Electron-velocity distribution functions in gases: The influence of anisotropic scattering and electron nonconservation by attachment and ionization

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Electron-velocity distribution functions have been calculated for electrons moving in a gas under the influence of an electric field. By assuming a differential scattering cross section such that scattering is entirely at 0° and 180°, it is shown analytically that the electron drift velocity w, the mean electron energy $\langle\epsilon\rangle$, the transverse diffusion coefficient D_T, and the longitudinal diffusion coefficient D_L are not, in general, determined by the momentum-transfer cross section alone. The magnitude of the errors incurred by neglecting the higher-order terms in the spherical-harmonic expansion of the velocity distribution function for this collision model are indicated. Velocity distribution functions have also been calculated for attaching gases. It is found that the velocity distribution function can be considerably altered by attachment for pure gases and gas mixtures. Consequently, any attempt to determine collision cross sections from electron-swarm measurements of w, D_T, and D_L in attaching gases should include attachment processes in the solution of the Boltzmann equation. The magnitude of this dependence has been found to be determined largely by the ratio of the attachment collision frequency to the energy-transfer collision frequency and the velocity dependences of the momentum transfer and attaching collision frequencies.

I. INTRODUCTION

Electron transport and rate coefficients measured in swarm experiments are related to the microscopic collision processes occurring in the gas by the Boltzmann equation.[1] The solution of this equation, which involves determining the velocity distribution function $f(\mathbf{r},\mathbf{v},t)$ has been the subject of numerous investigations in recent years.[2] Approximations are required in order to simplify and thus to solve this six-dimensional time-dependent partial differential equation. Most solutions are based on the assumption that the electron swarm has reached equilibrium and that the velocity distribution function can be expanded as an infinite Legendre polynomial series.

It has generally been assumed in the past that since the ratio of the electron to the molecular mass (m/M) is small, then elastic electron-molecule scattering in velocity space is almost isotropic and is, in fact, no more anisotropic than $\cos\theta$. This approximation implies that $f(\mathbf{r},\mathbf{v},t)$ is given with sufficient accuracy by only the first two terms of the Legendre expansion. Further assumptions implied by this approximation are that the average fractional gain or loss of energy by the electrons in collisions with the gas is small and that the electron scattering in inelastic collisions is isotropic. A scalar and vector equation involving the first two terms of the distribution function can now be derived and solved by numerical analyses to obtain the velocity distribution functions.[1,3] The relationship between the transport and rate coefficients measured in swarm experiments and the microscopic electron collision cross sections can then be found. As a consequence, the determination of the distribution function using this approximation requires only a knowledge of the momentum-transfer cross section σ_m (or "effective" momentum-transfer cross section when inelastic collisions are included[1]). Several recent studies have investigated the validity of this approximation[4–7] by devising numerical techniques which allow solutions of the Boltzmann equation to be obtained when higher-order terms in the distribution function are retained. In general, these studies have concentrated on the situation where the average electron energy gain or loss at collision may not be small and have shown that, indeed, large errors can arise in the calculated transport coefficients if the ratio of the total inelastic to elastic scattering cross section is large.[4,7] Fewer studies have explicitly looked at the effect of highly anisotropic (i.e., large-momentum-transfer) electron-molecule collisions,[8–10] although all these techniques are capable of studying these effects in detail. Studies by Haddad *et al.*[10] using the multiterm moment method solution of the Boltzmann equation devised by Lin *et al.*[6] have shown that highly anisotropic electron scattering can lead to significant errors in the derived transport coefficients if only the first two terms of the Legendre expansion of the distribution function are retained.

It is instructive to consider an idealized collision model in which the extreme case of electron scattering occurring

at 0° and 180° is considered. This approximation enables us to solve the Boltzmann equation analytically, which is equivalent to retaining all the terms in the Legendre expansion of the velocity distribution function. Consequently, we are able to derive explicit relationships for the dependence of the electron drift velocity w, transverse and longitudinal diffusion coefficients D_T and D_L, respectively, and the mean electron energy $\langle\epsilon\rangle$ on the functional speed dependence of the momentum-transfer collision frequency $\nu_m(c)$ and compare these coefficients with those derived by the two-term expansion of the velocity distribution function (i.e., in the situation where the electron scattering is only weakly anisotropic). (The symbol c will be used to denote speed in three dimensions and the symbol v for speeds in one dimension.) This analysis shows that both D_T and D_L are more sensitive to anisotropies in the electron scattering than are w or $\langle\epsilon\rangle$ and is described in Sec. II.

Another assumption that has been made in conventional analyses of the Boltzmann equation is that the generation of new electrons by ionization or the loss of electrons by attachment can be treated simply as energy-loss processes. This assumption fails to account for the effect of the time and spatial dependences in the number density on $f(\mathbf{r},\mathbf{v},t)$ (and hence the effect on the derived transport parameters w, $\langle\epsilon\rangle$, D_T, and D_L and electron ionization and attachment coefficients α/N and η/N, respectively). Experiments designed to measure the transport coefficients analyze an isolated swarm of electrons that possess time-dependent spatial gradients in the mean electron energy across the swarm. Consequently, unless the rate of electron attachment or ionization is independent of $\langle\epsilon\rangle$, electron gain and loss will be highly nonuniform across the swarm, leading to a shift in the centroid of the swarm in addition to that caused by the drift of the original electrons.

Lucas[11] has attempted to incorporate the influence of the spatial gradients in the distribution function on the calculation of the transport coefficients, but the technique is based upon an arbitrary expansion of $f(x,c)$ (Ref. 12) and contains errors in the analysis.[13] Thomas,[14] along with several other subsequent studies,[2] has attempted to include the influence of the spatial gradients in $n(x,t)$ due to the growth in the electron swarm by ionization on the calculation of the transport coefficients. Most of these studies, though, have not explicitly shown the effect of the velocity dependence of the electron ionization or attachment cross sections on the derivation of the electron transport parameters. It is necessary to include the ionization and attachment collisions in the calculation of the distribution function even for a uniform concentration of electrons since the variation of the attachment or ionization collision frequency with speed, $\nu_a(c)$ and $\nu_i(c)$, respectively, means that different regions of the velocity space will decrease or increase in population at different rates. Thus, if $\nu_a(c)$ or $\nu_i(c)$ are comparable to or greater than the energy-transfer collision frequency $[\approx(m/M)\nu_m(c)]$ for elastic collisions], it might be expected that the velocity distribution function is strongly influenced by attaching and ionizing collisions. This subject is discussed in Sec. III.

II. ANISOTROPIC SCATTERING

We adopt the following collision model in order to show the influence of anisotropic scattering on the derivation of the transport coefficients.

(1) The gas temperature is assumed to be 0 K (i.e., the electrons do not gain kinetic energy from the gas molecules).

(2) Elastic scattering only and $m/M \ll 1$.

(3) Electron scattering is entirely at 180°, and hence the fractional electron energy loss at collision is $\approx 4m/M$. (Scattering at 0° is a nonevent for elastic collisions since there is no change in momentum or energy.) Thus, if the velocity of an electron immediately after a collision is $\mathbf{v}$, then the velocity before a collision $\mathbf{v}'$ is

$$\mathbf{v}' \approx -\mathbf{v}/(1-4m/M)^{1/2}$$

and since $m/M \ll 1$,

$$\mathbf{v}' \approx -\mathbf{v}(1+2m/M) . \tag{1}$$

(4) The total collision cross section is assumed to have the following functional speed dependence $\sigma_T(v)=AV^p$, so that the total collision frequency is $\nu(v)=NAv^{p+1}$, where N is the gas number density and the momentum-transfer collision frequency is

$$\nu_m(v)=2NAv^{p+1} . \tag{2}$$

The Boltzmann equation describing the motion of electrons under the influence of a uniform electric field $\mathbf{E}$, when inelastic collisions are absent, is[1]

$$\frac{\partial}{\partial t}(nf)+\mathrm{div}_{\mathbf{r}}(nf\mathbf{v})+\mathrm{div}_{\mathbf{v}}\left[\frac{nfe\mathbf{E}}{m}\right]+S=0 . \tag{3}$$

When E is in the $-\mathbf{x}$ direction, at equilibrium, the electrons move only in the $\pm\mathbf{x}$ direction, and consequently electron diffusion transverse to the field does not occur. The problem now reduces to a solution of the one-dimensional Boltzmann equation which can be written in the following form:

$$\left[\frac{\partial}{\partial t}[nf(v)]+v\frac{\partial}{\partial x}[nf(v)]+\frac{Ee}{m}\frac{\partial}{\partial v}[nf(v)] +n\nu(v)f(v)\right]dv=n\nu(v')f(v')\,|\,dv'\,| , \tag{4}$$

where $nf(v)dv\,dx \equiv n(x,t)f(x,v,t)dv\,dx$ is the number of electrons between x and $x+dx$ and with velocities in the interval v to $v+dv$.

