# Energy-diffusion calculation of the electron-swarm distribution function

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An approximate treatment of the Boltzmann collision integral for electrons in a gas, valid for small fractional average energy loss, is studied. It is essentially a Fokker-Planck expansion in energy space, including mean energy loss (dynamical friction) and energy straggling (coefficient of diffusion). When applied to electron swarms in weakly ionized gases, treating angle variables in the two-term Legendre series, there results a useful, physically meaningful, differential equation for the time evolution of the energy spectrum in a time-dependent electric field. Elastic scattering, and inelastic and superelastic energy-transfer collisions are included. The time-independent solution in a constant field is a simple approximate expression for the steady-state energy spectrum of swarm electrons. The physical meaning of its functional form is made clear by showing its relation to ordinary diffusion-convection theory. Previous spectra by Pidduck [Proc. R. Soc. London Ser. A 88, 296 (1913); Proc. London Math. Soc. 15, 89 (1916); Q. J. Math. 7, 199 (1936)]; Druyvesteyn [Physica 10, 61 (1930)]; Davydov [Phys. Z. Sowjetunion 8, 59 (1935)]; Morse, Allis, and Lamar [Phys. Rev. 48, 412 (1935)]; Chapman and Cowling [ The Mathematical Theory of Non-Uniform Gases, 2nd ed. (Cambridge University Press, Cambridge, 1952), p. 350]; and Wannier [Am. J. Phys. 39, 281 (1971)] are special cases. The reasons for the inadequacy of the continuous-slowing-down approximation (CSDA) become apparent. The new spectrum is exact in the limit of small quantum transition energies. It is further shown that the CSDA violates detailed balance. Consequences of detailed balance on the loss function and related functions are investigated, and the Boltzmann H theorem is studied. During non-steady-state behavior, collisions may increase or decrease the swarm entropy, but the effect of the electric field is always to increase entropy. The spectrum is used with experimental cross sections to compute transport coefficients in O<sub>2</sub> and N<sub>2</sub>, in both of which fractional average energy loss is acceptably small over most energy ranges. Agreement with compiled swarm data is excellent over more than four orders of magnitude in E/N for most coefficients, except at certain energies in  $N_2$  that strain the approximation's validity. In the absence of an electric field, the inclusion of energy straggling provides a treatment of spectral relaxation valid for arbitrary energies that is an improvement over common mean-stopping-power formulas.

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# I. INTRODUCTION

The behavior of the electron-energy spectrum in a weakly ionized gas in an electric field is a problem of continuing interest in plasma dynamics. In the "swarm" regime electrons are generally considered to have energies from zero to several electron volts or several tens of electron volts, or possibly higher. The spectrum is controlled by the Boltzmann equation, and is determined by a balance between energy gain in an electric field in the presence of momentum-transfer collisions, and energy loss to elastic recoil and inelastic collisions with host molecules. The spectrum controls quantities of interest such as mean swarm energy, mean momentum- and energy-transfercollision frequencies, rates of chemical reactions, electrical conductivity, diffusion, avalanching, etc. Weakly ionized gases (here defined as electron-neutral collisions dominating electron-ion or electron-electron collisions) occur frequently in natural and laboratory situations (e.g., the ionosphere, or gas discharges).

For the Boltzmann distribution function  $f(\mathbf{r}, \mathbf{v}, t)$  it is customary to treat angle variables in velocity space by an expansion in Legendre polynomials in the angle  $\theta$  between the velocity  $\mathbf{v}$  and the electric field  $\mathbf{E}$ , enabling one to take advantage of the small drift energy compared with random thermal energy, which implies that the series converges quickly. Further progress must then contend with the resulting coupled equations for the coefficient functions and with the collision integral.

Early analytic work concentrated on the first two terms in this Legendre expansion (not uncommon in recent work also), sufficient to obtain the energy spectrum (the  $P_0$  term), and the first-order anisotropy in the distribution function  $(P_1)$  which determines drift velocity. The collision integral was handled by assuming only elastic collisions with constant cross section (e.g., the Druyvesteyn case [1]) or with variable cross section (Morse, Allis, and Lamar [2]). Finite-gas-temperature effects correcting for thermal motion of scatterers could also be taken into account (Davydov [3], Chapman and Cowling [4], and Wannier [5]). With these simplifications the steady-state energy spectrum could be obtained explicitly in closed form. The restriction to essentially elastic collisions limited applicability to only weak electric fields or to monatomic gases. These treatments all had in common that the collisional energy loss was treated in the continuous-slowing-down approximation (CSDA) in which all electrons of energy w were taken to lose energy

at the same rate, the mean rate for electrons of that energy. The elastic-recoil-energy-loss rate is quite small, and the approximation is not bad. The literature details this classical approach [6-8] and contains historical surveys [7,9,10]. Later work relaxed the CSDA for elastic collisions. Accounts of these methods are presented in texts [11-13].

Attempts to obtain closed-form expressions for the energy spectrum at higher  $E/N_0$  were thwarted by complicated electron-molecule interactions such as rotational and vibrational collisions in diatomic gases, with attendant larger energy jumps. Their cross sections were only poorly known, if at all. One could, however, consider these interactions as given, providing a generalized mean loss rate  $N_0L$  (eV/cm), where

$$L(w) = \sum_{k} w_k \sigma_k(w) . \qquad (1.1)$$

Here  $\sigma_k$  is the cross section for exciting state k, and  $w_k$  is electron energy loss upon excitation.  $N_0$  is background gas density, and we have written L for the case that all molecules are in the ground state. Again approximating the complete collision integral by only mean energy loss, one can obtain the generalized CSDA expression for the spectrum in closed form,

$$F = F_0 \exp\left[-\int_0^w \frac{3\sigma_m L}{\left(eE/N_0\right)^2} dw\right], \qquad (1.2)$$

where  $F_0$  is a normalization constant, and  $\sigma_m$  is the momentum-transfer cross section.

More recently, cross sections have become better known in important gases. At the same time numerical techniques have allowed actual calculation of the energy spectrum by direct solution of the Boltzmann equation, apparently obviating the need for further approximate analytic studies. More terms in the Legendre expansion can be retained and their effect studied.

In the present article we reinvestigate analytic treatments of the collision integral. It is emphasized that the actual physical process that determines the spectrum is spread of energy gain and loss about the mean rates, and that this spread is as important as the mean rates. This makes clear the physical reason for the inadequacy of the CSDA, which neglects spread in energy loss about the mean. It is simple to retain an approximation to the loss spread, valid when fractional average energy loss per energy-transfer collision is small, which is often the case. The fact that inelastic energy loss is discontinuous does not preclude such a treatment, and much physics can be learned from it. The procedure is essentially a onedimensional Fokker-Planck approximation to the inelastic collision integral in energy space. This reduces the collision integral to differential form, and results in a relatively simple differential (rather than integro-differential) equation for the time evolution of the energy spectrum in time-dependent electric fields or prescribed sources. It is valid for time variations slow compared with the momentum-transfer-collision frequency, but on any time scale relative to the energy-transfer-collision frequency.

