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Theory of Electron Diffusion Parallel to Electric Fields. I. Theory

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Recent experimental results in many gases demonstrate that the apparent rate of electron diffusion parallel to an electric field can differ significantly from that in the perpendicular direction. We have explained this anomalous behavior by taking account of the effect of electron density gradients on the solution of the Boltzmann equation representing a pulse of electrons under the influence of a uniform electric field. When the electron collision frequency increases with energy, the theory predicts that the leading edge of the pulse has a reduced mobility because of a higher-average electron speed and collision rate. Similarly the mobility of the trailing edge is enhanced, and consequently the half width of the pulse in the field direction is characterized by a new diffusion coefficient. The ratio of the longitudinal diffusion coefficient to the transverse diffusion coefficient is given as integrals involving the momentum transfer cross section and the unperturbed energy distribution. This ratio at high electric fields is found to be approximately one-half and one-fifth, for momentum transfer cross sections that are independent of and linearly proportional to the electron energy.

I. INTRODUCTION

Many experimental studies of the mobility μ and diffusion coefficient D for electrons in gases have been carried out over the years.[1] In most cases, these studies have depended on the Townsend method[2,3] for obtaining D/μ and the time of flight (TOF) method[4,5] for obtaining μ. In the Townsend method, electrons which are emitted at a steady rate from a point source, drift under the action of a uniform electric field and diffuse laterally to produce an ever widening radial spread to the electron swarm. It is the measured width of the radial distribution of the electrons at a given drift distance that gives D/μ. In the TOF method, a one-dimensional pulse of electrons is formed, and subsequently drifts under the action of an electric field. The measured speed of the center of the pulse gives μ.

The measured electron transport coefficients D and μ have been identified in the past with theoretical coefficients derived on the assumption that the electron energy distribution has no spatial dependence.[6,7] That is, it has been assumed that an energy distribution that is strictly correct only when the electron density is spatially uniform, can be used to describe the transport properties of electrons when the electron density is nonuniform, i.e., in cases where diffusion is present. Using this assumption, the theory predicts that D/μ and μE will be a function of E/N and the collision cross sections.[8] The experimental data obtained with the Townsend and TOF methods have been found to be consistent with this theory in that (1) D/μ and μE are indeed functions of E/N,[9] and (2) the elastic cross section for helium, for example, that is constructed to give consistency between theoretical and experimental values of μ, also gives consistency between theoretical and experimental values for D/μ.[10,11] The experimental transport coefficients when analyzed on this basis have yielded information on the elastic and inelastic cross sections for many gases.[6,10–13]

It has been recognized for many years[4,14] that the TOF method should be capable of giving D/μ as well as μ. In this case D/μ is obtained by measuring the increasing width of the electron pulse in the field direction, as the pulse drifts under the action of the field. Assuming the electron energy distribution is independent of position, the diffusion coefficient parallel to the electric field determined by the TOF method should be identical to the diffusion coefficient of the Townsend method in which the diffusion is predominantly perpendicular to the field direction. Within the last two years, measurements of D/μ by the TOF method have been carried out by Wagner, Davis, and Hurst for many different gases.[15] They found that D_L/μ, where D_L is the diffusion coefficient parallel to the field, is considerably different from D_T/μ, where D_T is the diffusion coefficient transverse to the field as given by the Townsend method. For example, in argon, D_L/μ was found to be approximately one-seventh of D_T/μ at high E/N.

Previously Wannier[16] has shown that the influence of density gradients on the energy distribution function generally results in differences between the theoretical longitudinal and transverse diffusion coefficients. By considering the case where the logarithmic derivative of the ion density is uniform in the field direction, the distribution function is still independent of position, and Wannier was able to calculate for ions of mass equal to the gas molecules and for constant cross section, the longitudinal diffusion coefficient in the high field limit.

The purpose of the present work[17] is to theoretically describe the motion and spreading of an electron pulse in a TOF experiment by means of Boltzmann transport theory, and to relate the theoretical predictions with experimental measurements. The effect of the density gradients leads to the distribution function becoming a function of position. In Sec. II, the conventional transport theory, which utilizes a position independent energy distribution, is reviewed. A semiquantitative model is developed in Sec. III that takes the effect of electron-density gradients on the energy distribution into account, and yields a simple physical picture of the dominant process that leads to the anomalous longitudinal diffusion observed in the TOF experiments. In Sec. IV, a solution of the Boltzmann transport equation applicable to elastic collisions is obtained, which describes the TOF experiment and yields a formula for the longitudinal diffusion coefficient D_L. This formula is then applied to cases where the elastic cross section has a simple functional dependence on the electron energy.

For simplicity, only elastic collisions are considered in the present Paper I. In the following Paper II, the theory is extended to take inelastic collisions into account and is used to obtain D_L/μ as a function of E/N for various real gases. These results are compared with available experimental data.

II. CONVENTIONAL APPROACH

A typical TOF experiment can be described as follows. A narrow pulse of electrons is injected into a uniform electric field region containing gas atoms at a given density. After injection, the pulse will drift under the action of the electric field and spread by diffusion. Because the initial electron energy distribution does not, in general, match that characteristic of a steady state in the gas, the energy distribution as well as the drift and diffusion rates will change as the pulse moves away from the point of injection. Most of this change occurs while the pulse travels the order of an energy relaxation distance d_ϵ. This quantity, when only elastic collisions are considered, can be approximately expressed as[18]

$$d_\epsilon \simeq MeE/2m^2\nu^2 , \tag{1}$$

where M and m are the atomic and electronic masses, respectively, e is the electron charge, and ν is the electron collision frequency. In conventional transport theory, it has been implicitly assumed that after the pulse has traveled a distance large compared to d_ϵ, the electron energy distribution assumes a steady state characterized by a balance between the electrons gaining energy from the field acting on the drift current and losing energy through collisions with the gas atoms. It is at this point of the conventional approach that the effect of electron-density gradients on the electron energy distribution is neglected. The equation that expresses this balance when only elastic collisions are considered can be written as[8]

$$\frac{\partial}{\partial\epsilon}\left\{\epsilon^2 Q\left[F(\epsilon)+\frac{M}{6m}\left(\frac{eE}{NQ}\right)^2\frac{1}{\epsilon}\,\frac{\partial F(\epsilon)}{\partial\epsilon}\right]\right\}=0, \tag{2}$$

where $F(\epsilon)$ is the electron energy distribution, ϵ is the electron kinetic energy, and Q is the momentum transfer cross section which is, in general, a function of ϵ. In writing Eq. (2) it is assumed that the gas temperature T is zero. The solution of this equation, which is regular at $\epsilon = 0$ and gives the steady-state distribution, is

$$F(\epsilon)=A\exp\left[-\frac{6m}{M}\left(\frac{N}{eE}\right)^2\int_0^\epsilon \epsilon Q^2 d\epsilon\right], \tag{3}$$

where A is a normalization constant[19] such that

$$\frac{4\pi}{m}\left(\frac{2}{m}\right)^{1/2}\int_0^\infty \epsilon^{1/2}F d\epsilon = 1 . \tag{4}$$