A. Uniform spatial distribution

We will first restrict ourselves to the situation of a uniform electron stream in which spatial gradients in the electron number density and f are negligible. In these circumstances, Eqs. (1) and (4) give

$$\frac{Ee}{m}\frac{d}{dv}f(v)=-\nu f(v)+\left[1+\frac{2m}{M}\right]\nu f(-v) +\frac{2m}{M}v\nu\frac{d}{dv}f(-v)+\frac{2m}{M}\nu f(-v)\frac{dv}{dv} . \tag{5}$$

Similarly, for the interval $-v$ to $-(v+dv)$

$$\frac{Ee}{m}\frac{df}{dv}(-v)=\nu f(-v)-\left[1+\frac{2m}{M}\right]\nu f(v) -\frac{2m}{M}v\nu\frac{d}{dv}f(v)-\frac{2m}{M}vf(v)\frac{d\nu}{dv} . \quad (6)$$

Define the symmetric and antisymmetric distribution functions as

$$F_0(v)=[f(v)+f(-v)]/2$$

and

$$F_1(v)=[f(v)-f(-v)]/2 ,$$

where $f(v)\equiv F_0(v)+F_1(v)$.

Adding Eqs. (5) and (6) and using $m/M\ll 1$ and $\nu_m=\nu_m(v)=2\nu$ gives

$$\frac{Ee}{m}\frac{dF_0}{dv}=-\nu_m\left[F_1+\frac{1}{\nu_m}\frac{m}{M}\frac{d}{dv}(\nu_m vF_1)\right] , \quad (7)$$

while subtracting Eq. (6) from Eq. (5) and integrating gives

$$\frac{Ee}{m}F_1=\frac{m}{M}v\nu_m F_0 . \quad (8)$$

Substituting Eq. (8) into Eq. (7) gives

$$\left[\left[\frac{Ee}{m}\right]^2+\left[\frac{m}{M}v\nu_m\right]^2\right]\frac{dF_0}{dv} =-\left[\frac{m}{M}v\nu_m^2+2\left[\frac{m}{M}\right]^2 v\nu_m^2 +2\left[\frac{m}{M}\right]^2 v^2\nu_m\frac{d}{dv}\nu_m\right]F_0 . \quad (9)$$

Using Eq. (2) and where $p\ll M/m$, only the first term on the right-hand side of Eq. (9) is significant, so that

$$F_0=C\exp\left[-\frac{m}{M}\int_0^v\frac{v}{\left[\left[\frac{Ee}{m\nu_m}\right]^2+\left[\frac{m}{M}\right]^2 v^2\right]}dv\right] ,$$

where $\{v^2\}_{\rm av}=[(m/M)v]^2$ and is defined as the mean-square speed of the gas molecules. In the present analysis, at sufficiently large values of E/N, $\{v^2\}_{\rm av}\ll(Ee/m\nu_m)^2$ over the whole range of v except when $mv^2/M\gtrsim\{v^2\}_{\rm av}$, in which case F_0 is negligibly small. Hence,

$$F_0=C\exp\left[-\frac{m}{M}\int_0^v\frac{v}{\left[\frac{Ee}{m\nu_m}\right]^2}dv\right] . \quad (10)$$

Equation (10) can also be obtained directly from Eqs. (7) and (8) by neglecting the second term on the right-hand side of Eq. (7). Using Eq. (2) and the normalizing condition that $\int_{-\infty}^{+\infty}F_0dv=1$,

$$F_0(v)=\frac{(2p+4)}{2\alpha\Gamma(1/(2p+4))}\exp\left[-\left[\frac{v}{\alpha}\right]^{2p+4}\right] , \quad (11)$$

where Γ is the gamma function, and

$$\alpha^{2p+4}=\frac{M}{m}\left[\frac{Ee}{2mNA}\right]^2(2p+4) . \quad (12)$$

From Eqs. (8) and (11)

$$F_1(v)=\frac{1}{2\alpha^{p+3}}\left[(2p+4)^3\frac{m}{M}\right]^{1/2} \times\frac{v^{p+2}}{\Gamma(1/(2p+4))}\exp\left[-\left[\frac{v}{\alpha}\right]^{2p+4}\right] . \quad (13)$$

Define the electron drift velocity as $w\equiv\int_{-\infty}^{+\infty}vF_1(v)dv$. Thus,

$$w=\alpha\left[(2p+4)\frac{m}{M}\right]^{1/2} \times\Gamma((p+4)/(2p+4))/\Gamma(1/(2p+4)) . \quad (14)$$

The mean electron energy is

$$\langle\epsilon\rangle\equiv\tfrac{1}{2}m\{v^2\}_{\rm av} =\tfrac{1}{2}m\alpha^2\Gamma(3/(2p+4))/\Gamma(1/(2p+4)) . \quad (15)$$

The application of Eqs. (14) and (15) to the calculation of w and $\langle\epsilon\rangle$ for specific energy dependences of the total scattering cross section is discussed in Sec. II C after we have derived expressions for the electron diffusion for this anisotropic scattering model.

B. Isolated electron swarm

Generalizing the electron motion to include spatial gradients in the electron number density but still considering electron motion in one dimension (i.e., the transverse diffusion coefficient $D_T=0$), Eq. (4) and its counterpart for $nf(-v)$ can be added and subtracted to give

$$\frac{\partial}{\partial t}(nF_0)+v\frac{\partial}{\partial x}(nF_1)+\frac{Ee}{m}\frac{\partial}{\partial v}(nF_1) -\frac{m}{M}\frac{\partial}{\partial v}(v\nu_m nF_0)=0 , \quad (16)$$

and

$$\frac{\partial}{\partial t}(nF_1)+v\frac{\partial}{\partial x}(nF_0)+\frac{Ee}{m}\frac{\partial}{\partial v}(nF_0)+n\nu_m F_1 +\frac{m}{M}\frac{\partial}{\partial v}(v\nu_m nF_1)=0 . \quad (17)$$

The last term in Eq. (17) is negligible as shown above [Eq. (10)], while the term $(\partial/\partial t)(nF_1)$ can be neglected provided spatial gradients in the electron concentration are not large.[1] Thus,

$$nF_1=-\frac{1}{\nu_m}\left[v\frac{\partial}{\partial x}(nF_0)+\frac{Ee}{m}\frac{\partial}{\partial v}(nF_0)\right] . \quad (18)$$

Transforming to coordinates moving with the centroid of the swarm (i.e., $X=x-wt$), Eqs. (16) and (18) give

$$\frac{d}{dt}(nF_0)-\frac{v^2}{\nu_m}\frac{\partial^2}{\partial X^2}(nF_0)-\frac{v}{\nu_m}\frac{Ee}{m}\frac{\partial^2}{\partial v\,\partial X}(nF_0)-w\frac{\partial}{\partial X}(nF_0)-\frac{Ee}{m}\frac{\partial}{\partial v}\left[\frac{1}{\nu_m}\left[v\frac{\partial}{\partial X}(nF_0)+\frac{Ee}{m}\frac{\partial}{\partial v}(nF_0)\right]\right]$$
$$=\frac{m}{M}\frac{\partial}{\partial v}(v\nu_m nF_0)\,. \quad (19)$$