In the steady state the equation can be solved analyti-

cally (reduced to quadratures), resulting in a closed-form expression for the energy spectrum essentially no more complicated in form than the CSDA, but substantially more accurate. It involves the momentum-transfer cross section and two sums over energy-transfer cross sections: L and a second moment  $\mathcal{M}$  describing straggling (spread of energy loss). Straggling allows some electrons to lose energy more slowly than the mean rate, thereby supporting the high-energy tail and, among other things, raising the avalanche rate above the CSDA. The spectrum's functional form is readily understandable in terms of ordinary diffusion and convection theory, and terms in the expression have simple physical meanings. Earlier spectra by Pidduck [14]; Davydov [3]; Druyvesteyn [1]; Morse, Allis, and Lamar [2]; Chapman and Cowling [4]; and Wannier [5] are special cases, and the domain of validity of each can be seen from a unified physical perspective. We demonstrate that the new spectrum is exact in the limit of small molecular quantum transition energies (fractional average energy loss going to 0). Consideration of this limit permits the direct demonstration that the CSDA violates detailed balance.

The expression is applied to  $O_2$ , which has relatively small fractional energy loss. We also apply it to  $N_2$  even though the 2.5-eV resonance spike and the high first electronic state stress the validity of the Fokker-Planck-type approximation. Swarm parameters and elastic, rotational, vibrational, and electronic cross sections are relatively well known for these two gases. Using these cross sections, the spectrum reproduces swarm parameters remarkably well over nearly five orders of magnitude in  $E/N_0$  with exceptions at certain energies in  $N_2$ .

The spectrum and time-dependent equation should be useful for approximate calculations in both steady-state and time-dependent cases, for basic theoretical studies, for developing physical insight, for parameter studies, and for scaling into regions not presently covered by experiments.

In the swarm regime, McCormack [15] and Braglia [16] have previously investigated effects of inelastic collisions, but have not presented the closed-form expression for the spectrum in terms of cross-section sums, or directly compared with data. Braglia and Ferrari [17] use a similar Fokker-Planck-type expansion to study plasma conductivity at microwave frequencies. Gurevich [18] has studied a model of velocity diffusion for the problem of runaway electrons, the opposite regime from a nearisotropic swarm.

Section II discusses the Boltzmann-equation formalism and summarizes the usual Legendre polynomial expansion for angle variables. Section III discusses the collision integral and the  $L, \mathcal{M}$  approximation to it. Section IV presents the equation for the time evolution of the energy spectrum and its steady-state solution, and shows its relation to ordinary diffusion-convection theory. Section V draws inferences from detailed balance, while Sec. VI investigates the limit of small quantum transition energies, showing the relation between L and  $\mathcal{M}$ , and demonstrates that the CSDA violates detailed balance. Section VII studies the Boltzmann H theorem, giving its explicit form in terms of L and  $\mathcal{M}$ . Sections VIII and IX compute and compare swarm coefficients with data in  $O_2$  and  $N_2$ .

## **II. BOLTZMANN EQUATION**

Ignoring inessential spatial variation or a magnetic field, the Boltzmann equation for the electron distribution function  $f(\mathbf{v}, t)$  in an electric field E is

$$\frac{\partial f}{\partial t} - \frac{e\mathbf{E}}{m} \cdot \nabla_v f = C + (\text{sources}) - (\text{sinks}) . \qquad (2.1)$$

Here e is the magnitude of the electron charge and m its mass. Sources may be x-ray ionization, avalanching, or ionization by the passage of fast charged particles. Sinks include recombination or attachment. Actual sources or sinks are problem specific, and are not considered in detail here. We concentrate on the effects of E and collision integral C in determining f. We shall also use  $F(v) = \int f(\mathbf{v}) d\Omega_{v},$ and the energy spectrum g(w) = (v/m)F, normalized to  $\int F(v)v^2 dv = \int g(w)dw$ = n (the electron density), where  $w = \frac{1}{2}mv^2$  is the electron energy. F will be considered a function of w and is also referred to as the energy spectrum.

#### A. Legendre expansions

For reduced electric fields  $E/N_0$  not too large, where  $N_0$  is the gas density,  $V_{\text{drift}} \ll V_{\text{thermal}}$ , and the departure from isotropy is small. Then f is usefully developed in the usual Legendre-polynomial series [6,8] in the angle  $\theta$  between v and E.

$$f = \sum_{l} f_{l}(v) P_{l}(\cos\theta)$$
  
=  $f_{0} + f_{1} \cos\theta + (\text{small terms})$ . (2.2)

When electron-neutral collisions dominate, C is linear in f. C is also expanded,  $C = C_0 + C_1 \cos\theta + \cdots$ , and the coefficient functions in Eq. (2.2) obey

$$\frac{\partial f_0}{\partial t} - \frac{eE}{3m} \left[ 2 \frac{f_1}{v} + \frac{\partial f_1}{\partial v} \right] = C_0 , \qquad (2.3a)$$

$$\frac{\partial f_1}{\partial t} - \frac{eE}{m} \frac{\partial f_0}{\partial v} = C_1 . \qquad (2.3b)$$

 $f_0$  is essentially the energy spectrum, for  $F = \int f d\Omega_v = 4\pi f_0$ , while  $f_1$  controls bulk electron motion with drift velocity  $\mathbf{v}_d = (1/n) \int f \mathbf{v} d^3 v$ =  $-(4\pi/3n) \hat{\mathbf{E}} \int f_1 v^3 dv$ , where  $\hat{\mathbf{E}}$  is a unit vector in the direction of  $\mathbf{E}$ . (We do not concern ourselves with gases such as methane in which the two-term Legendre expansion is known to be poor, although the treatment of the collision integral in Sec. III would be just as valid.)

 $C_0$  is the contribution of the collision integral to the time rate of change of the energy spectrum; it is discussed in Sec. III.  $C_1$  is the contribution to that part of the spectrum that controls the swarm momentum.

In general, for a weakly ionized gas in which electronneutron collisions dominate, and when elastic collisions dominate the momentum transfer,  $C_1 = -v_m f_1$ , where  $v_m = N_0 v \sigma_m$  is the monoenergetic momentum-transfercollision frequency and  $\sigma_m$  is the momentum-transfer cross section.

### B. Slowly varying fields

When  $\partial/\partial t \ll v_m$ , Eq. (2.3b) then becomes  $f_1 = (eE/mv_m)\partial f_0/\partial v$ . Inserting this in Eq. (2.3a) gives a single equation for  $f_0$ . Transforming it to an equation for g(w), we have

$$\frac{\partial g}{\partial t} + \frac{\partial}{\partial w} \left[ \frac{e^2 E^2}{m v_m} \left[ g - \frac{2}{3} \frac{\partial (wg)}{\partial w} \right] \right] = C_g , \qquad (2.4)$$

where  $C_g$  is the collision integral for g. In this equation we have exhibited the electric-field term in two parts, one essentially proportional to  $\partial g / \partial w$ , and one to  $\partial^2 (wg) / \partial w^2$ , and the expression appears in fluxconservative form. The quantity in square brackets is the energy flux due to the electric field.

