $l = 1$ and (c) $l = -1$.

and the equation for $u(x, K^2)$ is then

$$\frac{d^2u}{dx^2} + \left(\frac{2-l}{2}\frac{1}{x} - (l+2)x^{l+1} - (l+2)bx^{\frac{1}{2}(2s+l)}\right)\frac{du}{dx}$$
$$- K^2u + \{(l+2)x^{l+1} + (l+2)bx^{\frac{1}{2}(2s+l)}\}\beta u = 0. \qquad (6)$$

If we now write

$$u(x, K^2) = C_0\{1 + K^2h(x) + O(K^4)\}, \qquad \beta(K^2) = \beta_0^{(1)}K^2 + O(K^4),$$

and substitute into equation (6) then, neglecting terms of order K^4 or higher, the equation for $h(x)$ is

$$\frac{d^2h}{dx^2} + \left(\frac{2-l}{2}\frac{1}{x} - (l+2)x^{l+1} - (l+2)bx^{\frac{1}{2}(2s+l+2)}\right)\frac{dh}{dx}$$
$$= 1 - (l+2)(x^{l+1} + bx^{\frac{1}{2}(2s+l)})\beta_0^{(1)} \qquad (7)$$

and g_1 is simply given by $g_1(x) = h(x)$.

Equation (7) was solved numerically using a Runge–Kutta program and the values of D_L/D_T were constructed by numerical integration from the resulting solutions using equation (5). The results are described in the next section.

Results

We looked at the constant cross-section model ($l=1$) first. Equation (7) was solved numerically for s values ranging from $-0·5$ to $2·5$ in steps of $0·5$, and for values of b ranging from $0·00$ to $0·90$ in steps of $0·05$. The results are summarized in Fig. 1a.

The first point to note is that when $b = 0·00$, i.e. inelastic effects discarded, the program gives a value of $0·573$ for D_L/D_T. This is in excellent agreement with the value of $0·574$ that we found earlier by expanding $g_1(x)$ in Laguerre polynomials.

For $s = -0·5$ the value of D_L/D_T decreases from $0·573$ to $0·471$ as b increases from $0·00$ to $0·90$. For $s = 0$, D_L/D_T still decreases with increasing b but less quickly, i.e. from $0·573$ to only $0·516$. The same behaviour is observed again for $s = 0·5$, still decreasing with increasing b but only very slowly. For $s = 1·0$, the value of D_L/D_T remains *constant* at $0·573$ whatever the value of b, and then, for $s = 1·5$, $2·0$ and $2·5$, D_L/D_T begins to *increase* with increasing b, the larger the value of s the quicker the increase.

Similar results to the above are found for the $l = 1$ model (see Fig. 1b). For small s values D_L/D_T is below its elastic value and decreases very strongly with an increase in the strength of the inelastic collisions. At larger s values this decrease is less substantial until finally there is a value of s for which D_L/D_T remains equal to its elastic value even though quite strong inelastic effects may be present. For s values larger than this, D_L/D_T increases only very slowly above its elastic value for any increase in b.

An interesting case to consider is the constant collision frequency model ($l = -1$). When inelastic collisions are absent this is the only interaction which continues to have an isotropic diffusion coefficient even in arbitrarily large electrostatic fields. However, the addition of even a small number of inelastic collisions destroys this isotropy, as our results in Fig. 1c show.

A surprising feature of the $l = -1$ results, which has not been present in the previous data, is the appearance of a maximum in the D_L/D_T values as a function of b. For s values larger than about $1 \cdot 0$, D_L/D_T first increases above its isotropic value of $1 \cdot 0$ to some maximum value dependent on s, and then decreases once more with a further increase in b until it is again below the isotropic value. The constant collision frequency model appears to be the only case where this effect occurs.

We would now like to apply these results to some real gases, in particular to explain some of the D_L/μ data of Wagner *et al.* (1967), and this is discussed in the next section.

Application to Real Gases

Even though the present results are only applicable to model gases with very simple inelastic energy dependences it is still interesting to try and use them to explain some of the D_L/μ data of Wagner *et al.* (1967). Hydrogen is a particularly good gas to consider first, as its elastic cross section is almost independent of energy. We can illustrate this behaviour quite clearly by examining the E/P dependence of W and D_T/μ.