Let F_0^* be the solution for a homogeneous stream of electrons free of spatial gradients in the number density.[1] Thus, rewriting Eq. (10) with $F_0^*\equiv F_0$ gives

$$\left[\frac{Ee}{m}\right]^2\frac{dF_0^*}{dv}=-\frac{m}{M}\nu_m^2 vF_0^*\,,$$

and

$$\left[\frac{Ee}{m}\right]^2\frac{1}{\nu_m}\frac{\partial}{\partial v}(nF_0)+\frac{m}{M}v\nu_m nF_0=\frac{1}{\nu_m}\left[\frac{Ee}{m}\right]^2 nF_0^*\frac{\partial}{\partial v}(F_0/F_0^*)\,.$$

Substituting this expression into Eq. (19) gives

$$\frac{d}{dt}(nF_0)-\frac{v^2}{\nu_m}\frac{\partial^2}{\partial X^2}(nF_0)-\frac{v}{\nu_m}\frac{Ee}{m}\frac{\partial^2}{\partial v\,\partial X}(nF_0)-w\frac{\partial}{\partial X}(nF_0)-\frac{Ee}{m}\frac{\partial}{\partial v}\left[\frac{v}{\nu_m}\frac{\partial}{\partial X}(nF_0)\right]$$
$$=\left[\frac{Ee}{m}\right]^2\frac{\partial}{\partial v}\left[\frac{1}{\nu_m}nF_0^*\frac{\partial}{\partial v}\frac{F_0}{F_0^*}\right]. \quad (20)$$

Let nF_0 be represented by the expansion

$$nF_0=F_0^*\sum_{k=0}^{\infty}b_k(v)\frac{\partial^k n}{\partial X^k}\,,$$

with $b_0(v)\equiv 1$, and let $n(X,t)$ satisfy the equation

$$\frac{dn}{dt}=\sum_{m=2}^{\infty}D_m\frac{\partial^m n}{\partial X^m}\,.$$

Then

$$\frac{d}{dt}(nF_0)=F_0^*\sum_{k=0}^{\infty}\sum_{m=2}^{\infty}b_k(v)D_m\frac{\partial^{k+m}n}{\partial X^{k+m}}\,.$$

Substituting this expression into Eq. (20) and separately equating the coefficients of $\partial n/\partial X$ and $\partial^2 n/\partial X^2$ to zero, the following expressions can be obtained:

$$-\frac{v}{\nu_m}\left[\frac{Ee}{m}\right]\frac{dF_0^*}{dv}-wF_0^*-\frac{Ee}{m}\frac{d}{dv}\left[\frac{vF_0^*}{\nu_m}\right]=\left[\frac{Ee}{m}\right]^2\frac{d}{dv}\left[\frac{F_0^*}{\nu_m}\frac{db_1}{dv}\right], \quad (21)$$

from which $b_1(v)$ can be found by integration, and

$$D_2F_0^*-\frac{v^2}{\nu_m}F_0^*-\frac{v}{\nu_m}\frac{Ee}{m}\frac{d}{dv}(b_1F_0^*)-wb_1F_0^*-\frac{Ee}{m}\frac{d}{dv}\left[\frac{v}{\nu_m}b_1F_0^*\right]=\left[\frac{Ee}{m}\right]^2\frac{d}{dv}\left[\frac{F_0^*}{\nu_m}\frac{db_2}{dv}\right]. \quad (22)$$

Integrating over all velocities in Eq. (22) gives

$$D_2=\int_{-\infty}^{+\infty}\frac{v^2}{\nu_m}F_0^*dv+\int_{-\infty}^{+\infty}\frac{v}{\nu_m}\frac{Ee}{m}\frac{d}{dv}(b_1F_0^*)dv\,,$$

or

$$D_2=2\int_0^{\infty}\frac{v^2}{\nu_m}F_0^*dv-\frac{Ee}{m}\int_{-\infty}^{+\infty}b_1F_0^*\frac{d}{dv}\left[\frac{v}{\nu_m}\right]dv\,. \quad (23)$$

The coefficient D_2 is the coefficient of diffusion in the direction of the applied electric field and is designated the longitudinal diffusion coefficient D_L.

The transport parameters w^*, $\langle\epsilon\rangle^*$, and D_L given by Eqs. (14), (15) (where $w^*\equiv w$ and $\langle\epsilon\rangle^*\equiv\langle\epsilon\rangle$), and (23), respectively, are now explicitly dependent on the functional speed dependence of the momentum-transfer collision frequency $\nu_m(v)$. The values of these transport coefficients obtained for various speed dependences of $\nu_m(v)$

TABLE I. Comparison between the transport coefficients obtained from the present analysis and the "two-term" expansion of the distribution function for $\nu_m = \text{const}$; $p = -1$.

Present results	Two-term expansion results
$w^* = \frac{Ee}{m\nu_m}$	$w^* = \frac{Ee}{m\nu_m}$
$\langle\epsilon\rangle^* = \frac{m\{v^{2*}\}_{\text{av}}}{2} = \frac{M}{2}\left[\frac{Ee}{m\nu_m}\right]^2 = \frac{M}{2}w^{2*}$	$\langle\epsilon\rangle^* = \frac{m\{c^{2*}\}_{\text{av}}}{2} = \frac{M}{2}\left[\frac{Ee}{m\nu_m}\right]^2 = \frac{M}{2}w^{2*}$
$D_L = \frac{\{v^2\}_{\text{av}}}{\nu_m} = \frac{M}{m\nu_m}\left[\frac{Ee}{m\nu_m}\right]^2$	$D_L = \frac{1}{3}\frac{\{c^2\}_{\text{av}}}{\nu_m} = \frac{1}{3}\frac{M}{m\nu_m}\left[\frac{Ee}{m\nu_m}\right]^2$
$D_T = 0$	$D_T = D_L$

can be directly compared with those obtained by the conventional "two-term" expansion approximation of the distribution function.

C. Special cases

1. $\nu_m(v) = \nu_m = const$ (i.e., $p = -1$)

The values of w^*, $\langle\epsilon\rangle^*$, D_L, and D_T obtained when ν_m is independent of the electron speed are given in Table I along with the values obtained from the two-term approximation analysis using this speed dependence. These analyses indicate that whereas w^* and $\langle\epsilon\rangle^*$ are identical in both of the approximations, D_L is three times larger for the anisotropic electron scattering case than for the weakly anisotropic scattering situation, and although $D_L = D_T$ for the two-term approximation, by definition $D_T = 0$ for the present anisotropic scattering model.

The variation in the mean energy across the electron swarm in the direction of the applied electric field can readily be found for the situation where $\nu_m = \text{const}$. In this case

$$\langle\epsilon\rangle = \frac{m\{v^2\}_{\text{av}}}{2} = \frac{m}{2}\int_{-\infty}^{+\infty} v^2 F_0 dv = \frac{m}{2}\int_{-\infty}^{+\infty} v^2 F_0^* \sum_{k=0}^{\infty} b_k \frac{1}{n}\frac{\partial^k n}{\partial X^k} dv \ .$$

For small spatial gradients in n, only the first two terms of the summation are important in the region where most of the electrons are found (i.e., when $X \approx wt$). Thus,

$$\langle\epsilon\rangle = \frac{m}{2}\int_{-\infty}^{+\infty} v^2 F_0^* \left[1 + b_1 \frac{1}{n}\frac{\partial n}{\partial X}\right] dv \ . \tag{24}$$

From Eq. (21) b_1 can be found, i.e.,

$$b_1 = \frac{1}{\nu_m w}(\{v^{2*}\}_{\text{av}} - v^2) \ . \tag{25}$$

For an isolated swarm, the spatial distribution of the electron concentration is given by

$$\frac{dn}{dt} - D_L \frac{\partial^2 n}{\partial X^2} = 0 \ ,$$

where higher-order spatial derivatives are assumed to be negligibly small. This equation has the solution

$$n(X) \propto \exp\left[-\frac{X^2}{4D_L t}\right] = \exp\left[-\frac{(x - wt)^2}{4D_L t}\right] .$$

Thus, Eq. (24) gives

$$\langle\epsilon\rangle = \frac{m\{v^{2*}\}_{\text{av}}}{2}\left[1 + \frac{x - \bar{x}}{\bar{x}}\right] = \frac{mx}{2wt}\{v^{2*}\}_{\text{av}} \ ,$$

where $\bar{x} = wt$ and $D_L = \{v^{2*}\}_{\text{av}}/\nu_m$. Consequently, the mean electron energy increases linearly across the swarm in the direction of the swarm motion when ν_m is constant.