After the electrons in the pulse have assumed this steady-state distribution, they are characterized by a mobility and diffusion coefficient that are independent of position and given by[8]

$$\mu=-\frac{8\pi e}{3m^2N}\int_0^\infty \frac{\epsilon}{Q}\frac{\partial F}{\partial\epsilon}d\epsilon , \tag{5}$$

and

$$D=\frac{8\pi}{3m^2N}\int_0^\infty \frac{\epsilon F}{Q}\,d\epsilon . \tag{6}$$

The electron density n will obey the equation of continuity given by

$$\frac{\partial n}{\partial t}=-\mu E\frac{\partial n}{\partial z}+D\nabla^2 n , \tag{7}$$

where the electric field is taken as $\vec{E}=-E\hat{k}$ where $\hat{k}$ is a unit vector along the z axis. If the pulse is still quite narrow when the electrons have reached their steady state, the solution of Eq. (7) that represents the motion and spreading of the pulse is given by

$$n=n_0\frac{\exp\{[-\rho^2-(z-\mu Et)^2]/4Dt\}}{(4\pi Dt)^{3/2}} , \tag{8}$$

where ρ is a cylindrical radial coordinate and n_0 is the total number of electrons in the pulse. It is evident from Eqs. (7) and (8) that conventional theory predicts that the diffusion coefficients parallel and perpendicular to the field are the same.

It is clear from Eq. (8) that μ can be evaluated by measuring the time it takes the pulse to travel a given distance after the electrons have assumed a steady-state distribution. In turn, D can be evaluated from the measured width of the pulse for a given drift distance. In practice, the effect due to d_ϵ can be made insignificant by working at sufficiently high gas densities, as is evident from Eq. (1) which shows that d_ϵ is proportional to $1/N$ at a given E/N. The experimentalist assumes that effects due to d_ϵ are negligible if μE and DN are found to be density independent at fixed E/N.

In order to carry out the measurement of drift time and pulse width, it is necessary to introduce a metallic boundary which perturbs the electron density from that given by Eq. (8). The effect due to boundaries can, in principle, be taken into account by using the conventional theory in the form of Eq. (7) along with the boundary condition. However, in practice, the effect due to boundaries for measurements of both D_T/μ and μE is usually small because of the high gas density used in the experiments.[20,21]

III. SEMIQUANTITATIVE MODEL

As has been stated above, it is assumed in conventional transport theory that the electrons in the pulse relax from their initial energy distribution into a distribution that is determined by a balance between the electrons gaining energy through the field acting on the drift current and losing energy through collisions with the gas atoms. This two-component balance is strictly applicable only when the electron density is spatially uniform. When the electron density is nonuniform and diffusion currents are present, the balance must also include the effect of the electrons gaining energy through the field acting on the diffusion current. In the TOF experiments, diffusion currents lead to an energy distribution that is a function of position within the pulse, and in turn leads to changes in the predicted drift and spreading characteristics of the pulse.

Before developing a quantitative description of the TOF experiment based on the Boltzmann equation, we will first give a semiquantitative discussion of the problem. The purpose of the discussion is to clarify the role that diffusion plays in affecting the energy distribution of the electrons and modifying conventional transport theory.

We assume that each electron can be characterized by a mean energy $\epsilon_m(z)$. In the steady state, the rate at which electrons gain energy from the field is equal to the rate at which they lose energy through elastic collisions with the gas atoms. Therefore,

$$n\nu(2m/M)\epsilon_m = -e\vec{E}\cdot\vec{\Gamma}\,, \tag{9}$$

where ν is the electron collision frequency and $2m/M$ is the fractional energy loss per collision. The particle current density, $\vec{\Gamma}$ is given by

$$\vec{\Gamma} = -\mu\vec{E}n - D\nabla n\,. \tag{10}$$

The quantities ν, D, and μ that appear in Eq. (9) and (10) are considered to be functions of ϵ_m. Taking $\vec{E} = -E\hat{k}$ and using Eq. (10), the energy balance given by Eq. (9) can be expressed as

$$\frac{2m}{M}\nu\epsilon_m = e\mu E^2 - eED\frac{1}{n}\frac{\partial n}{\partial z}\,. \tag{11}$$

Equation (11), after ν, μ, and D are expressed in terms of ϵ_m, can in principle be solved for ϵ_m in terms of $(1/n)\,\partial n/\partial z$. We will approximate μ and D by forms which are strictly correct only for constant collision frequency,[8] i.e., $\mu = e/m\nu$ and $D = 2\epsilon_m/3m\nu$. It is evident from Eq. (11) that when the density-gradient term is zero, the electron energy ϵ_0 is given by

$$\epsilon_0 = (M/2m^2)(eE/\nu_0)^2\,,$$

where ν_0 is the value of ν evaluated at $\epsilon_m = \epsilon_0$. By substituting $\epsilon_m = \epsilon_0 + \Delta\epsilon$ and $\nu = \nu_0 + \partial\nu/\partial\epsilon|_0\Delta\epsilon$ into Eq. (11) and solving for $\Delta\epsilon$, we can then express ϵ_m as

$$\epsilon_m = \epsilon_0\left[1 - \frac{2\epsilon_0}{3eE\left(1 + 2\dfrac{\partial\nu}{\partial\epsilon}\Big|_0\dfrac{\epsilon_0}{\nu_0}\right)}\frac{1}{n}\frac{\partial n}{\partial z}\right], \tag{12}$$

where $\partial\nu/\partial\epsilon|_0$ is the derivative of ν with respect to energy evaluated at $\epsilon_m = \epsilon_0$. In obtaining Eq. (12), we have considered only first-order terms in $\Delta\epsilon$ and $(1/n)\,\partial n/\partial z$ on the assumption that the effect of the density gradient on the electron energy is small. Equation (12) expresses the fact that ϵ_m is greater than ϵ_0 when the diffusion current adds to the drift current and is smaller when diffusion subtracts from the drift current. The electron energy is, therefore, a function of position within the electron pulse.[22]

Returning to Eq. (10) and using the expression for ϵ_m given in Eq. (12), the current density can be expressed as

$$\vec{\Gamma} = \mu_0 En\hat{k} - D_0\left(\frac{\partial n}{\partial x}\hat{i} + \frac{\partial n}{\partial y}\hat{j}\right) - D_0\left(1 - \frac{\gamma}{1+2\gamma}\right)\frac{\partial n}{\partial z}\hat{k}\,. \tag{13}$$

and where $\mu_0 = e/m\nu_0$, $D_0 = 2\epsilon_0/3m\nu_0$, and where we have defined the quantity γ as $\gamma = (\epsilon_0/\nu_0)\, \partial\nu/\partial\epsilon|_0$. It is evident from Eq. (13) that while the coefficient describing diffusion perpendicular to the field corresponds to the usual diffusion coefficient, the coefficient for diffusion parallel to the field is modified due to the dependence of μ on $(1/n)\, \partial n/\partial z$. Then, D_L and D_T can be expressed as

$$D_L = D_0[1 - \gamma/(1+2\gamma)] \ ,$$

$$\text{and} \quad D_T = D_0 \ . \tag{14}$$

It is evident from Eq. (14) that D_L can be greater or smaller than D_T depending on how ν changes with energy. That is

if $\left.\frac{\partial\nu}{\partial\epsilon}\right|_0 = 0$, then $D_L = D_T = D_0$;

or if $\left.\frac{\partial\nu}{\partial\epsilon}\right|_0 > 0$, then $D_L < D_T$;

and if $\left.\frac{\partial\nu}{\partial\epsilon}\right|_0 < 0$, then $D_L > D_T$.