### C. Energy diffusion due to the electric field

The two parts of the field term in Eq. (2.4) correspond mathematically to a mean flux ( $\sim \partial g / \partial w$ ) and a diffusive flux [ $\sim \partial^2 (wg) / \partial w^2$ ]. Thus elastic scattering in the presence of an electric field produces both a mean gain in energy (rate  $\sim e^2 E^2 / m v_m$ ) and a diffusion in energy (diffusion coefficient  $\sim \frac{2}{3}we^2 E^2 / m v_m$ ). The diffusion results from successive scatterings parallel or antiparallel to **E**, spreading out the swarm in the field's potential energy.

That energy diffusion produces a significant contribution to the spectrum can be seen by comparing the effect of diffusive gain  $G_d$  in Eq. (2.4) to that of mean energy gain  $G_m$  on a Maxwellian of temperature  $T_e$  (eV):

$$\frac{G_d}{G_m} = \frac{-\frac{2}{3}\frac{\partial}{\partial\omega}(wg)}{g} = -1 + \frac{2w}{3T_e} . \qquad (2.5)$$

This is of order unity, and is therefore important. It changes sign over the average energy  $3T_e/2$ . Diffusion allows particles of energy  $w > 3T_e/2$  to gain energy faster than the mean rate, and particles with  $w < 3T_e/2$  to gain energy more slowly than the mean rate, thus spreading out the spectrum and giving it body.

### **III. COLLISION INTEGRAL**

The general form for the collision integral for excitations to discrete molecular states k of energy  $w_k$  and cross section  $\sigma_k(w)$  is

$$C_{g} = N_{0} \sum_{k} \left[ \left( \sigma_{k} vg \right)_{w+w_{k}} - \left( \sigma_{k} vg \right)_{w} \right]$$
(3.1)

assuming all host molecules in the ground state. This assumption will be relaxed momentarily.

Since the cross sections are not exact step functions, each term, and the sum itself, is a continuous function of w. When molecular transition energies  $w_k$  are small compared with the width of g it is sensible to expand the summand in a Taylor series. Exhibiting the first two terms,

$$C_g = N_0 \frac{\partial}{\partial w} \left[ vgL + \frac{\partial}{\partial w} (vg\mathcal{M}) \right] + \cdots, \qquad (3.2)$$

where

$$L = \sum_{k} w_k \sigma_k(w) , \qquad (3.3a)$$

$$\mathcal{M} = \sum_{k} \frac{1}{2} w_k^2 \sigma_k(w) .$$
 (3.3b)

L is the energy-loss function describing mean energy loss, and  $\mathcal{M}$ , which may be called the straggling function, accounts for spread about the mean. This approximates the random walk in energy space by diffusion, a Fokker-Planck-type approximation, and is most valid when fractional energy transfer per energy-transfer collision is small, so that large energy changes occur predominantly by a succession of small ones. L and  $\mathcal{M}$  are constructed from measured cross sections. Energy loss to heavyparticle recoil from elastic scatterings can easily be incorporated in the definitions. The CSDA is that only the L term is retained.

Thermally populated excited states, of energy  $E_i$  and degeneracy  $D_i$ , are accounted for by taking L and  $\mathcal{M}$  to be

$$L = \Pi^{-1} \sum_{i,k} D_i e^{-E_i/T} (E_k - E_i) \sigma_{ik}(w) , \qquad (3.4)$$

$$\mathcal{M} = \Pi^{-1} \sum_{i,k} D_i e^{-E_i/T} \frac{1}{2} (E_k - E_i)^2 \sigma_{ik}(w) , \qquad (3.5)$$

rather than Eqs. (3.3), where  $\Pi = \sum_i D_i \exp(-E_i/T)$  is the partition function,  $\sigma_{ik}(w)$  is the cross section for transition from *i* to *k*, and *T* is the gas temperature.

Using Eq. (3.2) in Eq. (2.4), one obtains

$$\frac{\partial g}{\partial t} + \frac{\partial \phi}{\partial w} = 0 , \qquad (3.6a)$$

where

$$\phi = \frac{e^2 E^2}{m v_m} \left[ g - \frac{2}{3} \frac{\partial(wg)}{\partial w} \right] - N_0 vgL - N_0 \frac{\partial}{\partial w} (vg\mathcal{M})$$
(3.6b)

is the energy flux. Equations (3.6) determine the evolution of the energy spectrum in the Fokker-Planck approximation.

Third and higher derivatives in the expansion Eq. (3.2)have been neglected. The main properties of any normalized distribution with a decaying tail such as F are its average energy and the width of the function about the average. The first-derivative term L determines the average energy, and the second-derivative term  $\mathcal{M}$  determines the width, together with corresponding terms from the field contribution. The third derivative (skewness) alters the asymmetry about the mean, and the fourth sets the kurtosis, both being more detailed properties of F. Transport coefficients of interest are weighted integrals over the spectrum, and details of the spectral shape integrate out. Thus there is physical reason to expect that stopping with L is insufficient, but stopping with  $\mathcal{M}$  is sufficient to calculate a spectrum which reproduces bulk transport coefficients with some acceptable accuracy. This is consistent with earlier mathematical observations [16,19]. These arguments may be less true for the avalanche coefficient at low  $E/N_0$ , which requires an accurate high-energy tail.

#### A. Spread in energy loss

The ratio  $\mathcal{M}/L$  is more slowly varying than L or  $\mathcal{M}$  itself, since irregular cross-section behavior, such as the  $N_2$  resonance spike near 2.5 eV, will occur in both L and  $\mathcal{M}$  and divide out in the ratio.

Spread about the mean-energy-loss rate L can be compared with L. From Eq. (3.6b) it is of order of the diffusive-loss rate  $L_d$  divided by the mean loss rate L,

$$\frac{L_d}{L} \sim \frac{1}{vgL} \frac{\partial}{\partial w} (vg\mathcal{M}) \sim \frac{\mathcal{M}}{\overline{w}L} , \qquad (3.7)$$

where  $\overline{w}$  is the energy over which  $\mathcal{M}g = (\mathcal{M}/L)Lg$ changes much, being of the order of the swarm temperature or a characteristic energy over which L itself changes. Ratio (3.7) is not negligibly small, and can be of order unity (or larger near thermal energies where L changes sign), showing that diffusive contributions to energy loss can be comparable to the mean loss, as was the case for energy gain in the electric field. Since in steady state mean loss essentially balances mean gain, diffusive loss can be as important as diffusive gain in determining the spectrum.  $\mathcal{M}$  represents a critical piece of physics that must not be neglected.

### B. Importance of energy diffusion

The steady-state spectrum is that for which  $\phi = 0$ , and results from a balance between total energy gain from E and total energy loss to collisions. It is instructive to temporarily neglect the diffusive contributions to the flux, that is, the  $\mathcal{M}$  term in the collision integral and the term  $-\frac{2}{3}\partial(wg)/\partial w$  in the electric-field expression. The spectrum is then a balance between the mean rates. The mean loss rate  $N_0 vL$  increases with energy, and the mean gain rate  $e^2 E^2 / m v_m$  decreases with energy. The rates are equal at some energy  $w_1$ . An electron with energy  $w > w_1$  loses energy faster than it gains it, and one with energy  $w < w_1$  gains energy faster than it loses it. Consequently all electrons end up with energy  $w_1$ ; the spectrum collapses to a  $\delta$  function at the energy where the rates cross. The physical process which actually determines the energy spectrum is spread in gain and loss rates about the mean; mean rates determine only the average energy, cf. Fig. 1. It is clear that for electrons with a spread in energies to be in steady state there must be a balance between gain and loss rates over a spread in energies, and this spread determines the spectrum.