2. $\nu_m(v) \propto v$ (i.e., $p = 0$) (constant elastic collision cross section)

The transport parameters derived from the present analysis assuming that ν_m is proportional to the electron speed are given in Table II. These results indicate that, in this case, both w^* and $\langle\epsilon\rangle^*$, calculated using the anisotropic scattering model, are significantly different from those calculated using the two-term approximation, being approximately 15% higher and 5% lower, respectively, than the two-term results. The longitudinal diffusion coefficient calculated using the anisotropic scattering model is almost five times as large as that calculated using the two-term approximation. These results indicate that although the effects of anisotropic scattering on w and $\langle\epsilon\rangle$ are small, they may still be significant for certain speed dependences of the total scattering cross section. The changes in D_L and D_T for this scattering model are, on the other hand, very significant for both of the special cases considered and indicate that more modest anisotropies in the electron scattering will still have a large effect on the accuracy of the calculation of the diffusion coefficients if these anisotropies are not taken into account.

D. Expansion of the distribution function in spherical harmonics

The velocity distribution function calculated using the present anisotropic scattering model can be expanded in spherical harmonics in order to show that the higher-

TABLE II. Comparison between the transport coefficients obtained from the present analysis and the two-term expansion of the distribution function for $\nu_m = \text{const} \times v$; $p = 0$.

Present results	Two-term expansion results
$w^* = 0.7801 \left[\frac{m}{M}\right]^{1/4} \left[\frac{Ee}{2mNA}\right]^{1/2}$	$w^* = 0.8974 \left[\frac{m}{M}\right]^{1/4} \left[\frac{Ee}{2mNA}\right]^{1/2}$
$\langle \epsilon \rangle^* = \frac{m\{v^{2*}\}_{\text{av}}}{2}$	$\langle \epsilon \rangle^* = \frac{m\{c^{2*}\}_{\text{av}}}{2}$
$= 0.338m \left[\frac{M}{m}\right]^{1/2} \left[\frac{Ee}{2mNA}\right]$	$= 0.427m \left[\frac{M}{m}\right]^{1/2} \left[\frac{Ee}{2mNA}\right]$
$= 0.555Mw^{2*}$	$= 0.530Mw^{2*}$
$D_L = 0.3457 \left[\frac{M}{m}\right]^{1/4} \frac{1}{(NA)} \left[\frac{Ee}{2mNA}\right]^{1/2}$	$D_L = 0.0716 \left[\frac{M}{m}\right]^{1/4} \frac{1}{(NA)} \left[\frac{Ee}{2mNA}\right]^{1/2}$
$D_T = 0$	$D_T = 2.041 D_L$

order terms in the expansion are not insignificant in comparison with the first two terms as is usually assumed.

Let the equilibrium distribution function in three-dimensional velocity space be denoted by

$$f(c,\theta) = \sum_{k=0}^{\infty} f_k(c) P_k(\cos\theta)$$

$$= (F_0 + F_1)\delta(+v) + (F_0 - F_1)\delta(-v) ,$$

where $P_k(\cos\theta)$ is the kth-order Legendre polynomial. Multiplying this expression by $P_n(\cos\theta)$ and integrating over a shell in velocity space for speeds lying between c and $c+dc$ yields the following:

$$2\pi c^2 \sum_{k=0}^{\infty} f_k(c) \int_{-1}^{+1} P_k(\cos\theta) P_n(\cos\theta) d(\cos\theta)$$

$$= (F_0 + F_1) P_n(1) + (F_0 - F_1) P_n(-1)$$

$$= (F_0 + F_1) + (-1)^n (F_0 - F_1);$$

alternatively,

$$f_n(c) = \frac{(2n+1)}{4\pi c^2} [(F_0 + F_1) + (-1)^n (F_0 - F_1)] .$$

Thus,

$$f_0(c) = \frac{1}{2\pi c^2} F_0(c) ,$$

$$f_1(c) = \frac{3}{2\pi c^2} F_1(c) ,$$

$$f_2(c) = \frac{5}{2\pi c^2} F_0(c) ,$$

etc., where $F_0(c)$ and $F_1(c)$ are given by Eqs. (11) and (13) with $v \equiv c$.

When this expression for $f_2(c)$ is substituted into Eq. (2.23) of Huxley and Crompton,[1] the present values for $f_0(c)$ and $f_1(c)$ are recovered from their analysis. In the usual two-term approximation, $f_2(c)$ and higher-order terms are assumed to be negligible in comparison to $f_0(c)$ and $f_1(c)$. This implies that the drift velocity of the electron swarm is small in comparison to the average random velocity of the electrons. The present analysis using the scattering model described above has shown that, on the contrary, the term $f_2(c)$ and higher-order terms can be comparable in magnitude to $f_0(c)$ when the electron scattering is highly anisotropic. Consequently, even if the electron drift velocity is considerably less than the average random electron velocity, this is not a *sufficient* condition for neglecting the higher-order terms in the Legendre expansion of $f(c)$.

III. ELECTRON ATTACHMENT

Several attempts have been made in recent years to include the effects of electron attachment and ionization upon the electron-velocity distribution function of electron swarms and the derivation of the transport and rate coefficients for these swarms.[2] When the rate of ionization or attachment is significant in comparison to the energy-transfer rate, the Boltzmann equation given by Eq. (3) must be modified to include terms to account for the electron loss or gain, which can be both spatially and temporally dependent within the swarm.

Most of these analyses find their origin in the work of Thomas,[14] who indicated that the influence of these electron nonconservation processes depended upon the type of experiment that was being performed. When the current in an external circuit produced by a continuous stream of electrons [the steady-state Townsend (SST) experiment[15]] is analyzed, there exists a region between the electrodes in which the electron stream is at equilibrium (i.e.,

$\partial nf/\partial t=0$), but the growth in the electron number density within the stream must be taken into account by including the term $[\partial n(v,x)/\partial x]f=\alpha_s n(v,x)f$ in Eq. (3), where $\alpha_s=\alpha-\eta$, and α and η are the unnormalized ionization and attachment coefficients, respectively. Alternatively, when the current in the external circuit is analyzed for a pulse or swarm of electrons which are liberated within the drift gap and drift to the anode under the applied field [the pulsed Townsend (PT) experiment[15]], the number density in the swarm changes with time such that $[\partial n(v,t)/\partial t]f=\nu_a n(v,t)f$, where $\nu_a=\bar{\nu}_i-\bar{\nu}_a$, and $\bar{\nu}_i \equiv\langle\nu_i(v)\rangle$ and $\bar{\nu}_a\equiv\langle\nu_a(v)\rangle$ are the average ionization and attachment collision frequencies, respectively. Tagashira *et al.*[15] have analyzed these experiments in detail and have defined a further type of experiment where the development of the electron number density within a swarm in a drift gap is analyzed as a function of both position and time [the time-of-flight (TOF) experiment[15]]. This experiment is distinct from that where the motion of the electrons causes a current to flow in an external circuit as in the pulsed Townsend experiment.

For the present analysis, it is initially assumed that the electron number density is spatially uniform and that the velocity distribution function is at equilibrium. We also assume that the E/N is sufficiently low, such that electron ionization processes are negligible and only attachment processes need be considered. The influence that the position and magnitude of the attachment process has on the shape of the electron-velocity distribution function and on the derivation of w and $\langle\epsilon\rangle$ will be described for two different functional dependences of the momentum-transfer cross section on the electron speed. The changes in the transport coefficients occur irrespective of the angular scattering model that is assumed. Finally, we will indicate the changes in the drift velocity that occur due to the spatial variation in the mean energy across an isolated electron swarm and how these changes are related to the functional velocity dependence of the attachment collision cross section.