Equation (14) also indicates that D_L can differ significantly from D_T when ν varies by an appreciable fraction over an energy interval equal to ϵ_0. If we take ν to vary as

$$\nu = \nu_0\,(\epsilon_m/\epsilon)_0^{(l+1)/2} \ ,$$

where l is an integer, then D_L/D_T becomes

$$D_L/D_T = (l+3)/2(l+2) \ .$$

For example for $l = -1$ (ν = const), $D_L = D_T$ and for $l = 0$ (constant cross section) $D_L = 0.75\, D_T$.

The difference between D_L and D_T in (14) arises from the change in the drift velocity μE that is associated with the increase (or decrease) of ϵ_m over ϵ_0 brought about by the electric field acting on the diffusion part of the current. In the TOF experiment, ϵ_m is greater than ϵ_0 in the leading edge of the pulse where the diffusion current adds to the drift current, and for the case of a constant cross section ($l = 0$), μE will be less than $\mu_0 E$. In the trailing edge where the diffusion current subtracts from the drift current, $\epsilon_m < \epsilon_0$ and, therefore, $\mu E > \mu_0 E$. It is evident that this change in the drift velocity on each side of the pulse leads to a narrowing of pulse and since this change is proportional to $\partial n/\partial z$, the narrowing can be characterized by a change in the coefficient for diffusion parallel to the field.

IV. QUANTITATIVE THEORY

(a) Boltzmann Transport Theory

The average properties of electrons moving through a gas, e.g., electron density, current density, mean energy, etc., can be obtained from the electron distribution function $f(\vec{r}, \vec{v}, t)$. The significance of this function is that $f(\vec{r}, \vec{v}, t)\,d\vec{r}\,d\vec{v}$ denotes the number of electrons at position $\vec{r}$ in $d\vec{r}$ and with velocity $\vec{v}$ in the range $d\vec{v}$. The distribution function in turn satisfies an equation of continuity in position and velocity space, i.e., the Boltzmann transport equation. This equation equates the rate change of the number of electrons in $d\vec{r}\,d\vec{v}$ to the net flow of electrons into this volume element. The flow in position space results from the velocity of the electrons, while in velocity space it results from their acceleration due both to collisions with the gas atoms and to the applied electric field.

There are several approximations commonly made in order to simplify the integral-differential Boltzmann equation when applied to electrons. The first is that the distribution function is *almost* spherically symmetric in velocity space, and therefore, can be adequately represented by the first two terms of an expansion in spherical harmonics involving the direction of the electron velocity. That is, $f(\vec{r}, \vec{v}, t)$ can be written as[23]

$$f(\vec{r}, \vec{v}, t) = f^0(\vec{r}, \vec{v}, t) + \vec{f}^1(\vec{r}, v) \cdot \hat{v} \ ,$$

where $\hat{v}$ is the unit velocity vector. The second approximation is that in the case of elastic collisions, to which the present Paper (I) is restricted, the fractional energy gain or loss by an electron upon colliding with a gas atom is small. This assumption is justified because of the small electron to atom mass ratio. With these approximations, the Boltzmann equation reduces to two partial differential equations for f^0 and $\vec{f}^1$ that can be expressed as[23]

$$\frac{4\pi}{m}\left(\frac{2}{m}\right)^{\frac{1}{2}} \epsilon^{\frac{1}{2}} \frac{\partial f^0}{\partial t} = \frac{16\pi N}{mM} \frac{\partial}{\partial\epsilon}\left[\epsilon^2 Q\left(f^0 + kT\frac{\partial f^0}{\partial\epsilon}\right)\right] - \frac{8\pi\epsilon}{3m^2}\nabla\cdot\vec{f}^1 - \frac{8\pi e E}{3m^2}\frac{\partial}{\partial\epsilon}(\epsilon\hat{k}\cdot\vec{f}^1) \ , \tag{15}$$

and
$$\vec{f}^1 = -\frac{1}{NQ}\left(\nabla f^0 + eE\frac{\partial f^0}{\partial \epsilon}\hat{k}\right), \tag{16}$$

where the electric field has been taken to be uniform and given by $\vec{E} = -E\hat{k}$, with $\hat{k}$ as a unit vector along the z axis, and where k is the Boltzmann constant.

The equation that f^0 must satisfy is obtained by substituting $\vec{f}^1$ from Eq. (16) into Eq. (15) and is

$$\frac{4\pi}{m}\left(\frac{2}{m}\epsilon\right)^{\frac{1}{2}}\frac{\partial f^0}{\partial t} = \frac{16\pi}{mM}\frac{\partial}{\partial \epsilon}\left[N\epsilon^2 Q\left(f^0 + kT\frac{\partial f^0}{\partial \epsilon}\right) + \frac{MeE}{6mN}\frac{\epsilon}{Q}\left(eE\frac{\partial f^0}{\partial \epsilon} + \frac{\partial f^0}{\partial z}\right)\right] + \frac{8\pi}{3m^2 N}\frac{\epsilon}{Q}\left(eE\frac{\partial^2 f^0}{\partial \epsilon\,\partial z} + \nabla^2 f^0\right). \tag{17}$$

The electron current density and the electron density, can be expressed in terms of f^0 as[23]

$$\vec{\Gamma}(\vec{r}, t) = -\frac{8\pi}{3m^2 N}\int_0^\infty \frac{\epsilon}{Q}\left(\nabla f^0 + eE\hat{k}\frac{\partial f^0}{\partial \epsilon}\right)d\epsilon, \quad \text{and} \quad n(\vec{r}, t) = \frac{4\pi}{m}\left(\frac{2}{m}\right)^{\frac{1}{2}}\int_0^\infty \epsilon^{1/2} f^0 d\epsilon. \tag{18}$$

By multiplying Eq. (17) by $d\epsilon$ and integrating from 0 to ∞, we obtain the equation of continuity in position space, i.e., $\nabla\cdot\vec{\Gamma} + \partial n/\partial t = 0$. It is to be noted that f^0 can be expressed as $f^0 = n(\vec{r}, t)F(\epsilon, \vec{r}, t)$, where F is the electron energy distribution as introduced in Sec. II, which now may be a function of $\vec{r}$ and t in addition to ϵ.