When inelastic collisions are present W and D_T are given by

$$W = \frac{8\pi e E}{3m^2 N} \frac{x_0^{\frac{1}{2}l}}{B} \frac{C}{Q_0} I^{(0)}, \qquad D_T = \frac{8\pi}{3m^2 N} \frac{C}{B^2} \frac{x_0^{\frac{1}{2}l}}{Q_0} I^{(1)}, \qquad (8a, b)$$

where

$$C = (B^{3/2}/I^{(1/2)})(m/4\pi)(\tfrac{1}{2}m)^{\frac{1}{2}},$$

and provided the inelastic contributions to these expressions remain constant (that is, $I^{(0)}$, $I^{(1)}$ etc.) then their E/P dependences are

$$W \propto (E/P)^{1/(l+2)} \qquad \text{and} \qquad D_T/\mu \propto (E/P)^{2/(l+2)}.$$

So for a constant cross section gas ($l = 0$) we expect to find W proportional to $(E/P)^{\frac{1}{2}}$ and D_T/μ directly proportional to E/P, and this is indeed the behaviour displayed by hydrogen. Fig. 2 shows the drift velocity data of Lowke (1963) plotted as a function of $(E/P)^{\frac{1}{2}}$, while Fig. 3 shows the D_T/μ data of Crompton *et al.* (1967). Both these graphs demonstrate the type of E/P dependence we would expect from a constant cross-section gas.

Fig. 3 also shows the D_L/μ results of Wagner *et al.* (1967). When there are no inelastic collisions present we expect the D_L/D_T ratio to be $0 \cdot 57$; however, in Fig. 3, between the E/P values of $0 \cdot 5$ and $1 \cdot 2$ V cm^{-1} mmHg^{-1} (1 mmHg $\approx$ 133 Pa), this ratio has the constant value $0 \cdot 48$. Above $1 \cdot 2$ the D_T/μ graph begins to deviate from straight-line behaviour and our model becomes inadequate, whereas below $0 \cdot 5$ we start to move into the area of thermal equilibrium where our theory is no longer applicable.

From Fig. 1a we can see that a D_L/D_T value of $0 \cdot 48$ implies $s = -0 \cdot 5$, with b lying somewhere between $0 \cdot 60$ and $0 \cdot 80$. To find the correct value of b we can fit our theoretical expression for the drift velocity (equation 8a) to the experimental results in Fig. 2. If we express E/P in units of V cm^{-1} mmHg^{-1}, W in cm s^{-1} and take M to be the mass of a hydrogen molecule, then equation (8a) becomes

$$10^{-5} W = 18 \cdot 5 \, Q_0^{-\frac{1}{2}} (I^{(0)}/I^{(1/2)})(E/P)^{\frac{1}{2}}. \qquad (9)$$

By using the experimental value of the gradient in Fig. 2 and the numerical values of $I^{(0)}$ and $I^{(1/2)}$ appropriate to $s = -0.5$ and $b = 0.70$ we can use equation (9) to find $Q_0 = 15.2\,\text{Å}^2$. We can check the consistency of these values by calculating the gradient of the D_T/μ graph in Fig. 3. From the equations (8) this is

$$D_\text{T}/\mu = 10.8\,Q_0^{-1}\,(I^{(1)}/I^{(0)})\,(E/P) + 0.025,$$

which gives a gradient of $0.21\,\text{cm mmHg}$. The experimental result is $0.22\,\text{cm mmHg}$. The good agreement here suggests that we can describe the system phenomenologically with a cross section of $15.2\,\text{Å}^2$ and inelastic parameters of $s = -0.5$ and $b = 0.70$.
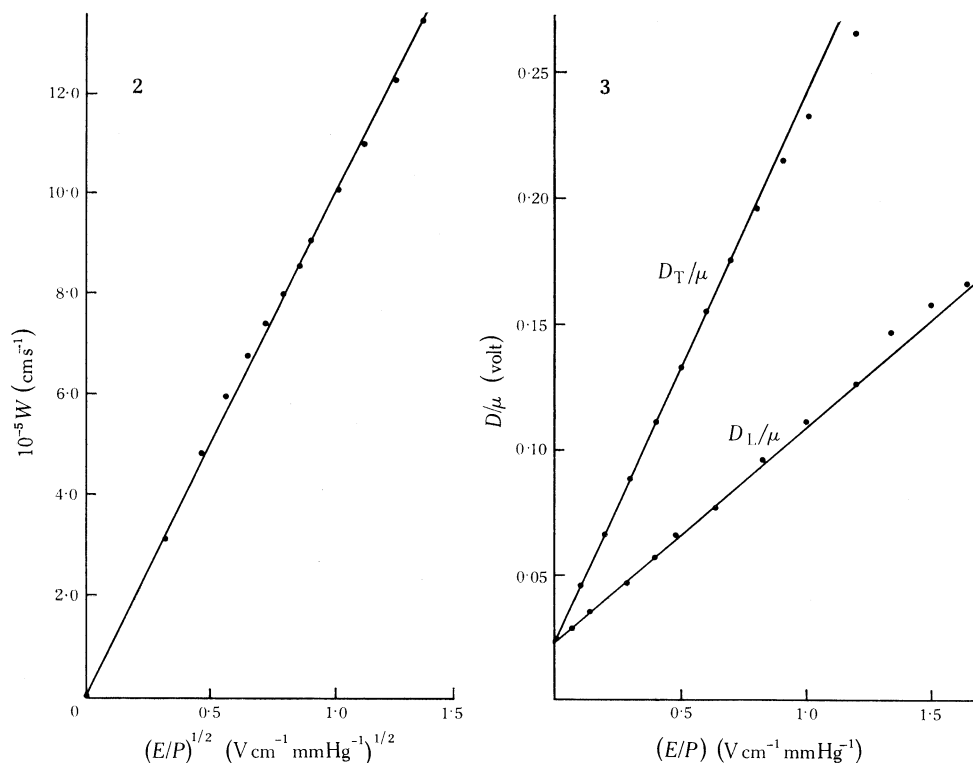