A. Anisotropic scattering model

In the present study we first assume that the electrons are distributed uniformly in space and that elastic electron scattering again occurs only at 0° or 180°. Inelastic collisions are assumed to be negligible. Thus, the one-dimensional continuity equation given by Eq. (4) applies, in which an extra term to account for electron attaching collisions $-n\nu_a(v)f(v)$ is included on the right-hand side. In this situation, Eqs. (16) and (17) become

$$\frac{\partial}{\partial t}(nF_0)+\frac{Ee}{m}n\frac{\partial F_1}{\partial v}-\frac{m}{M}n\frac{\partial}{\partial v}(v\nu_m F_0)=-n\nu_a F_0 , \quad (26)$$

and

$$\frac{\partial}{\partial t}(nF_1)+\frac{Ee}{m}n\frac{\partial F_0}{\partial v}+n\nu_m F_1=-n\nu_a F_1 , \quad (27)$$

where, as before, ν_m is the momentum-transfer collision frequency for elastic collisions. In many gases, $\nu_a\ll\nu_m$ and the attachment term can be neglected in Eq. (27) (or included in the total momentum-transfer cross section). However, in Eq. (26) the attachment collision frequency is comparable to the energy-transfer collision frequency, $\nu_u\approx(m/M)\nu_m$ for this scattering model, and it is not possible to neglect the term. These comments apply because we are only considering elastic and attaching collisions. In general, an attaching gas will possess considerable inelastic loss processes as well as electron attachment. In this situation ν_u can be considerably larger than ν_a over a wide range of E/N, allowing the transport coefficients to be obtained with sufficient accuracy by neglecting the attachment process. However, when $\nu_a(v)$ is large and peaks at near zero energy, as, for example, in SF_6 and F_2, these terms must be retained in the analysis if accurate transport coefficients are to be calculated, as the rate of energy transfer is comparable to or less than the attachment rate in these circumstances. In experiments where a strongly attaching gas is diluted (typically 0.1% to 10%) in a rare gas in order to perform drift velocity and attachment measurements over a wide range of E/N, ν_a may again be comparable to or larger than the energy exchange frequency. Such measurements have been performed in fluorine containing electronegative gases-rare-gas mixtures for use in excimer laser kinetic studies[16] and for diffuse discharge opening switch studies.[17] Conversely, the effect of electron attachment on $F_0(v)$ in experiments where the attaching gas is mixed in minute traces (<1 part in 10^6) in a high-pressure buffer gas[18] is again negligible, even if the buffer gas is a rare gas, as in this situation, $\nu_a\ll\nu_u$. For completeness, the attachment terms will be retained in both Eqs. (26) and (27).

To solve Eqs. (26) and (27), first integrate Eq. (26) over all speeds, i.e.,

$$\frac{dn}{dt}=-n\bar{\nu}_a ,$$

thus

$$n(t)=n(0)\exp(-\bar{\nu}_a t) . \quad (28)$$

Assuming that the velocity distribution function has attained equilibrium, then $\partial F_0/\partial t=\partial F_1/\partial t=0$. This assumption may be questionable when the electron attachment rate is large, as has been clearly shown in the work of Crompton *et al.*[19] on resonant three-body electron attachment to O_2. This work has shown that when the electron attachment process is large and strongly energy dependent, the electron energy distribution function never relaxes to the thermal Maxwellian distribution, even for "thermal" electrons. For the present model, we assume this approximation is valid, and substituting Eq. (28) into Eqs. (26) and (27) gives

$$\frac{Ee}{m}\frac{dF_1}{dv}-\frac{m}{M}\frac{d}{dv}(v\nu_m F_0)=(\bar{\nu}_a-\nu_a)F_0 ,$$

or

$$\frac{Ee}{m}\frac{dF_1}{dv}=\frac{mv}{M}\frac{d}{dv}(\nu_m F_0)+\left[\bar{\nu}_a-\nu_a+\frac{m}{M}\nu_m\right]F_0 , \quad (29)$$

and

$$\frac{Ee}{m}\frac{dF_0}{dv}=(\bar{\nu}_a-\nu_a-\nu_m)F_1 \ . \tag{30}$$

When $\nu_a(v)$ is a rapidly varying function of v over the range of speeds where F_0 is appreciable, then $\bar{\nu}_a$ will be much less than $\nu_a(v)$ for most of this range, and the preceding comments concerning the importance of the ratio ν_a/ν_u remain valid.

Equations (29) and (30) can be solved numerically for $F_0(E/N,v)$ and $F_1(E/N,v)$ when ν_m and ν_a are known. For illustrative purposes, calculations have been carried out for the following parameters:

$$M/m=1600 \ ,$$

$$\nu_m(v)=\nu_m=\text{const} \ ,$$

$$\nu_a/\nu_m=\begin{cases}0 \ \text{ for } \ |v|<v_{\text{th}} \\ A(BV-1)\exp-\left[\dfrac{B}{2}V\right] \ \text{ for } \ |v|>v_{\text{th}} \ ,\end{cases}$$

where A is a constant, $B=(\{v_0^2\}_{\text{av}})^{1/2}/v_{\text{th}}$, $V=|v|/(\{v_0^2\}_{\text{av}})^{1/2}$, v_{th} is the threshold velocity for the attachment process, and $(\{v_0^2\}_{\text{av}})^{1/2}$ is the root-mean-square velocity calculated from Eq. (15) using the velocity distribution function given earlier when attachment is neglected. In this example, $(\{v_0^2\}_{\text{av}})^{1/2}$ and hence B are proportional to E/N. The small M/m ratio was chosen in this example to enhance the influence (if any) of electron attachment on the electron drift velocity obtained when using a constant collision frequency model.

Figures 1 and 2 show the calculated distribution function $F_0(v)$ obtained for two values of B and several values of A. Values of relative mean energy, $\langle\epsilon\rangle/\langle\epsilon\rangle_{(\bar{\nu}_a=0)}$, and relative drift velocity, $w/w_{(\bar{\nu}_a=0)}$, were calculated from these distribution functions and are listed in Table III together with values of the relative attachment frequency $\bar{\nu}_a/\nu_m$. The mean energy and drift velocity are given in relation to the values obtained when attachment is neglected in Eqs. (29) and (30), and the relative changes in these parameters are independent of E/N for this collision model.

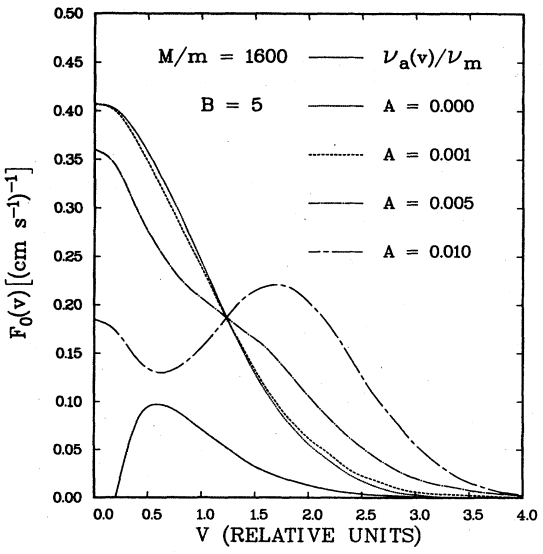

FIG. 1. Model calculations of the velocity distribution function $F_0(v)$, assuming only elastic and attaching collisions for anisotropic electron scattering. For these calculations, ν_m was assumed to be constant and M/m, A, and B were given the values shown on the graph. The curve for $\nu_a(v)/\nu_m$ is shown on an arbitrary scale.