It is useful to briefly describe the physical meaning of the various terms in Eq. (17), and thereby obtain some insight into the physical processes that are neglected under the assumption that F is independent of $\vec{r}$ and t. Equation (17) is an equation of continuity for electrons in energy and position space. After being multiplied by $d\epsilon d\vec{r}$, it describes the net rate at which electrons enter $d\epsilon d\vec{r}$ at $(\epsilon, \vec{r})$. This rate is associated with either electrons gaining or losing energy within $d\vec{r}$ or electrons entering $d\vec{r}$ with energy ϵ from points outside $d\vec{r}$. The first and second terms on the right side of Eq. (17) represent electrons gaining or losing energy due to collisions with the gas atoms. The third term represents the electrons gaining or losing energy due to the field acting on the electron drift current while the fourth term is associated with the energy gain or loss due to the field acting on the electron diffusion current. These last two terms show that the electrons can gain energy from the field when more electrons flow against the field than with it and that this net flow is associated with both the drift and diffusion of the electrons. These first four terms represent the electrons gaining or losing energy within d, i.e., a divergence in energy space. The fifth and sixth terms represent the electron flow into $d\vec{r}$, and, therefore, represent a divergence in r space. The fifth term represents the net flux into $d\vec{r}$ that is associated with electron drift, and the sixth term is associated with electron diffusion. The assumption in conventional transport theory that F is independent of $\vec{r}$ and t implies that (1) the fourth, fifth, and sixth terms are small in comparison to the first three terms, and (2) that the electron energy distribution is in steady state, i.e., $\partial F/\partial t \sim 0$. The first assumption is correct only when electron diffusion can be neglected in comparison with electron drift. This condition does not hold in the TOF experiments. The second assumption is correct for the TOF experiments in that drift times of electrons in the experiments are ordinarily long in comparison to energy relaxation times with the result that the initial energy distribution has had sufficient time to relax to almost a steady-state distribution.

(b) One Dimensional Pulse

In order to go beyond the simple model developed in Sec. III, it is necessary to find a solution of Eq. (17) which is appropriate for the TOF experiment. It is clear that the proper approach would be to obtain a solution that would describe the complete evolution in time of a one-dimensional δ-function pulse of electrons introduced at $z = 0$, $t = 0$ with initial energy of ϵ_i, i.e., to find the Green's function for Eq. (17). This solution would describe the motion and spreading of the pulse as well as the relaxation of the initial energy into the final steady-state distribution. In turn, this solution could be used to build up other solutions for different initial energy distributions and pulse shapes. However, this approach would lead to mathematical complexity and to a more detailed description of the TOF experiment than is needed for comparison with the presently available results from experiment. While certain aspects of this general approach will be developed in the Appendix for completeness and where they are pertinent to the TOF experiment, the object of the present section is to obtain the part of the general solution which is applicable when the pulse is far enough from the point of injection such that the energy distribution is essentially in steady state.

We will start by assuming a solution of the form

$$f_s^{\,0}(\epsilon, z, t) = e^{isz}e^{-\omega(s)t}H(\epsilon, s).$$

This is simply one Fourier component in z of the complete solution that we seek. When $f_S{}^0$ is substituted into Eq. (17), the resulting equation for H can be written as

$$\frac{8\pi(eE)^2}{3m^2N}\frac{\partial}{\partial\epsilon}\left[\frac{\epsilon}{Q}(1+kT\beta)\left(\frac{\beta H}{1+kT\beta}+\frac{\partial H}{\partial\epsilon}\right)\right]+is\frac{8\pi eE}{3m^2N}\left(\frac{\partial}{\partial\epsilon}\frac{\epsilon H}{Q}+\frac{\epsilon}{Q}\frac{\partial H}{\partial\epsilon}\right)+(is)^2\frac{8\pi}{3m^2N}\frac{\epsilon H}{Q}+\omega(s)\frac{4\pi}{m}\left(\frac{2\epsilon}{m}\right)^{\frac{1}{2}}H=0, \tag{19}$$

where β is given by $\beta=(6m/M)(NQ/eE)^2\epsilon$. Equation (19) can be considered as an eigenvalue problem with ω the eigenvalue and H the corresponding eigenfunction. Both ω and H are functions of the parameter s, which is a direct measure of the fractional change in $f_S{}^0$ associated with a change in z, i.e., $(f^0)^{-1}\partial f^0/\partial z = is$. It would be expected that for each value of s there would exist a series of eigenvalues for ω. For $s=0$, the solution of Eq. (19) that is finite at $\epsilon=0$ and corresponds to $\omega=0$, which is the lowest eigenvalue, is

$$H_0(\epsilon, 0)=\text{const}\times\exp\left[-\int_0^\epsilon d\epsilon\beta/(1+kT\beta)\right]. \tag{20}$$

This is the spatially independent energy distribution used in conventional transport theory, and reduces to Eq. (3) when $kT=0$. The higher energy functions ($\omega>0$) for the case of $s=0$ give the additional functions required for expanding an arbitrary initial energy distribution that eventually decays to that given by Eq. (20). Likewise, for $s\neq 0$, the higher functions would be needed to describe the decay of the initial energy distribution for cases where f^0 depends on z.

In the present case, we are concerned only with the energy function $H_0(\epsilon, s)$ which is associated with the electron distribution function far from the source point where the higher energy modes are negligible. It is clear that as s deviates from zero, $H_0(\epsilon, s)$ begins to deviate from the conventional energy distribution given in Eq. (20). We will expand $H_0(\epsilon, s)$ and $\omega_0(s)$ as a power series in s, i.e.,

$$H_0(\epsilon, s)=F_0(\epsilon)+is\,F_1(\epsilon)+(is)^2F_2(\epsilon)+\cdots, \tag{21}$$

and $$\omega_0(s)=is\,\omega_1-(is)^2\omega_2+\cdots. \tag{22}$$

It is to be noted that Eq. (22) gives $\omega(0)=0$ and this implies that $F_0(\epsilon)$ will be equal to $H_0(\epsilon, 0)$ as given by Eq. (20). A set of differential equations is obtained when the expansions for $H_0(\epsilon, s)$ and $\omega_0(s)$ are substituted into Eq. (19), and the coefficients of powers in (is) are equated to zero. The first three equations of this set are

$$\frac{\partial}{\partial\epsilon}\left[\frac{\epsilon}{Q}(1+kT\beta)\left(\frac{\beta F_0}{1+kT\beta}+\frac{\partial F_0}{\partial\epsilon}\right)\right]=0, \tag{23}$$