This shows that in the CSDA ( $\mathcal{M}=0$ ), the only physical process that gives body to the distribution function is energy diffusion due to elastic scattering in the electric field, since in the collision integral only the mean loss rate is retained. The CSDA is poor because it neglects "half" of the physics determining the spectrum. We shall later

show that it also violates detailed balance. In particular,  $\mathcal{M}$  allows some particles to lose energy more slowly than the mean, thereby supporting the high-energy tail and greatly increasing the avalanche rate or any process depending on the higher-energy parts of the spectrum.

So long as *average* energy loss per collision is small compared with the spectrum width, as is the case in  $N_2$ and especially  $O_2$  over wide energy ranges, a differential treatment including both L and  $\mathcal{M}$  is justified and insightful, and its accuracy for calculating transport coefficients, at least in these two gases, is borne out by direct calculation. This would almost certainly be true as well in many diatomic and polyatomic molecules.

#### C. Energy loss per collision

The electrons' mean energy loss per energy-transfer collision is

$$w_l = \frac{L}{\sum_k \sigma_k} . \tag{3.8}$$

The fractional energy loss  $\xi = w_l / w$  in N<sub>2</sub> and O<sub>2</sub> at 300 K is shown in Fig. 2.  $\xi$  includes inelastic and superelastic collisions with molecules in thermally populated rotational states.  $\xi$  is seen to be safely small except below about 0.01 eV, where rotational transitions with energies



FIG. 1. (a) Balance of mean gain and loss rates. Spectrum is a  $\delta$  function at  $w_1$  where the rates cross. (b) Balance of complete gain and loss rates. CSDA neglects spread in energy loss.



FIG. 2. Fractional energy loss per energy-transfer collision at 300 K in  $N_2$  and  $O_2$ . Below 0.01 eV rotational transfer is comparable to or larger than incident energy.

 $4JB_0 \sim 0.01$  eV are common. (Here  $B_0 \sim 2 \times 10^{-4}$  eV is the rotational constant, and  $J \sim 10$  is a typical populated rotational quantum number.) Except for this low energy, one would expect the energy-space Fokker-Planck approximation to be quite good.

Even at energies large enough for electronic excitation, which cause large single energy jumps, vibrational transitions still occur, reducing the average fractional energy loss. Figure 2 shows at 10 eV, say, that this is more true for  $O_2$  than for  $N_2$ . Some computed swarm parameters will depart from experimental values in  $N_2$  when energy jumps due to electronic transitions are important in reducing the tail. Thus the characteristic energy will be computed to be too large when it is near 1 or 2 eV. Agreement is better in  $O_2$ .

## D. Thermal gas motion

The cross sections, and L and  $\mathcal{M}$ , defined above are for the target molecule at rest. Thermal motion would guarantee that when E=0 the equilibrium distribution function is Maxwellian. However, thermally populated internal states will guarantee this as well and are included in Eqs. (3.4) and (3.5). Furthermore, since rotational energy transfer is faster than elastic transfer, the rate at which swarms exchange energy with neutral particles is controlled by inelastic transfers. Thus corrections for gas motion may be neglected when L and  $\mathcal{M}$  in the form of Eqs. (3.4) and (3.5) are used.

## **IV. ENERGY SPECTRUM**

#### A. Equation for time dependence of the distribution function

Equation (3.6) controls the time evolution of the spectrum in time varying fields in the absence of sources and sinks; these are to be added to the right-hand side as appropriate. The equation is valid for E varying slowly compared with the swarm mean momentum-transfer-collision frequency  $\overline{\nu}_m$ , but on any time scale relative to

the swarm mean energy-transfer frequency.

When E=0, the resulting equation

$$\frac{\partial g}{\partial t} - N_0 \frac{\partial}{\partial w} \left[ vLg + \frac{\partial (v\mathcal{M}g)}{\partial w} \right] = 0$$
(4.1)

determines the relaxation of g from an initial condition toward thermal equilibrium. Without the E term, Eq. (4.1) is no longer limited by  $V_{\text{drift}} \ll V_{\text{thermal}}$ , and so applies to electrons of any energy. It includes mean energy loss, straggling, and thermal heating.

If straggling were to be neglected (CSDA,  $\mathcal{M}=0$ ) in Eq. (4.1), the resulting equation would show simple convection in energy space, and therefore laminar flow; electrons of higher energy would never overtake ones of lower energy. Straggling destroys laminar flow and restores passing in energy space.

Equation (3.6) can be written as well for F,

$$\frac{\partial F}{N_0 \partial t} - \frac{v}{w} \frac{\partial}{\partial w} \left[ w \left[ L + \frac{1}{w} \frac{\partial (w\mathcal{M})}{\partial w} \right] F + w \left[ \frac{(eE/N_0)^2}{3\sigma_m} + \mathcal{M} \right] \frac{\partial F}{\partial w} \right] = 0 , \quad (4.2)$$

which will permit simpler understanding later.

#### B. Steady-state spectrum

When  $\partial/\partial t = 0$ , the steady-state solution of (4.2) is

$$F = F_0 \exp \left| -\int_0^w \frac{L + \frac{1}{w} \frac{\partial}{\partial w} (w\mathcal{M})}{\frac{(eE/N_0)^2}{3\sigma_m} + \mathcal{M}} dw \right|, \qquad (4.3)$$

where  $F_0$  is a normalization constant. The CSDA, Eq. (1.2), is recovered when  $\mathcal{M}$  is neglected.

The value of Eq. (4.3) lies both in its simplicity and (approximate) correctness, as well in its directly exhibiting the dependence of the distribution function on the most important molecular parameters  $\sigma_m$ , L, and  $\mathcal{M}$ , and on the experimental parameter  $E/N_0$ . Furthermore, it has a simple interpretation in terms of ordinary diffusion-convection theory.

# C. Diffusion-convection theory

Let a quantity  $\psi$  diffuse and convect in one dimension x with prescribed diffusion coefficient D(x) and convection velocity V(x):

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial x} (V\psi) = \frac{\partial}{\partial x} D \frac{\partial \psi}{\partial x} . \qquad (4.4)$$

In steady state the flux must be constant in t and x:

$$V\psi - D\frac{\partial\psi}{\partial x} = \text{const} = 0$$
, (4.5)

where the constant is taken to be zero since we assume  $\psi$  vanishes at an end point. Then  $(1/\psi)\partial\psi/\partial x = V/D$ ; in steady state the logarithmic derivative of  $\psi$  is the ratio of convection velocity to diffusion coefficient. Consequently  $\psi$  is distributed according to

$$\psi = \psi_0 \exp\left[\int \frac{V}{D} dx\right] . \tag{4.6}$$

If we now take x to be the electron energy w and  $\psi$  the spectrum F, the controlling equation (4.2), of diffusive-convective form, identifies

$$V = -N_0 v \left[ L + \frac{1}{w} \frac{\partial}{\partial w} (w \mathcal{M}) \right] , \qquad (4.7)$$

$$D = N_0 v \left[ \frac{(eE/N_0)^2}{3\sigma_m} + \mathcal{M} \right] , \qquad (4.8)$$

so that solution (4.6) is the steady-state spectrum (4.3) already obtained.