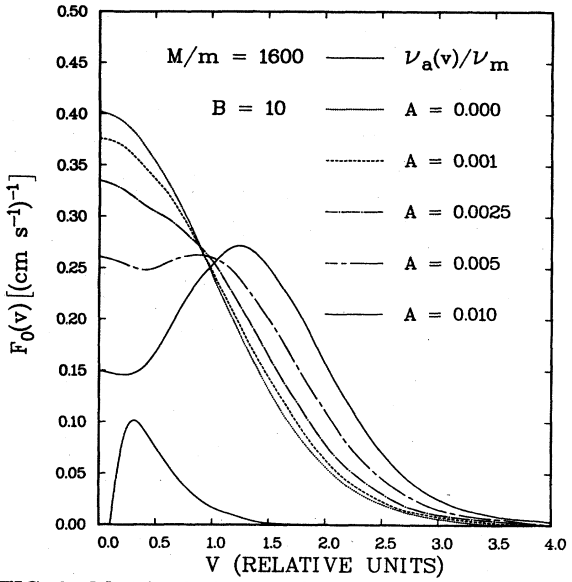

FIG. 2. Model calculations of the velocity distribution function $F_0(v)$ for the same parameters given in Fig. 1, except for the different values of A and B shown in the figure.

As expected, the drift velocity is not appreciably altered for this collision model, as can be seen from multiplying both sides of Eq. (30) by v and integrating over all velocities. For $\bar{\nu}_a/\nu_m \ll 1$, then $w=Ee/m\nu_m$ to a very good approximation, and the small differences from unity shown for $w/w_{(\bar{\nu}_a=0)}$ in Table III may be partly due to errors in the numerical integrations. The marked changes in the distribution function, which produce the very large changes in the calculated values of $\langle\epsilon\rangle$ shown in Table III, indicate that, apart from the particular case when $\nu_m=\text{const}$, significant changes in the drift velocity would also be produced in general. Rather than pursue this further with the anisotropic scattering model, calculations have also been performed using the two-term spherical harmonic expansion of the distribution function since this should give a more realistic assessment of the influence of attachment in practical cases.

B. Two-term spherical harmonic expansion

We will again limit the discussion to a model gas where only elastic scattering and attachment occur. Following the same procedure outlined above, then for a uniform concentration gradient, Eqs. (5.40) and (5.41) of Huxley and Crompton[1] become

TABLE III. The influence of electron attachment on the mean energy and drift velocity of the electrons—anisotropic scattering model, with $\nu_m = \text{const}$ and $M/m = 1600$.

	$\bar{\nu}_a/\nu_m$	$\langle\epsilon\rangle/\langle\epsilon\rangle_{(\bar{\nu}_a=0)}$	$w/w_{(\bar{\nu}_a=0)}$
$B=5$			
$A=0.001$	2.37×10^{-4}	1.062	0.9999
$A=0.005$	1.042×10^{-3}	1.598	0.9999
$A=0.01$	1.526×10^{-3}	3.045	1.001
$B=10$			
$A=0.001$	1.59×10^{-4}	1.107	1.000
$A=0.0025$	3.62×10^{-4}	1.293	1.001
$A=0.005$	6.04×10^{-4}	1.639	1.003
$A=0.01$	8.38×10^{-4}	2.23	1.008

$$\frac{1}{3}\left[\frac{Ee}{m}\right]\frac{d}{dc}(c^2 f_1) = \frac{m}{M}c^3\frac{d}{dc}(\nu_m f_0) + \left[\bar{\nu}_a - \nu_a + \frac{3m}{M}\nu_m\right]c^2 f_0 , \quad (31)$$

and

$$(\bar{\nu}_a - \nu_a - \nu_m) f_1 = \frac{Ee}{m}\frac{\partial}{\partial c} f_0 . \quad (32)$$

Model calculations have been performed using $f_0(E/N,c)$ and $f_1(E/N,c)$ obtained from Eqs. (31) and (32) for the following parameters:

$$M/m = 5\times10^4 ,$$

$$\nu_m(c) \propto c$$

(i.e., constant collision cross section),

$$\nu_a/\nu_m(\alpha) = \begin{cases} 0 \text{ for } |v| < v_{\text{th}} \\ A\left[V - \frac{1}{B}\right]\exp\left[-\frac{B}{2}V\right] \text{ for } |v| > v_{\text{th}} , \end{cases}$$

where $\nu_m(\alpha)$ is the momentum-transfer collision frequency for the speed α, which is defined by Eq. (12) with $p=0$, and in this case, $V=c/\alpha$ and $B=\alpha/v_{\text{th}}$. Equation (12) shows that in this situation, B is proportional to $(E/N)^{1/2}$. A more realistic M/m ratio was chosen in this example to indicate that, in general, appreciable modifications to w and $\langle\epsilon\rangle$ can occur, even for very small $\bar{\nu}_a/\nu_m$ ratios.

Equations (31) and (32) have been used to calculate $f_0(c)$ and $f_1(c)$ for two values of B and several values of A, and the distribution functions $f_0(c)$ are shown in Figs. 3 and 4. Values for $\bar{\nu}_a/\nu_m(\alpha)$, $\langle\epsilon\rangle/\langle\epsilon\rangle_{(\bar{\nu}_a=0)}$, and $w/w_{(\bar{\nu}_a=0)}$ calculated using these distribution functions are listed in Table IV. The results given in Tables III and IV indicate that $\langle\epsilon\rangle$ increases with increases in the magnitude of the attachment cross section. This phenomenon may be termed "attachment heating" and occurs when $\nu_a(c)$ peaks at energies well below the mean energy of the electrons. Conversely, when the peak in $\nu_a(c)$ occurs at higher electron energies than $\langle\epsilon\rangle$, high-energy electrons will be lost from electron-velocity distribution, and the resultant $\langle\epsilon\rangle$ values will be lower (i.e., "attachment cooling" will occur). An analogous situation occurs when ionization processes are significant. In this case the sharing of the initial electron energy between the two electrons after an ionizing collision results in a lowering of $\langle\epsilon\rangle$ ("ionization cooling") for the electron distribution as a whole.[13,15]

The calculations given in Tables III and IV also indicate that, in general, attaching collisions will modify the drift velocity of the electron swarm. Although Naidu and Prasad[20] have found that $w(E/N)$ is independent of the gas pressure P_T within the experimental error in the perfluoroalkanes, recent accurate measurements by Hunter *et al.*[21] have found that $w(E/N)$ is dependent on P_T for both C_3F_8 and n-C_4F_{10} but independent of P_T for CF_4 and C_2F_6. Both the molecules C_3F_8 and n-C_4F_{10} possess strongly pressure-dependent three-body electron attachment processes at gas pressures $P_T \lesssim 400$ kPa, in contrast to CF_4 and C_2F_6, in which the electron attachment rate is independent of gas pressure over this pressure range.[18] Aschwanden[22] has also observed that $w(E/N)$ is dependent on P_T in 1-C_3F_6, which is also known to possess strongly pressure-dependent apparent three-body attachment processes.[23] In both of these studies the drift velocity measurements were performed at sufficiently low gas pressures ($P_T < 10$ kPa) such that multiple scattering effects are negligible.[24] Naidu and Prasad[20] observed that D_T/μ values (which, as a rule, are more sensitive to changes in the velocity distribution function[1]) in C_3F_8 and n-C_4F_{10} were pressure dependent, while those in CF_4 and C_2F_6 were independent of gas pressure. Similarly, Aschwanden[22] has found that D_L/μ in 1-C_3F_6 is also dependent on P_T. We propose that the pressure dependence in w, D_T/μ, and D_L/μ observed for these molecules may be related to the changes in the velocity distribution function that we have observed in the present model calculations.