$$\frac{8\pi(eE)^2}{3m^2N}\frac{\partial}{\partial\epsilon}\left[\frac{\epsilon}{Q}(1+kT\beta)\left(\frac{\beta F_1}{1+kT\beta}+\frac{\partial F_1}{\partial\epsilon}\right)\right]+\frac{8\pi eE}{3m^2N}\left(\frac{\partial}{\partial\epsilon}\frac{\epsilon F_0}{Q}+\frac{\epsilon}{Q}\frac{\partial F_0}{\partial\epsilon}\right)+\omega_1\frac{4\pi}{m}\left(\frac{2}{m}\epsilon\right)^{\frac{1}{2}}F_0=0, \tag{24}$$

and

$$\begin{aligned}\frac{8\pi(eE)^2}{3m^2N}\frac{\partial}{\partial\epsilon}\left[\frac{\epsilon}{Q}(1+\beta kT)\left(\frac{\beta F_2}{1+kT\beta}+\frac{\partial F_2}{\partial\epsilon}\right)\right]+\frac{8\pi eE}{3m^2N}\left(\frac{\partial}{\partial\epsilon}\frac{\epsilon F_1}{Q}+\frac{\epsilon}{Q}\frac{\partial F_1}{\partial\epsilon}\right)+\frac{8\pi}{3m^2N}\frac{\epsilon F_0}{Q}\\+\frac{4\pi}{m}\left(\frac{2\epsilon}{m}\right)^{\frac{1}{2}}(\omega_1F_1-\omega_2F_0)=0.\end{aligned} \tag{25}$$

These equations determine, in succession, the functions $F_i(\epsilon)$ and the values for ω_i for $i>0$ starting from F_0 given by Eq. (20). We will take F_0 to be normalized according to Eq. (4). Multiplying Eq. (24) by $d\epsilon$ and integrating from 0 to ∞ gives

$$\omega_1=-(8\pi eE/3m^2N)\int_0^\infty(\epsilon/Q)(\partial F_0/\partial\epsilon)d\epsilon=\mu_0E, \tag{26}$$

where μ_0 is the usual mobility coefficient given by Eq. (5). It is evident that ω_1 is the usual drift velocity. The solution of Eq. (24) that is finite at $\epsilon=0$ is

$$F_1=-\frac{F_0(\epsilon)}{eE}\int_0^{\epsilon}\frac{Q(x)}{x[1+kT\beta(x)]F_0(x)}\left[\frac{xF_0(x)}{Q(x)}+\int_0^x\frac{y}{Q(y)}\frac{\partial F_0(y)}{\partial y}\,dy+\frac{3\omega_1 N}{eE}\left(\frac{m}{2}\right)^{\frac{1}{2}}\int_0^x y^{1/2}F_0(y)dy\right]dx, \tag{27}$$

where $F_1(0)$ has been set equal to zero.[24]

The quantity ω_2 is obtained by integrating Eq. (25) over energy from 0 to ∞ and is

$$\omega_2=D_0+\frac{8\pi eE}{3m^2N}\int_0^{\infty}\frac{\epsilon}{Q}\frac{\partial F_1}{\partial\epsilon}\,d\epsilon+\frac{\omega_1 4\pi}{m}\left(\frac{2}{m}\right)^{\frac{1}{2}}\int_0^{\infty}\epsilon^{1/2}F_1 d\epsilon, \tag{28}$$

where D_0 is the usual diffusion coefficient given by Eq. (6). The higher-order F_i's and ω_i's can be obtained in a similar manner.

We can now express $f_s{}^0$ as

$$f_s{}^0(\epsilon,z,t)=e^{is(z-\omega_1 t)}e^{-s^2\omega_2 t}[F_0+isF_1+(is)^2F_2+(is)^3(F_3+\omega_3 tF_0)\cdots], \tag{29}$$

where the function $\exp(-(is)^p\omega_p t)$ has been expanded in a power series in (is) for $p>3$. We now form a Fourier integral, using $f_s{}^0$ given in Eq. (29), i.e.,

$$f^0(\epsilon,z,t)=(2\pi)^{-1}\int_{-\infty}^{\infty}ds f_s{}^0(\epsilon,z,t).$$

If we note that

$$\int_{-\infty}^{\infty}ds\, e^{is(z-\omega_1 t)}e^{-s^2\omega_2 t)}(is)^m=\frac{\partial^m}{\partial z^m}\int_{-\infty}^{\infty}ds\, e^{is(z-\omega_1 t)}e^{-s^2\omega_2 t)},$$

and that[25]

$$(2\pi)^{-1}\int_{-\infty}^{\infty}dse^{is(z-\omega_1 t)}e^{-s^2\omega_2 t}=\exp[-(z-\omega_1 t)^2/4\omega_2 t]/(4\pi\omega_2 t)^{1/2},$$

then f^0 can be expressed as

$$f^0(\epsilon,z,t)=\left(F_0+F_1\frac{\partial}{\partial z}+F_2\frac{\partial^2}{\partial z^2}+(F_3+\omega_3 tF_0)\frac{\partial^3}{\partial z^3}+\cdots\right)P(z), \tag{30}$$

where $P(z)=\exp[-(z-\omega_1 t)^2/4\omega_2 t]/(4\pi\omega_2 t)^{1/2}$.

It will be shown in the Appendix that this solution is the far distance part of the Green's function for Eq. (17) for electrons that are initially injected with zero energy. This solution should, therefore, be appropriate for describing the one-dimensional electron pulse of a TOF experiment far from the source point.

The electron density corresponding to f^0 as given by Eq. (30) can be obtained by using Eq. (18). The density can be written as

$$n(z,t)=\left(1+A_1\frac{\partial}{\partial z}+A_2\frac{\partial^2}{\partial z^2}+\cdots\right)P(z), \tag{31}$$

where $A_1=(4\pi/m)(2/m)^{1/2}\int_0^{\infty}\epsilon^{1/2}F_1 d\epsilon,$ (32)

and A_i, with $i>1$, are given by similar expressions.

The two quantities that are measured in a TOF experiment are the position of the center of the pulse as a function of time and the width of the pulse as a function of time. We will consider the average distance z_{av}, and the average square of the deviation from z_{av}, $(z-z_{\text{av}})_{\text{av}}{}^2$, as corresponding to the experimentally measured quantities, where

$$z_{\text{av}}=\int_{-\infty}^{\infty}zn(z,t)dz, \quad\text{and}\quad (z-z_{\text{av}})_{\text{av}}{}^2=\int_{-\infty}^{\infty}(z-z_{\text{av}})^2 n(z,t)dz.$$

Using the properties of the Gaussian function, it is easily shown that

$$z_{\mathrm{av}} = \omega_1 t - A_1, \tag{33}$$

and $$(z - z_{\mathrm{av}})_{\mathrm{av}}{}^2 = 2\omega_2 t - A_1{}^2 + 2A_2. \tag{34}$$

It is to be noted that in calculating the above parameters which characterize the position and the width of the pulse, it is only necessary to consider terms in Eq. (31) up to the second derivative in z. The higher terms are necessary only in describing higher-order shape characteristics of the pulse.