In Eq. (4.7),  $-N_0vL$  is the prescribed convection velocity, and the  $(1/w)\partial(wM)/\partial w$  term is the additional convection due to the energy dependence of the diffusion coefficient. Their sum is the total convection velocity. The first term in Eq. (4.8) is the diffusion coefficient due to elastic scattering in *E*, and the *M* term is that due to energy-loss straggling. Their sum is the total diffusion coefficient.

The electric field  $E_D$  at which the two diffusion coefficients are equal is

$$\frac{eE_D}{N_0} = \sqrt{3\sigma_m \mathcal{M}} , \qquad (4.9)$$

which is a function of w. It is the dividing field strength above or below which one or the other diffusion coefficient may be neglected. In O<sub>2</sub> it is as small as 0.1 Td for  $w \leq 0.1$  eV, about 1 Td near 0.3 eV, 10 Td at 4.0 eV, and greater than 100 Td for  $w \geq 9$  eV. (1 Td =  $10^{-17}$ V cm<sup>2</sup>.) In N<sub>2</sub> it is more widely variable because of the resonance spike which causes both  $\sigma_m$  and  $\mathcal{M}$  to peak near 2.5 eV.

[The mean gain velocity  $e^2 E^2 / m v_m$  and the velocity  $-\frac{2}{3}e^2 E^2 / m v_m$  due to the energy dependence of the electric-field diffusion coefficient would also appear in V, as they should, if we had applied these ideas directly to Eq. (3.6) for g. They drop out algebraically in the coefficients of F and  $\partial F / \partial w$  in the transformation to Eq. (4.2), as well as in the numerator of the final expression for F.]

### V. DETAILED BALANCE

In a collision between an electron of energy w and a molecule in state *i*, in which the molecule ends up in state k, the cross section is  $\sigma_{ik}(w)$ , and the electron has energy  $w' = w - (E_k - E_i)$ . The cross section  $\sigma_{ki}$  for the inverse process is related by detailed balance [20],

$$D_i w \sigma_{ik}(w) = D_k w' \sigma_{ki}(w') .$$
(5.1)

This may be used to show certain moments of the cross sections vanish.

The pth moment of the inelastic cross sections,

$$L^{(p)} = \Pi^{-1} \sum_{i,k} D_i e^{-E_i/T} (E_k - E_i)^p \sigma_{ik}(w) , \qquad (5.2)$$

with p an integer, may be integrated with weight function  $w \exp(-w/T)$ ,

$$I^{(p)} = \int_{0}^{\infty} e^{-w/T} w L^{(p)} dw$$
  
=  $\Pi^{-1} \int_{0}^{\infty} dw \ e^{-w/T} \sum_{i,k} e^{-E_i/T} (E_k - E_i)^p D_i w \sigma_{ik}(w) .$   
(5.3)

Invoking detailed balance, Eq. (5.1), this becomes

$$I^{(p)} = \Pi^{-1} \sum_{i,k} \int_{0}^{\infty} dw \ e^{-(w + E_{i} - E_{k})/T} D_{k}$$
$$\times e^{-E_{k}/T} (E_{k} - E_{i})^{p} [w - (E_{k} - E_{i})]$$
$$\times \sigma_{ki} (w - (E_{k} - E_{i})) , \qquad (5.4)$$

adding and subtracting  $E_k/T$  in the exponent. Interchanging *i* and *k*, we have

$$I^{(p)} = \Pi^{-1} \sum_{i,k} \int_0^\infty dw \ e^{-w/T} D_i e^{-E_i/T} (E_i - E_k)^p w \sigma_{ik}(w) ,$$
(5.5)

since  $\sigma_{ik}(w)$  vanishes for argument less than threshold or less than zero. Comparing with (5.3),

$$I^{(p)} = (-1)^{p} I^{(p)} . (5.6)$$

The integral (5.3) over odd energy moments vanishes. In particular,  $L^{(1)} = L$ , and

$$\int_{0}^{\infty} e^{-w/T} w L(w) dw = 0 .$$
 (5.7)

Since  $wLdw \propto vLv^2dv$ , Eq. (5.7) is equivalent to  $\langle N_0vL \rangle = 0$  in thermal equilibrium. For then  $F = e^{-w/T}$ , and  $\langle N_0vL \rangle = \int dv v^2 F N_0 vL = 0$ , and detailed balance assures that in equilibrium the swarm exchanges no net energy with the gas. That odd moments for p > 1 should vanish is less obvious, and appears unrelated to usual dynamical quantities.  $L^{(3)}$  is related to the skewness of the cross-section sum considered as a function of w. The Fokker-Planck approximation turns out to preserve Eq. (5.7), as presently discussed.

## VI. EXACT LIMIT FOR SMALL QUANTUM TRANSITION ENERGIES

In order for the spectrum Eq. (4.3) to reduce to a Maxwellian when E=0, we must have

$$\frac{L + \frac{1}{w} \frac{\partial}{\partial w} (w\mathcal{M})}{\mathcal{M}} = \frac{1}{T} .$$
 (6.1)

For L and  $\mathcal{M}$ , Eqs. (3.4) and (3.5), constructed from experimental cross sections, Eq. (6.1) turns out to be only approximately obeyed, and Eq. (4.3) is, of course, only an approximation to the spectrum. It is a better approximation the smaller the molecular quantum transition energies. We now show that Eqs. (6.1) and (4.3) become exact in the limit of small transitions. More precisely, we need  $\sigma_{ik}(w)$  to be large only when

$$E_k - E_i | \ll T , \qquad (6.2a)$$

and  $|E_k - E_i|$  to be small compared with the energy over which  $w\sigma_{ik}(w)$  changes,

$$|E_k - E_i| \frac{\partial}{\partial w} \ln(w\sigma_{ik}) \ll 1$$
 (6.2b)

Imposing detailed balance, Eq. (5.1), in Eq. (3.4) for L,

$$wL = (1/\Pi) \sum_{i,k} D_i e^{-E_i/T} (E_k - E_i) w \sigma_{ik}(w)$$
  
= (1/\Pi) \sum\_{i,k} D\_k e^{-E\_i/T} (E\_k - E\_i) w' \sigma\_{ki}(w') . (6.3)

Expanding  $w'\sigma_{ki}(w')$  about w, we invoke (6.2b) to obtain

$$wL = (w/\Pi) \sum_{i,k} D_k e^{-E_i/T} (E_k - E_i) \sigma_{ki}(w)$$
$$-(1/\Pi) \frac{\partial}{\partial w} w \sum_{i,k} D_k e^{-E_i/T} (E_k - E_i)^2 \sigma_{ki}(w) .$$
(6.4)