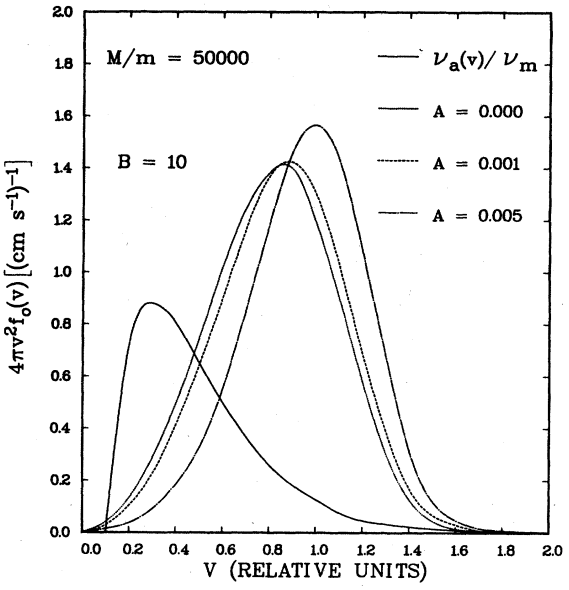

FIG. 3. Model calculations of the velocity distribution function $4\pi v^2 f_0(v)$ using the two-term spherical harmonic expansion of $f(v)$ for the values of M/m, A, and B shown in the figure. In this calculation the momentum collision frequency has the velocity dependence $\nu_m = \text{const} \times v$, and the curve $\nu_a(v)/\nu_m$ is shown on an arbitrary scale.

C. Spatial dependences in $\bar{\nu}_a$

Monte Carlo studies of the electron motion in H_2, in addition to the analysis given above, have shown that considerable spatial dependences in $\langle \epsilon \rangle$ can occur, even when the swarm has achieved equilibrium.[13,25] When ionization processes are significant, $\bar{\nu}_i$ is also highly spatially dependent within the swarm. By analogy, when spatial dependences in $\langle \epsilon \rangle$ occur for an attaching gas, the suggestion has been made that $\bar{\nu}_a$ and hence the transport parameters will also be spatially dependent.[25] Consequently, the centroid of an isolated swarm, and hence w, will be displaced due to the spatial dependence in $\bar{\nu}_a(x)$, while the swarm averaged value $\bar{\nu}_a^*$ retains the value calculated above.

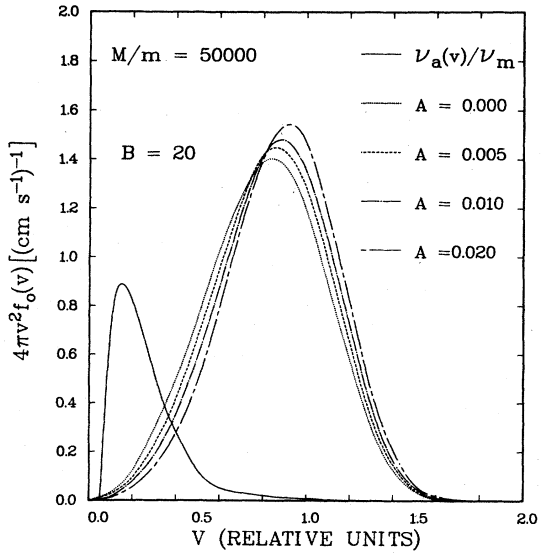

FIG. 4. Model calculations of the velocity distribution function $4\pi v^2 f_0(v)$ for the same parameters given in Fig. 3, except for the different values of A and B shown in the figure.

Following a similar procedure to that given above for a one-dimensional isolated swarm with constant ν_m, it is found that the drift velocity is changed by attachment to the value

$$w' = w^* + \int_{-\infty}^{+\infty} \nu_a f_0^* b_1(v) dv \ , \tag{33}$$

where f_0^* is the spatially uniform velocity distribution function, and $w^* \equiv Ee/m\nu_m$ as before. For $\nu_a \ll \nu_m$, the value of $b_1(v)$ given in Eq. (25) can be used in Eq. (33) to give

$$w' = w^* \left[1 + \frac{1}{\nu_m w^{*2}} \int_{-\infty}^{+\infty} \nu_a (\{v^{2*}\}_{\text{av}} - v^2) f_0^* dv \right] . \tag{34}$$

The influence of the spatial gradients in $\langle \epsilon \rangle$ on the value of w' can be shown from the following special cases.

(1) When $\nu_a(v)$ is approximately constant over the velocity interval $0 < v^2 < 2\{v^{2*}\}_{\text{av}}$, then $w' \approx w^*$ (i.e., the spatial gradient in $\langle \epsilon \rangle$ has a negligible effect on the drift velocity and the other transport coefficients).

(2) When $\nu_a(v)$ is only appreciable for $v^2 \ll \{v^{2*}\}_{\text{av}}$, then

$$w' \approx w^* \left[1 + \frac{\bar{\nu}_a \{v^{2*}\}_{\text{av}}}{\nu_m w^{*2}} \right] ,$$

or

$$w' \approx w^* \left[1 + \frac{M\bar{\nu}_a}{m\nu_m} \right] \approx w^* \left[1 + \frac{\bar{\nu}_a}{\nu_a} \right] .$$

Thus, for low energy or thermal electron attachment, the electron drift velocity will be larger than the spatially uniform value w^*.

(3) When $\nu_a(v)$ is only appreciable for $v^2 \gg \{v^{2*}\}_{\text{av}}$, then

$$w' \approx w^* \left[1 - \frac{1}{\nu_m w^{*2}} \int_{-\infty}^{+\infty} \nu_a v^2 f_0^* dv \right] .$$

Consequently, when electron attachment is significant only at higher electron energies, then the electron drift velocity will be smaller than the spatially uniform value w^*.

The presence of significant ionization processes has previously been shown to increase the electron-swarm drift velocity.[9,13] Thus, for gases which possess large thermal and near-thermal electron attachment cross sections, such as SF_6 and F_2, for example, at E/N values near breakdown (i.e., when $\bar{\nu}_a \approx \bar{\nu}_i$) electrons will be lost at the rear of the swarm by attachment and gained at the front by ionization. Both processes reinforce one another to considerably enhance the electron drift velocity. For gases

TABLE IV. The influence of electron attachment on the mean energy and drift velocity of the electrons—two-term spherical harmonic expansion model, with $\nu_m = \text{const} \times c$ and $M/m = 5 \times 10^4$.

	$\bar{\nu}_a/\nu_m(\alpha)$	$\langle\epsilon\rangle/\langle\epsilon\rangle_{(\bar{\nu}_a=0)}$	$w/w_{(\bar{\nu}_a=0)}$
$B=10$			
$A=0.001$	1.415×10^{-5}	1.077	0.952
$A=0.005$	5.06×10^{-5}	1.324	0.808
$B=20$			
$A=0.005$	6.28×10^{-6}	1.058	0.956
$A=0.010$	1.068×10^{-5}	1.104	0.920
$A=0.020$	1.653×10^{-5}	1.168	0.870

such as the perfluoroalkanes, which, on the other hand, only attach electrons at high energies, over a limited E/N range the drift velocity will be reduced by the presence of electron attachment and then increased by ionization at higher E/N values. This effect may possibly partly account for the negative differential conductivity region in the drift velocities as a function of E/N which has been observed for all of these gases at E/N values where electron attachment starts to become a significant electron-loss process.[17,21,26]

The increase in electron number density at the front of the electron swarm due to spatial gradients in $\langle\epsilon\rangle$ when ionization is significant has also been shown to lead to marked increases in the longitudinal diffusion coefficient ND_L.[9,13] In contrast, the transverse diffusion coefficient ND_T is relatively unaffected by these processes as transverse gradients in $\langle\epsilon\rangle$ have been shown to be negligible when the swarm has achieved equilibrium.[13,25] By analogy, then, although ND_L will be considerably modified by attachment, ND_T will remain relatively unaffected by spatial gradients in $\langle\epsilon\rangle$ in the field direction.

The work described in this paper has concentrated on the analysis of the electron motion in the presence of attachment, where the velocity distribution function has attained local equilibrium (i.e., where $\partial f_0/\partial t = \partial f_1/\partial t = 0$, but where spatial gradients in $\langle\epsilon\rangle$ have been included). Several other recent studies have considered the situation where temporal variations in $f_0(v)$ and $f_1(v)$ are significant.[15,27,28] These studies have shown that for both electron attachment and ionization the changes in the transport and rate coefficients due to temporal changes in the distribution function are, in general, less than those due to attachment and ionization modified electron diffusion and spatial gradients in $\langle\epsilon\rangle$.[2,15,27]

IV. CONCLUSIONS

This work has shown that anisotropic electron scattering and attachment can significantly modify the velocity distribution function for electrons in gases. Although the derivations and the numerical examples are related to specific and, in some cases, unrealistic models, the following general conclusions can be drawn from this work.