It follows from Eqs. (23), (24), and (25) that F_0 is independent of N, and F_1 and F_2 are proportional to $1/N$ and $1/N^2$, respectively. Therefore, ω_1 is independent of N, ω_2 and A_1 are proportional to $1/N$, and A_2 is proportional to $1/N^2$. Thus in the limit of high gas density, z_{av} and $(z_{\mathrm{av}})_{\mathrm{av}}{}^2$ can be expressed as

$$z_{\mathrm{av}} \simeq \omega_1 t = \mu_0 E t, \quad \text{and} \quad (z - z_{\mathrm{av}})_{\mathrm{av}}{}^2 \simeq 2\omega_2 t = 2D_L t,$$

where D_L has been set equal to ω_2. The electron density in this limit can be written as

$$n(z,t) = \exp[-(z - \mu_0 E t)^2/4D_L t]/(4\pi D_L t)^{1/2}.$$

We, therefore, have found a solution of Eq. (17), which in the limit of high gas density yields an electron-density pulse which has the conventional Gaussian shape of Eq. (8). While the usual mobility coefficient characterizes the motion of the pulse, the width of the pulse in the field direction is given in terms of a new longitudinal diffusion coefficient given by $D_L = \omega_2$, where ω_2 is given by Eq. (28).

(c) A Simple Application of the Theory

We will now consider the application of the theory in the case of a momentum transfer cross section that varies as,

$$Q(\epsilon) = Q_0(\epsilon/\epsilon_0)^{l/2},$$

where Q_0 is the cross section at the arbitrary reference energy ϵ_0 and l is an integer. The quantity D_L/D_0 has been calculated[26] along with the parameters which characterize the deviation of z_{av} and $(z - z_{\mathrm{av}})_{\mathrm{av}}{}^2$ from their high-pressure limits. This calculation was carried out by first determining F_0, F_1, and F_2 from Eqs. (23)–(25) and evaluating ω_2, A_1, and A_2 from Eqs. (28) and (32). It was found that D_L/D_0 approaches a definite limit at high E/N which is consistent with the results of Sec. III.

Table I gives values of D_L/D_0 as a function of l in the limit of high E/N.[27] The results for $l = -1$ (constant collision frequency) and $l = 0$ (constant cross section) are in qualitative agreement with the results of Sec. III. Figure 1 illustrates the variation of D_L/D_0 as a function of E/N for the various values of l. As is expected, D_L/D_0 approaches unity in the limit of low E/N, where the electron diffusion is governed primarily by the thermal motion of the gas atoms, rather than the electric field.

Figure 2 shows the functions F_0, NF_1, and N^2F_2 for the case of constant cross section ($l = 0$). The function F_0 is a Druyvesteyn distribution as is expected for this case at high E/N.

The quantities A_1 and $2A_2 - A_1{}^2$, which are pressure-dependent correction terms to $\mu_0 E t$ and $2D_L t$ in Eqs. (33) and (34), were also calculated. These quantities have the dimensions of cm and cm² and are proportional to $1/N$ and $1/N^2$, respectively. Using $D_0/\mu_0 E$ as a normalization factor, the normalized quantities were found to approach a definite limit at high E/N. Table I gives values for these quantities at high E/N for

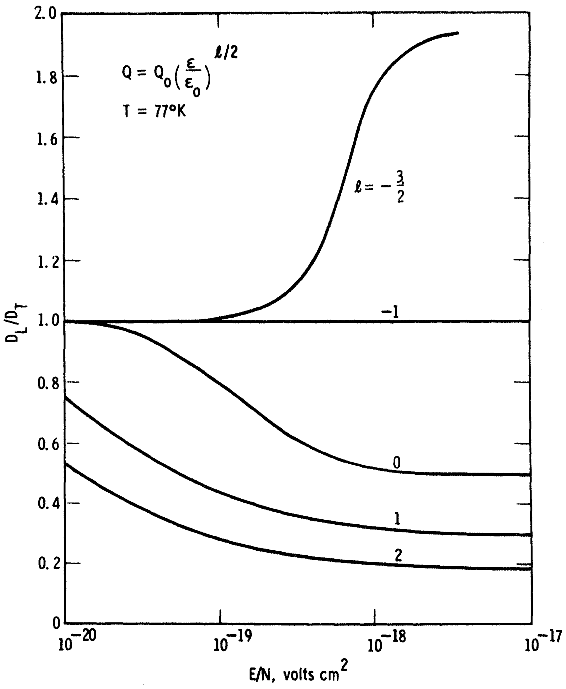

FIG. 1. D_L/D_T as a function of E/N for various values of the parameter l. The molecular weight is taken as 4.

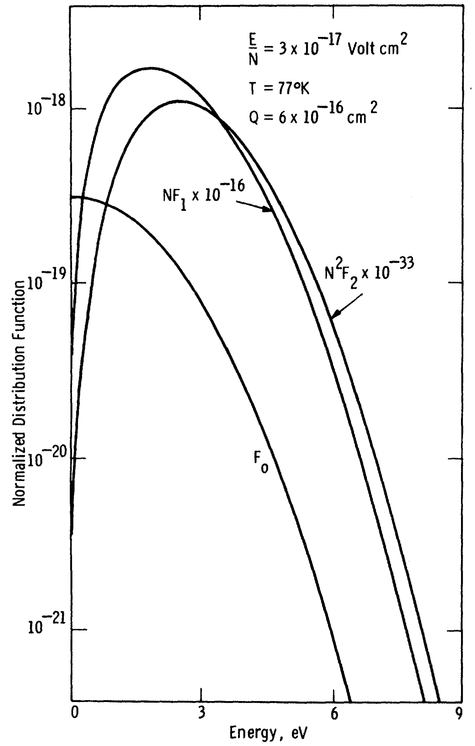

FIG. 2. F_0, NF_1, and N^2F_2 as a function of electron energy for the case of constant cross section in the high E/N limit. The units of F_0, F_1, and F_2 are cm^{-3} sec^3, cm^{-2} sec^3, and cm^{-1} sec^3, respectively. The molecular weight is taken as 4.

TABLE I. Results for D_L/D_0.

l	D_L/D_0	$A_1\mu_0E/D_0$	$(A_2-A_1^2/2)\ (\mu_0E/D_0)^2$
$-\frac{3}{2}$	1.95	~3.6	~13
-1	1.00	3.0	4.5
0	0.495	2.1	1.25
1	0.29	1.4	0.4
2	0.18	0.85	0.15

various values of l.