Now using condition (6.2a) to write  $\exp(-E_i/T) = \exp(-E_k/T)[1+(E_k-E_i)/T+\cdots]$ , Eq. (6.4) becomes

$$wL = (w / \Pi) \sum_{i,k} D_k e^{-E_k / T} (E_k - E_i) \sigma_{ki}$$
  
+  $\frac{w}{T\Pi} \sum_{i,k} D_k e^{-E_k / T} (E_k - E_i)^2 \sigma_{ki}$   
-  $(1/\Pi) \frac{\partial}{\partial w} w \sum_{i,k} D_k e^{-E_k / T} (E_k - E_i)^2 \sigma_{ki}$   
+  $O((E_k - E_i)^3)$ . (6.5)

Dropping terms of order  $(E_k - E_i)^3$ , interchanging *i* and *k*, and comparing with Eqs. (3.4) and (3.5), this is

$$wL = -wL + \frac{2w\mathcal{M}}{T} - \frac{\partial}{\partial w}(2w\mathcal{M}) , \qquad (6.6)$$

from which follows Eq. (6.1). This proves the necessary relation (6.1) that must hold between Fokker-Planck coefficients of friction and diffusion, and verifies that in zero field the form (4.3) correctly reduces to a Maxwellian when quantum jumps are small.

Equation (6.1) can be solved for  $\mathcal{M}$ ,

$$\mathcal{M} = \frac{1}{w} \int_{w}^{\infty} e^{(w-w')/T} w' L(w') dw' , \qquad (6.7)$$

showing that the straggling function is a weighted integral over the loss function over an energy equal to the gas temperature. Rewriting (6.7), and extending the lower limit, shows

$$\int_{0}^{\infty} e^{-w/T} w \ L \ dw = \lim_{w \to 0} (w e^{-w/T} \mathcal{M}) = 0 , \qquad (6.8)$$

so that taking the small quantum energy limit preserves the exact mean energy balance condition (5.7). Equation (6.7) gives physical meaning to the indefinite integral of  $e^{-w/T}wL$  as well.

Since  $L \neq 0$ , Eq. (6.1) for T > 0 is not satisfied by assuming  $\mathcal{M}=0$ . For a gas at nonzero temperature, excited

states are populated, and collisional deexcitation will occur. Therefore there is a spread in the energy loss rate:  $\mathcal{M} > 0$ . Equation (6.1), which follows from detailed balance, requires this. Thus the continuous-slowing-down approximation  $(L \neq 0, \mathcal{M} = 0)$  violates detailed balance. For small transitions the spreading term  $\mathcal{M}$  is given by Eq. (6.7), but the result is true in general. The *L* chosen for use in the CSDA must, of course, obey Eq. (5.7). Its indefinite integral (6.7) could then not vanish for all w.

## Previous distribution functions as special cases

Previous analytic distribution functions have been obtained by Pidduck [14]; Druyvesteyn [1]; Davydov [3]; Morse, Allis, and Lamar [2]; Chapman and Cowling [4]; and Wannier [5]. All of these are intended to apply in the case of elastic collisions only. The later work permits  $\sigma_m$ to be a function of energy, and accounts for thermal energy transfer. We now show these are all approximate special cases of Eq. (4.3).

Huxley and Crompton [7] show that previous spectra are included in that of Chapman and Cowling (Wannier's corrected derivation [5] is also). In our notation it is

$$F_{\rm CC} = F_0 \exp \left[ -\int_0^v \frac{mv \, dv}{\frac{M(eE/N_0)^2}{3(mv\sigma_m)^2} + T} \right], \qquad (6.9)$$

where M is the molecular mass. Thus we need only show that Eq. (6.9) is contained in (4.3).

For elastic collisions mean energy loss is [12]  $w_l = (2m/M)w$ , so that

$$L = \frac{2m}{M} w \sigma_m(w) , \qquad (6.10)$$

and Eq. (6.9) can be written

٢

$$F_{\rm CC} = F_0 \exp\left[-\int_0^w \frac{L \, dw}{\frac{(eE/N_0)^2}{3\sigma_m} + TL}\right].$$
 (6.11)

However, by using Eq. (6.1) to rewrite

$$\mathcal{M} = TL + \frac{T}{w} \frac{\partial(w\mathcal{M})}{\partial w}$$
(6.12)

١

in the denominator of the integrand in Eq. (4.3), the latter equation becomes

$$F = F_0 \exp\left[-\int_0^w \frac{L + \frac{1}{w} \frac{\partial(w\mathcal{M})}{\partial w}}{\frac{(eE/N_0)^2}{3\sigma_m} + T\left[L + \frac{1}{w} \frac{\partial(w\mathcal{M})}{\partial w}\right]} dw\right],$$
(6.13)

differing from the Chapman-Cowling spectrum (6.11) only by the  $(1/w)\partial(w\mathcal{M})/\partial w$  added to L. Thus we only need  $\partial(w\mathcal{M})/\partial w \ll wL$ . But for elastic collisions,

$$\mathcal{M} = \frac{1}{2} w_l^2 \sigma_m = \frac{1}{2} \left( \frac{2m}{M} w \right)^2 \sigma_m = \frac{1}{2} \frac{2m}{M} wL \qquad (6.14)$$

and

$$\frac{1}{w}\frac{\partial}{\partial w}(w\mathcal{M}) = \frac{2m}{M}L\left[1 + \frac{w}{2L}\frac{\partial L}{\partial w}\right] \ll L \quad . \tag{6.15}$$

Therefore the  $\mathcal{M}$  correction can be dropped and Eq. (6.13) reduces to the Chapman-Cowling distribution, proving the assertion. When inelastic collisions contribute, the contribution  $(1/w)\partial(w\mathcal{M})/\partial w$  is not necessarily small, and can no longer be neglected. Even though L in Eq. (6.10) is written for no thermal gas motion, T enters because of thermally excited discrete states in Eq. (6.12) which provide thermal energy transfer.

Using Eq. (6.1), one could eliminate L in Eq. (4.3) to obtain

$$F = F_0 \exp \left| -\frac{1}{T} \int_0^w \frac{1}{\frac{(eE/N_0)^2}{3\sigma_m \mathcal{M}} + 1}} dw \right|, \qquad (6.16)$$

reducing the dependence on molecular and experimental quantities to the single parameter  $(eE/N_0)^2/3\sigma_m\mathcal{M}$ . This form is appealing in its simplicity and is similar to the Chapman-Cowling result with LT replaced by  $\mathcal{M}$ . However, it focuses attention on the straggling function  $\mathcal{M}$  and detracts from the more physically transparent form of Eqs. (4.3) and (4.6). We shall therefore work with the distribution function in the form of Eq. (4.3).