Fig. 2 (*left*). Drift velocity W versus $(E/P)^{\frac{1}{2}}$ for hydrogen. The experimental data are from Lowke (1963).

Fig. 3 (*right*). Experimental values of D_T/μ and D_L/μ versus E/P for hydrogen. The D_T/μ data are from Crompton *et al.* (1967) and the D_L/μ data from Wagner *et al.* (1967).

We can make a further test of this approach by comparing calculated and experimental data for DP versus E/P. From equation (8b) we find

$$DP = 4.34 \times 10^3\,(E/P)^{\frac{1}{2}}\,(I^{(1)}/I^{(1/2)}) \quad \text{kg m s}^{-3}$$

and, using the appropriate values of $I^{(1)}$ and $I^{(1/2)}$, this becomes

$$10^{-3}\,DP = 2.66\,(E/P)^{\frac{1}{2}} \quad \text{kg m s}^{-3}. \tag{10}$$

Fig. 4 shows the experimental DP data, calculated from

$$DP = (D/\mu) \times W \times (E/P)^{-1},$$

plotted against $(E/P)^{\frac{1}{2}}$. From equation (10) we would expect a straight line with gradient $2 \cdot 66$ but this is obviously not the case. The poor agreement here is due to the fact that the experimental DP values increase much less quickly than the expected $(E/P)^{\frac{1}{2}}$; in fact the data appear to increase roughly as $(E/P)^{\frac{1}{4}}$ instead. This departure of the DP data from constant cross-section behaviour is probably caused by the inelastic effects, but why they should produce a change in the E/P dependence here and not in the W or D/μ data is still not clear.
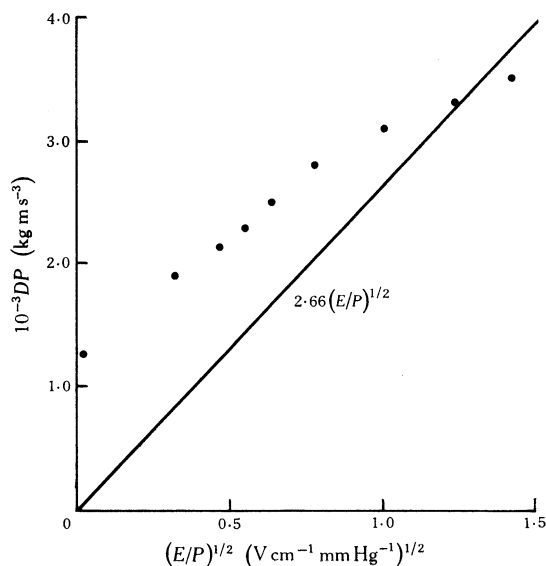

Fig. 4. Variation of the product DP versus $(E/P)^{\frac{1}{2}}$ for hydrogen. The points derived from the experimental data of Lowke (1963) and Crompton *et al.* (1967) are clearly not compatible with a straight line of gradient $2 \cdot 66$.

Discussion

There are several conditions which need to be met if the type of approach outlined in the previous section is to be successful. In the first place the cross section for momentum transfer Q must be a smoothly varying function of energy ε which is capable of expression in the form $Q = Q_0(\varepsilon/\varepsilon_0)^{\frac{1}{2}l}$. The easiest way to check for this type of behaviour is to use the drift velocity versus E/P data. If Q is proportional to $\varepsilon^{\frac{1}{2}l}$ then a log–log plot of W versus E/P should yield a straight line with a gradient of $(l+2)^{-1}$ (provided that the effect of the inelastic collisions remains constant). However, if we analyse the data for each of the gases used by Wagner *et al.* (1967) we find that, except for helium, argon and hydrogen, the only gases which display this behaviour are carbon monoxide, which corresponds to $l = 1$, and carbon dioxide, with $l = -1$.