Since it can be shown[28] that $D_0/\mu_0E \sim d_\epsilon$, it is evident from Table I that the correction terms to μ_0Et and $(4D_Lt)^{1/2}$ are almost of order d_ϵ. Thus provided $D_0/\mu_0E \ll z_{av}$ and $(D_0/\mu_0E)^2 \ll (z - z_{av})_{av}{}^2$, the corrections involved in the interpretation of measured transit times and pulse widths are small, and thus the pulse can be characterized by a mobility and diffusion coefficient which is proportional to $1/N$.

That the correction terms to μ_0Et and $(4D_Lt)^{1/2}$ are of the order of d_ϵ is a reflection of the fact that the "far distance" solution is affected by the initial electron distribution, and the effects are associated with the relaxation of the initial electron energy distribution to its steady-state form. Since the higher energy modes decay at least as fast as $\exp(-z_{av}/d_\epsilon)$, the corrections represented by A_1 and A_2 in the lowest mode should be accurate when $z_{av} \geq 10\, d_\epsilon$. It will be shown in the Appendix that the magnitude of A_1 and A_2 depend on the initial energy distribution. Since the values of Table I are for the case of an initial energy of zero, they can only be taken as a semiquantitative measure for the corrections in real experiments. The serious application of these corrections to actual experiments involves a calculation of A_1 and A_2 using the initial energy distribution of the electrons at the point of injection.

(d) Extension to Three Dimensions

In Sec. IV(b), a one-dimensional solution of Eq. (17) was obtained which in the limit of high gas density, a limit which is appropriate to actual TOF experiments, gives an electron pulse which is characterized by a new longitudinal diffusion coefficient D_L. In the present section, this solution will be generalized to three dimensions in order to show that in the high-gas-density limit the transverse diffusion is still given by the usual coefficient D_0.

We will consider a cylindrically symmetric case, and the ∇^2 term in Eq. (15) will now include the term

$$\nabla_\rho{}^2 = \frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial f^0}{\partial\rho}\right).$$

Now $f_s{}^0(\epsilon, \rho, z, t)$ can be written as

$$f_s{}^0 = \exp[-isz - \omega(s, K^2)t]\, J_0(K\rho) H(\epsilon, s, K^2), \qquad (35)$$

where $J_0(K\rho)$ is the zero-order Bessel function of the first kind. On substituting $f_s{}^0$ given by Eq. (35) into Eq. (17), we obtain an equation similar to Eq. (19) with the additional term $-K^2(8\pi/3m^2N)(\epsilon/Q)H$. Because there are two parameters K^2 and s, we will expand $H(\epsilon, s, K^2)$ and $\omega(s, K^2)$ in a double power series in (is) and K^2, i.e.,

$$H(\epsilon,\ s, K^2) = F_{00} + F_{10}(is) + F_{01}K^2 + F_{20}(is)^2 + F_{11}(is)K^2 + F_{02}K^4 + \cdots,$$

and $\omega(s,K^2)=\omega_{10}(is)+\omega_{01}K^2-\omega_{20}(is)^2+\omega_{11}isK^2+\cdots$.

When these expressions are substituted into the equation analogous to Eq. (19), a series of differential equations analogous to Eqs. (23), etc., are obtained corresponding to various orders of (is) and K^2. These equations can be solved in succession to give F_{ij}'s and ω_{ij}'s starting from $F_{00}=F_0$. In this way it can be shown that

$$F_{10}=F_1,\quad F_{20}=F_2,\quad \omega_{10}=\omega_1=\mu_0 E,\quad \omega_{01}=D_0 \text{ and } \omega_{20}=\omega_2=D_L\ .$$

Then using $f_S{}^0$ given in Eq. (35), a Fourier-Bessel integral for f^0 can be written as

$$f^0(\epsilon,z,\rho,t)=(2\pi)^{-2}\int_{-\infty}^{\infty}ds\int_0^{\infty}KdK\,e^{is(z-\omega_{10})t}\,e^{-s^2\omega_{20}t}\,e^{-\omega_{01}K^2t}\,J_0(K\rho)$$

$$\times\left[F_{00}+isF_{10}+(is)^2F_{20}+K^2F_{01}+isK^2(F_{11}-\omega_{11}tF_{00})+K^4(F_{02}-\omega_{02}tF_{00})+\cdots\right]\ .$$

This can be expressed as

$$f^0=\left(F_{00}+F_{10}\frac{\partial}{\partial z}+F_{20}\frac{\partial^2}{\partial z^2}-F_{01}\nabla_\rho{}^2-(F_{11}-\omega_{11}tF_{00})\frac{\partial}{\partial z}\nabla_\rho{}^2+\cdots\right)Q(z,\rho)\ ,$$

where[29]

$$Q(z,\rho)=\left\{\exp[-(z-\mu_0Et)^2/4D_Lt]/(4\pi D_Lt)^{1/2}\right\}\exp(-\rho^2/4D_0t)/4\pi D_0t\ . \tag{36}$$

In turn the electron density is given by

$$n(z,\rho,t)=\left(A_{00}+A_{10}\frac{\partial}{\partial z}+A_{20}\frac{\partial^2}{\partial z^2}-A_{01}\nabla_\rho{}^2+\cdots\right)Q(\rho,z)\ ,$$

where A_{ij} are defined in the same way as A_i in Sec. IV(b).

We can again calculate the quantities z_{av}, $(z-z_{\text{av}})_{\text{av}}{}^2$, and in addition $\rho_{\text{av}}{}^2$, where

$$\rho_{\text{av}}{}^2=\int_{-\infty}^{\infty}\int_0^{\infty}\rho^2 n(z,\rho,t)2\pi\rho d\rho dz\ .$$

Using the properties of the Gaussian function and noting that $\int_0^\infty \rho\nabla_\rho{}^2Qd\rho=0$, the above averages are

$$z_{\text{av}}=\mu_0Et-A_{10}\ ,\quad (z-z_{\text{av}})_{\text{av}}{}^2=2D_Lt-A_{10}{}^2+2A_{20}\ ,\quad \text{and}\quad \rho_{\text{av}}{}^2=4D_0t-4A_{01}\ .$$

Since A_{10} is proportional to $1/N$, and A_{20} and A_{01} are proportional to $1/N^2$, in the limit of high gas densities the motion of the pulse and the width parallel to the field can be described in terms of μ_0 and D_L, while the width in the transverse direction is characterized by the conventional diffusion coefficient D_0. In this limit the density is given by $Q(z,\rho)$ of Eq. (36).

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APPENDIX

It was stated without proof in Sec. IV(b) that the magnitude of A_1 and A_2 depends on the initial energy distribution of the electrons. It is the purpose of this Appendix to demonstrate this dependence by means of the Green's function for Eq. (17).