## VII. H THEOREM

Boltzmann's H theorem may be applied to the electron swarm and its consequences expressed in terms of L and  $\mathcal{M}$ . The swarm is considered a system by itself, with distribution function f, and the host gas is considered an external system interacting with the swarm. Defining Boltzmann's H function [21]

$$H = \int f \ln(f) d^3 v , \qquad (7.1)$$

f may be developed as in Eq. (2.2),  $H = \int (f_0 + f_1 \cos \theta) \ln(f_0 + f_1 \cos \theta) d^3 v$ . Expanding the logarithm, one obtains

$$H = 4\pi \int f_0 \ln(f_0) v^2 dv + O(f_1^2 / f_0) . \qquad (7.2)$$

Dropping higher-order terms, and considering only the case in which electron number density is conserved, we may use

$$H = \int F \ln F v^2 dv = \langle \ln F \rangle .$$
 (7.3)

The swarm entropy is S = -kH, where k is the Boltzmann constant. Then

$$\frac{dH}{dt} = \int (1 + \ln F) \frac{\partial F}{\partial t} v^2 dv \quad . \tag{7.4}$$

For constant number density the first term does not contribute, and, using Eq. (4.2) for  $\partial F / \partial t$ , we have

$$\frac{dH}{dt} = N_0 \int \ln F \frac{v}{w} \frac{\partial \Phi}{\partial w} v^2 dv , \qquad (7.5)$$

$$\frac{dH}{dt} = -\frac{2N_0}{m^2} \int \frac{\Phi}{F} \frac{\partial F}{\partial w} dw \quad . \tag{7.6}$$

In the expression for  $\Phi$  in Eq. (4.2) the electric-field term appears in the diffusive part and contributes to dH/dt an amount

$$\frac{dH}{dt}\bigg|_{E} = -\frac{2N_{0}}{m^{2}} \left(\frac{eE}{N_{0}}\right)^{2} \int \frac{w}{3\sigma_{m}} \frac{1}{F} \left(\frac{\partial F}{\partial w}\right)^{2} dw \quad . \tag{7.7}$$

The integrand is positive definite;  $dH/dt|_E \leq 0$ . The effect of the electric force per se, or of the acquired drift velocity, does not, of course, change the entropy, and the net effect of the field is always to increase the swarm's entropy, due to energy diffusion by momentum-transfer scatterings.

Using Eq. (6.1) the convective part of  $\Phi$  may be written  $(w\mathcal{M}/T)F$ , and, with the  $\mathcal{M}$  term from the diffusive part, the contribution from collisions to dH/dt is

$$\frac{dH}{dt}\Big|_{c} = -\frac{2N_{0}}{m^{2}}\int \left[w\frac{\mathcal{M}}{T}\frac{\partial F}{\partial w} + w\mathcal{M}\frac{1}{F}\left[\frac{\partial F}{\partial w}\right]^{2}\right]dw$$
$$= -\frac{2N_{0}}{m^{2}}\int w\mathcal{M}\left[\frac{1}{T} + \frac{1}{F}\frac{\partial F}{\partial w}\right]\frac{\partial F}{\partial w}dw \quad .$$
(7.8)

For example, if F starts at a Maxwellian of temperature  $T_{e} \neq T$ , then

$$\left. \frac{dH}{dt} \right|_c = -\frac{2N_0}{m^2} \int w \mathcal{M} \left[ \frac{1}{T} - \frac{1}{T_e} \right] \frac{-F}{T_e} dw \quad . \tag{7.9}$$

If  $T_e > T$ , then  $dH/dt|_c > 0$ , and collisions decrease swarm entropy as the electrons cool. If  $T_e < T$ , collisions increase the electrons' entropy as they heat up. Thus collisions may increase or decrease swarm entropy, but the electric field always increases it. Equations (7.7) and (7.8)are explicit expressions for the corresponding rates, assuming the gas persists with a Maxwellian distribution of states. The total rate is

$$\frac{dH}{dt} = \frac{dH}{dt} \bigg|_{E} + \frac{dH}{dt} \bigg|_{c} .$$
(7.10)

Equations (7.7), (7.9), and (7.10) express the rate of change of entropy explicitly in terms of gas parameters  $\sigma_m$  and  $\mathcal{M}$ .

# VIII. APPLICATION TO O<sub>2</sub>

There is no doubt as to the conceptual correctness of the Fokker-Planck approximation, but its accuracy for any given gas is not a priori obvious. In this section we apply the  $L, \mathcal{M}$  approximation to  $O_2$ , in which relevant cross sections are relatively well known. The application involves constructing L and  $\mathcal{M}$  from experimental cross sections and calculating steady-state swarm parameters

 $L(10^{-16} eV - cm^2)$ ,  $M(10^{-16} eV^2 - cm^2)$ 101 100 10-10-10-3 10 10 10-3  $10^{-2}$ 10-1 100 101 102 Energy (eV)

FIG. 3. L and  $\mathcal{M}$  for O<sub>2</sub> at 300 K. Quadrupole moment equals 1.8.

using the spectrum Eq. (4.3) and the same cross sections.  $N_2$  is discussed in Sec. IX.

Considered purely as a mathematical approximation, the appropriate test of the  $L, \mathcal{M}$  approach would be to use the same cross sections as in an accurate numerical solution and compare resulting distribution functions or bulk parameters. However, published calculations do not always thoroughly reveal cross sections used, making comparison difficult. In addition, some are digitized at wide spacing, making it difficult to construct the needed



FIG. 4. Swarm energy spectrum in  $O_2$  at  $E/N_0 = 10$  and 100 Td.

103

102

02



FIG. 5. Characteristic energy (transverse diffusion coefficient divided by mobility) in  $O_2$  at 300 K. Large open circles are calculations with Eq. (4.3) using the momentum-transfer cross section compiled by Wadzinski and Jasperse [29] corrected by Kieffer's low-energy tail [30]. Open triangles are with the momentum-transfer cross section presented by Phelps [27]. Small data points are representative of those tabulated by Dutton [32] (Table 2.13). Dots below 1 Td are calculations from Hake and Phelps [23].

derivatives in  $\mathcal{M}$ . Also, some experimental cross sections are known more accurately now than when some published calculations were performed. These and other practical limitations have made it impossible for us to directly compare the  $L, \mathcal{M}$  approximation with a more accurate calculation using identical cross sections. Instead, therefore, we test the Fokker-Planck approximation by using most recent recommended cross sections, and comparing calculated swarm parameters in  $O_2$  and  $N_2$  with experimental values. Swarm measurements change less in time than cross sections. In one case ( $\sigma_m$ in  $O_2$  at low energies), in which there is nearly an order of



FIG. 6. Swarm drift velocity in  $O_2$  in 300 K. Large open circles and triangles are the same as in Fig. 5. Smaller data points are from measurements as tabulated by Dutton [32]. Dots below 0.2 Td are calculations by Hake and Phelps [23].



FIG. 7. Swarm momentum-transfer-  $(v_m)$  and energytransfer-  $(v_u)$  collision frequencies per molecule in O<sub>2</sub> at 300 K. Large open circles and triangles are the same as in Fig. 5. Small data points are calculations and data from Hake and Phelps [23]. In the Fokker-Planck  $(L,\mathcal{M})$  approximation the momentum-transfer cross section compiled by Wadzinski and Jasperse [29] with Kieffer's low-energy tail [30] produces better agreement with the more accurate calculations of Ref. [23].

magnitude discrepancy between two recommended sets, we compute with both. The excellent comparison obtained in this procedure substantiates the value of the  $L, \mathcal{M}$  approximation, but leaves open an accurate quantitative comparison of errors.