(1) Anisotropic electron scattering will, in general, modify the transport coefficients as derived from a two-term spherical harmonic expansion of the Boltzmann equation. The diffusion coefficients ND_L and ND_T appear to be more sensitive to the scattering anisotropy than w or $\langle\epsilon\rangle$, and this sensitivity is dependent upon the functional velocity dependence of the momentum-transfer cross section $\sigma_m(c)$ or collision frequency $\nu_m(c)$.

(2) In principle, higher-order terms in the spherical harmonic expansion of $f(c)$ are required when the scattering anisotropy is large. The present analysis indicates that the condition that $w \ll (\{c^2\}_{\text{av}})^{1/2}$ is not a sufficient condition to neglect the terms $f_2(c)$, $f_3(c)$, etc. in this expansion. A similar conclusion has been reached in the work of Reid[8] and Haddad *et al.*[10] Other studies have shown that although anisotropy in the electron scattering can lead to significant errors in the derivation of the electron transport parameters if this anisotropy is neglected, the most significant errors occur when the average energy exchange collision frequency is large, as occurs, for example, when the ratio of the elastic to inelastic scattering cross sections approaches unity.[4,6]

(3) The velocity distribution function is modified by the presence of electron attachment and ionization, and consequently, all the transport and rate coefficients will be a function of the magnitude and speed dependence of $\nu_a(c)$.

(4) For an isolated electron swarm, an additional modification to w (and ND_L) is introduced by spatial variations in the attachment rate. The magnitude of w has been shown to increase or decrease depending on whether electron attachment occurs at thermal or higher electron energies.

(5) When three-body attachment processes occur, the transport parameters may depend on N as well as E/N.

The modifications to the distribution function, and hence the electron transport coefficients, described in this paper, which occur due to electron attachment and ionization, must not be confused with the changes in the definition of the transport coefficients which occur due to the different experimental methods used to perform these measurements,[15] with the possible exception of the spatial gradients in $\langle\epsilon\rangle$ which occur in PT and TOF experiments but not in SST experiments, although $f(\mathbf{v})$ in the SST experiments will be different if these gradients are neglected in the analysis of the electron motion.

It must be stressed that the present results are only indicative of the possible modifications to the theoretically derived transport parameters. The magnitude of the changes produced for particular gases can only be assessed by carrying out detailed calculations for realistic differential scattering and attachment cross sections. In particular, it is expected that the results will be strongly influenced by the inclusion of inelastic collision processes.

ACKNOWLEDGMENTS

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[1]L. G. H. Huxley and R. W. Crompton, *The Drift and Diffusion of Electrons in Gases* (Wiley, New York, 1974), Chaps. 2, 4, and 5.

[2]For example, see discussion and references in S. R. Hunter and L. G. Christophorou, in *Electron-Molecule Interactions and Their Applications,* edited by L. G. Christophorou (Academic, New York, 1984), Vol. 2, Chap. 3.

[3]For example, L. S. Frost and A. V. Phelps, Phys. Rev. **127**, 1621 (1962); A. G. Engelhardt, A. V. Phelps, and C. G. Risk, *ibid.* **135**, A1566 (1964).

[4]L. C. Pitchford, S. V. ONeil, and J. R. Rumble, Jr., Phys. Rev. A **23**, 294 (1981); L. C. Pitchford and A. V. Phelps, *ibid.* **25**, 540 (1982).

[5]P. Segur, M. C. Bordage, J. P. Balaguer, and M. Yousfi, J. Comput. Phys. **50**, 116 (1983).

[6]S. L. Lin, R. E. Robson, and E. A. Mason, J. Chem. Phys. **71**, 3483 (1979).

[7]H. Tagashira, Y. Sakai, and S. Sakamoto, J. Phys. D **10**, 1051 (1977); K. Kitamori, H. Tagashira, and Y. Sakai, *ibid.* **11**, 283 (1978).

[8]I. D. Reid, Aust. J. Phys. **32**, 231 (1979).

[9]I. D. Reid and S. R. Hunter, Aust. J. Phys. **32**, 255 (1979).

[10]G. N. Haddad, S. L. Lin, and R. E. Robson, Aust. J. Phys. **34**, 243 (1981).

[11]J. Lucas, Int. J. Electron. **29**, 465 (1970); J. Lucas and H. T. Saelee, J. Phys. D **8**, 640 (1975).

[12]H. R. Skullerud, Aust. J. Phys. **27**, 195 (1974).

[13]H. A. Blevin, J. Fletcher, and S. R. Hunter, J. Phys. D **11**, 1653 (1978).

[14]W. R. L. Thomas, J. Phys. B **2**, 551 (1969).

[15]H. Tagashira, in Proceedings of the XVth International Conference on Phenomena in Ionized Gases, Minsk, 1981, Invited Papers, p. 377, and references therein (unpublished).

[16]K. J. Nygaard, S. R. Hunter, J. Fletcher, and S. R. Foltyn, Appl. Phys. Lett. **32**, 351 (1978); K. J. Nygaard, J. Fletcher, S. R. Hunter, and S. R. Foltyn, *ibid.* **32**, 612 (1978); K. J. Nygaard, H. L. Brooks, and S. R. Hunter, IEEE, J. Quantum Electron. **QE-15**, 1216 (1979).

[17]S. R. Hunter, J. G. Carter, L. G. Christophorou, and V. K. Lakdawala, in *Gaseous Dielectrics IV,* edited by L. G. Christophorou (Pergamon, New York, 1984), pp. 224–237.

[18]S. R. Hunter and L. G. Christophorou, J. Chem. Phys. **80**, 6150 (1984).

[19]R. W. Crompton, in Proceedings of the XVIth International Conference on Phenomena in Ionized Gases, Duesseldorf, 1983, Invited Papers, p. 58 (unpublished); R. W. Crompton, R. Hegerberg, and H. R. Skullerud, J. Phys. B **13**, L455 (1980). See also R. Hegerberg and R. W. Crompton, Aust. J. Phys. **36**, 831 (1983); H. R. Skullerud, *ibid.* **36**, 845 (1983).

[20]M. S. Naidu and A. N. Prasad, J. Phys. D **5**, 983 (1972).

[21]S. R. Hunter, J. G. Carter, and L. G. Christophorou (unpublished).

[22]Th. Aschwanden, presented at the 37th Gaseous Electronics Conference, Boulder, Colorado, 1984 (unpublished), and private communication.

[23]S. R. Hunter, L. G. Christophorou, D. L. McCorkle, I. Sauers, H. W. Ellis, and D. R. James, J. Phys. D **16**, 573 (1982); D. L. McCorkle, L. G. Christophorou, and S. R. Hunter, in Proceedings of the Third International Swarm Seminar, Innsbruck, 1983, edited by W. Lindinger, H. Villinger, and W. Federer, p. 37 (unpublished).

[24]L. G. Christophorou and S. R. Hunter, in *Swarms of Ions and Electrons in Gases,* edited by W. Lindinger, T. D. Märk, and F. Howorka (Springer, New York, 1984), p. 243.

[25]S. R. Hunter, Ph.D. thesis, The Flinders University of South Australia, 1977.

[26]Studies to determine the significance of electron nonconservation on the derivation of a set of electron scattering cross sections for the perfluoroalkanes are presently being conducted.

[27]N. L. Aleksandrov, I. V. Kochetov, A. P. Napartovich, V. G. Pevgov, and A. N. Starostin, Fiz. Plazmy **6**, 1365 (1980) [Sov. J. Plasma Phys. **6**, 748 (1980)].

[28]S. Yoshida, A. V. Phelps, and L. C. Pitchford, Phys. Rev. A **27**, 2858 (1983); L. C. Pitchford and A. V. Phelps, Bull. Am. Phys. Soc. **28**, 182 (1983).