We wish to find the solution of Eq. (17) when a source term of the form $-\delta(z)\delta(t)\delta(\epsilon-\epsilon_i)$ is included on the left-hand side of the equation. This term represents one electron being introduced at $z=0$ with energy ϵ_i at $t=0$. The solution $G(z,t,\epsilon,\epsilon_i)$ can be expressed as

$$G=(m/4\pi)(m/2\epsilon_i)^{1/2}\int_{-\infty}^{\infty}ds\,e^{isz}\left[\textstyle\sum_l S(t)\,e^{-\Omega_l(s)t}\,r(\epsilon_i,s)H_l(\epsilon_i,s)H_l(\epsilon,s)\right]\ , \tag{A1}$$

where the sum is taken over the complete set of eigenfunctions $H_l(\epsilon,s)$, each of which corresponds to an eigenvalue $\Omega_l(s)$, and which are generated by the differential equation

$$\frac{8\pi(eE)^2}{3m^2N}\frac{\partial}{\partial\epsilon}\left[\frac{\epsilon(1+kT\beta)}{Q}\left(\frac{\beta H_l}{1+kT\beta}+\frac{\partial H_l}{\partial\epsilon}\right)\right]+is\frac{8\pi eE}{3m^2N}\left[\frac{\partial}{\partial\epsilon}\left(\frac{\epsilon H_l}{Q}\right)+\frac{\epsilon}{Q}\frac{\partial H_l}{\partial\epsilon}\right]-s^2\frac{8\pi}{3m^2N}\frac{\epsilon H_l}{Q}$$

$$=-\frac{4\pi}{m}\left(\frac{2\epsilon}{m}\right)^{\frac{1}{2}}\Omega_l H_l\,.$$

The functions $H_i(\epsilon, s)$ are orthogonal to each other with respect to the density-function $r(\epsilon,s)$, i.e.,

$$\int_0^\infty rH_lH_j\,d\epsilon=\delta_{lj}\,,\quad\text{where}\quad r(\epsilon,s)=\left(\frac{2\epsilon}{m}\right)^{\frac{1}{2}}\frac{3mN}{2(eE)^2}\exp\int_0^\epsilon\left(\frac{\beta}{1+\beta kT}+\frac{2is}{eE(1+\beta kT)}\right)d\epsilon\,.$$

In Eq. (A1), $S(t)$ is the unit or step function.

It is clear that $\Omega_0(0)$ is zero and $H_0(\epsilon,0)$ is equal to F_0. The functions $H_l(\epsilon,s)$ and $\Omega_l(s)$ for l and s greater than zero cannot be expressed as known functions for a general $Q(\epsilon)$. However, in the special case of constant collision frequency, these functions can be represented by known functions, and this special case can serve as a qualitative representation of the more general case. For constant collision frequency $\Omega_l(s)$ is given by

$$\Omega_l(s)=\frac{2m\nu}{M}\left\{\frac{3}{4}\left[\left(1+i\frac{4MeEs}{3(m\nu)^2}\right)^{\frac{1}{2}}-1\right]+l\left(1+i\frac{4MeEs}{3(m\nu)^2}\right)^{\frac{1}{2}}\right\}.$$

We see that for $s=0$, Ω_0 is zero and the higher eigenvalues are

$$\Omega_l(0)=2m\nu l/M=l/\tau_\epsilon\,.$$

That is, $\Omega_l(0)$ is given as a multiple of the reciprocal of the energy relaxation time for the electrons. When s differs from zero, the real part of $\Omega_l(s)$ for any l is positive and greater than $\Omega_l(0)$. Therefore, after a time of the order of τ_ϵ, the contribution to the Green's function by the higher modes ($l>1$) becomes small in comparison to the lowest mode ($l=0$). The pulse can then accurately be described in terms of $H_0(\epsilon,s)$ alone. It is this part of the Green's function that was obtained in Sec. IV(b) and which is appropriate to actual TOF experiments. We will assume that the magnitude of the eigenvalues $\Omega_l(s)$, as obtained for the case of a constant collision frequency, gives a reasonable representation of the magnitude for the general case with any $Q(\epsilon)$.

We now return to Eq. (A1) and consider only $l=0$ terms. We proceed as in the text and expand $H_0(\epsilon,s)$, $\Omega_0(s)$, and $r(\epsilon,s)$ in power series in (is). When these expansions are substituted into Eq. (A1), the form of $r(\epsilon_i,s)H_0(\epsilon_i,s)H_0(\epsilon,s)$ carried out to order $(is)^2$ can be written as

$$F_0+is\left\{F_1(\epsilon)+\frac{F_0(\epsilon)F_1(\epsilon_i)}{F_0(\epsilon_i)}+\frac{2F_0(\epsilon)}{eE}\int_0^{\epsilon_i}\frac{d\epsilon}{1+kT\beta}\right\}+(is)^2\left\{F_2(\epsilon)+\frac{F_0(\epsilon)F_2(\epsilon_i)}{F_0(\epsilon_i)}+\frac{2}{eE}\left[F_1(\epsilon)+\frac{F_1(\epsilon_i)F_0(\epsilon)}{F_0(\epsilon_i)}\right]\right.$$

$$\left.\times\int_0^{\epsilon_i}\frac{d\epsilon}{1+kT\beta}+\frac{F_1(\epsilon_i)F_1(\epsilon)}{F_0(\epsilon_i)}+\frac{2F_0(\epsilon)}{(eE)^2}\left(\int_0^{\epsilon_i}\frac{d\epsilon}{1+kT\beta}\right)^2\right\},\tag{A2}$$

where the functions F_0, F_1, and F_2 are the same as those in the text.[30] The coefficients of is and $(is)^2$ are now functions of ϵ_i, and therefore the magnitude of the constants that correspond to A_1 and A_2 will now be functions of the initial energy. When ϵ_i is zero, the expression in (A2) reduces to that given in Eq. (21) and, therefore, the solution of Eq. (17) as obtained in the text corresponds to zero initial energy. It is to be noted that ω_1 and ω_2 are still defined by Eqs. (26) and (28). The Green's function ($l=0$) could now be used to evaluate the constants corresponding to A_1 and A_2 for any initial energy distribution.

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[27] The result that, in general, $D_L \neq D_T$ should also apply to hot electrons in semiconductors. In fact, the value of D_L/D_T, as given in Table I for constant Q, should be valid when acoustic mode scattering is dominant; for a discussion of acoustic mode scattering and its relation to constant Q for electrons in gases, see Esther M. Conwell, *High Field Transport in Semiconductors* (Academic Press, Inc., New York, 1967), Chap. V.

[28] From Eq. (11), $\epsilon_m/\tau_\epsilon \sim e\mu E^2$ and noting that $D_0/\mu_0 E \sim \epsilon_m/eE$, it follows that $D_0/\mu_0 E \sim d_\epsilon$.

[29] Use is made of the integral

$$\int_0^\infty K dK e^{-\nu K^2 t} J_0(K\rho) = \exp[-\rho^2/4\nu t]/2\nu t\,;$$

see G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, New York 1952), Chap. 13, p. 393.

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