A second condition is that the inelastic effects, expressed through the two parameters s and b, must remain constant over the E/P range of interest, and this is only partly true of carbon monoxide. Fig. 5 shows a graph of W versus $(E/P)^{1/3}$ for this gas. In the E/P range from $1 \cdot 0$ to $4 \cdot 0 \, \text{V cm}^{-1} \, \text{mmHg}^{-1}$, W is directly proportional to $(E/P)^{1/3}$ and since the gradient is constant so the values of s and b should also be

constant. According to our model then, we expect D_L/D_T not to vary within this range. But this is not the case, as Fig. 6a shows that D_L/D_T decreases uniformly from 0·474 to 0·338 in this E/P range.
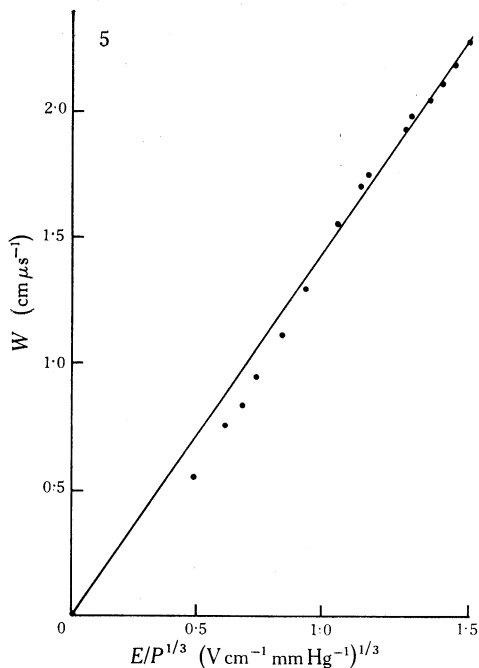

Fig. 5. Drift velocity W versus $(E/P)^{1/3}$ for carbon monoxide. The experimental data are from Wagner *et al.* (1967).
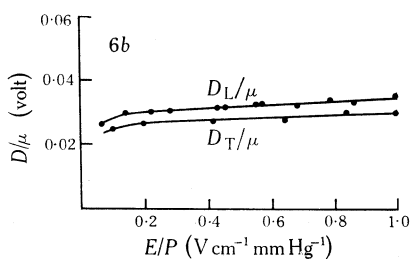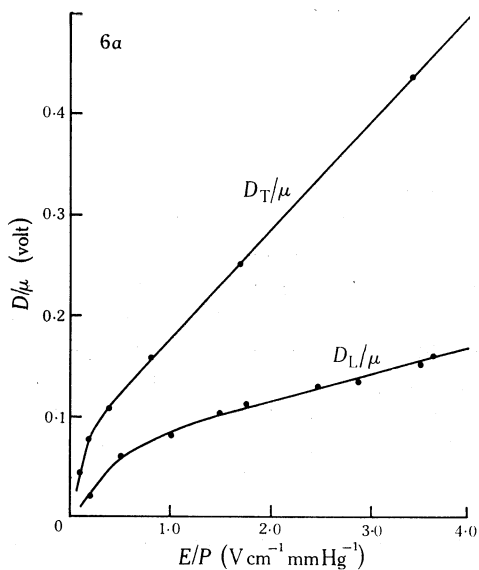

Fig. 6. Plots of D_T/μ and D_L/μ versus E/P for (*a*) carbon monoxide, and (*b*) carbon dioxide. The values for D_T/μ in (*a*) are from Skinker and White (1923; quoted after Wagner *et al.* 1967) and the remaining data are from from Wagner *et al.*

A further restriction is that we must always work in the large E/P limit because of our neglect of the term accounting for the background gas temperature in the original equation. This was necessary because the equation could not be separated with this additional term present, but it does prevent us from applying our results to gases

whose characteristic energies are only fractionally greater than the thermal equilibrium value of kT/e, or $0\cdot025$ V at room temperature. A particular case of this is carbon dioxide, as shown by the D/μ data of Wagner *et al.* (1967) in Fig. 6*b*.

Conclusions

We have shown that the addition of inelastic collisions can either add to or subtract from the anisotropy, depending on the particular energy dependence of the inelastic cross section. Perhaps the most interesting result we have found is that for some elastic cross sections there are particular variations of inelastic cross section with energy which do not alter the value of D_L/D_T even when their strength is increased so that they become comparable with the elastic cross section. Surprisingly though, the constant collision frequency model does not appear to be one of these cases.

Acknowledgments

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