#### A. Cross sections and L and $\mathcal{M}$ functions

For rotational excitations we use the Gerjuoy-Stein [22] cross sections with a quadrupole moment of 1.8 (in units of  $ea_0^2$ , where  $a_0$  is the Bohr radius). This relatively large value was meant to achieve agreement with drift ve-



FIG. 8. Avalanche rate in  $O_2$  at 300 K. Small circles are data representative of those compiled by Dutton [32]. The Fokker-Planck approximation is about a factor of 4 too high at 100 Td; agreement improves at larger  $E/N_0$ .



FIG. 9. L and  $\mathcal{M}$  in N<sub>2</sub> at 300 K. Quadrupole moment equals 1.04.

locity at low  $E/N_0$  [23], and presumably accounts for the enhancing effect of the negative ion resonance. Neither experiment nor theory has definitively resolved O<sub>2</sub> rotational cross sections [24,25], and it does not behoove us to become embroiled in the rotational fray.

We have smoothed out the sharp peaks in the vibrational cross sections, maintaining the general shape of the energy dependence [26,27] and preserving the energy integral of Phelps's [27] recommended normalization. This smooths out small jumps in energy loss and permits constructing reasonable derivatives. The electronic and ionization cross sections are those compiled by Archer [28], in use in the auroral physics community for some years.

We use two sets of momentum-transfer cross sections, representative of the discrepancy of nearly an order of magnitude in this quantity at low energies. One set recommended by Phelps [27] is as small as  $3.5 \times 10^{-17}$ cm<sup>2</sup> at the low end, and transport coefficients computed using this set are denoted by open triangles ( $\triangle$ ) in Figs. 5-8. The second set is that compiled by Wadzinski and Jasperse [29] corrected by Kieffer's low-energy tail [30], which is  $3.0 \times 10^{-16}$  cm<sup>2</sup>, and renormalized as suggested by Phelps [27]. Results based on this set are denoted by open circles ( $\bigcirc$ ). Differences in swarm parameters be-



FIG. 10. Swarm energy spectrum in  $N_2$  at 100 Td. Dashed line is calculation by Pitchford and Phelps [36].



FIG. 11. Drift velocity in  $N_2$  at 300 K. Large open circles are our computed points. Smaller symbols are experimental points as compiled by Dutton [32] (Tables 1.16–1.18).

tween the two sets occur mostly below 0.1 Td.

L and  $\mathcal{M}$  constructed from these cross sections are shown in Fig. 3. Rotational transitions are responsible for almost all energy loss below about 0.19 eV. The hump between 0.2 and 1 eV is vibrational.

## **B.** Distribution function

The distribution function, Eq. (4.3), for T=300 K, at 10 and 100 Td, is shown in Fig. 4. Attachment has been ignored. The CSDA results are also shown, and depart seriously from the  $L, \mathcal{M}$  approximation only in the highenergy tail. Many transport coefficients computed in the CSDA are not wildly different from either the  $L, \mathcal{M}$  approximation or data, except for avalanching at low  $E/N_0$ , because they do not depend sensitively on the tail. Swarm parameters in the CSDA in air are commonly in error [31] by 5-30 % over limited ranges of  $E/N_0$ .

#### C. Swarm parameters

Figures 5-8 show calculated points ( $\bigcirc$  and  $\triangle$ ) along with recent data tabulated by Dutton [32]. In general the agreement is remarkably good over more than four or-



FIG. 12. Swarm characteristic energy in  $N_2$  at 300 K. Large open circles are our computed points. Smaller symbols are experimental points as compiled by Dutton [32] (Table 2.10).

ders of magnitude in  $E/N_0$ , using recommended cross sections.

The characteristic energy, Fig. 5, is computed to be too large at 100 Td, because of the large single energy loss in electronic transitions which lowers the average swarm energy. Likewise, at the higher energies, large electronic transitions produce a more rapid energy transfer rate, Fig. 7, than the continuous Fokker-Planck approximation. Similarly, the avalanche rate, Fig. 8, is computed to be too large, especially at relatively small  $E/N_0$ . That the CSDA avalanche rate is small, while the  $L,\mathcal{M}$  approximation is too large, raises speculation that the  $L,\mathcal{M},\ldots$  series would alternate.

We have used currently recommended cross sections, and compared with compiled data. Except for the avalanche rate at low  $E/N_0$ , which depends on the tail above 12 eV, and for characteristic energies above about 4 eV where large electronic energy jumps are poorly modeled, disagreements appear to be within the bounds of cross-section uncertainties, as evidenced, for example, in the low-energy behavior in Fig. 6.

## IX. APPLICATION TO N<sub>2</sub>

In this section we apply the  $L, \mathcal{M}$  approximation to  $N_2$ , in which cross sections are also relatively well known. The resonance near 2.5 eV and the high first electronic state of  $N_2$  stress the validity of the Fokker-Planck approximation more than  $O_2$ , and prepare us to expect poorer agreement.

## A. Cross sections and L and $\mathcal{M}$ functions

We again use the Gerjuoy-Stein rotational cross sections, with quadrupole moment 1.04. Vibrational excitations are based on the measurements by Schulz [33] as normalized by Haas [34]. A low-energy (0.29-1.7 eV)tail for the v = 0 to v = 1 transition was added as suggested by Englehardt, Phelps, and Risk [35]. Numerical values for the tail were taken from Kieffer [30]. Electronic and ionization cross sections are those of Archer [28], and agree quite well with the tabulation of Wadzinski and Jasperse [29]. Figure 9 shows the resulting L and  $\mathcal{M}$ .

#### **B.** Distribution function

Figure 10 shows the distribution function, Eq. (4.3), at 100 Td, together with the CSDA and the more precise calculation of Pitchford and Phelps [36]. This is a particularly stressful field strength, since at this field the spectrum straddles the resonance spike and the Fokker-Planck approximation is not at its best. In particular, the L, M approximation puts too many electrons at intermediate and high energies. The approximation tends to be better at different  $E/N_0$ . Furthermore, when moments are taken a higher level of accuracy is achieved, and swarm parameters are in quite good agreement with both data and more accurate calculations.

## C. Swarm parameters

The open circles in Fig. 11 show calculated drift velocity along with data compiled by Dutton [32]. In general

FIG. 13. Swarm momentum-transfer-  $(v_m)$  and energytransfer-  $(v_u)$  collision frequencies per molecule in N<sub>2</sub> at 300 K. Large open circles are our calculations using Eq. (4.3). Solid curves are averaged data and small solid diamonds are discrete energy loss calculations by Frost and Phelps [37].

the agreement is excellent over some five orders of magnitude in  $E/N_0$ . It is slightly too small below about  $3 \times 10^{-19}$  V cm<sup>2</sup>; here rotational transitions become comparable to swarm energies, stressing the Fokker-Planck validity. It is also too small near  $10^{-16}-10^{-15}$  V cm<sup>2</sup>, where the swarm straddles the 2.5-eV resonance spike.

The characteristic energy, Fig. 12, is computed to be too large below  $3 \times 10^{-19}$  V cm<sup>2</sup> and above  $10^{-16}$  V cm<sup>2</sup>, accounting for the drift velocity behavior.

The swarm momentum and energy-transfer-collision frequencies are shown in Fig. 13, together with data and calculations by Frost and Phelps [37]. Again, agreement is excellent except for the energy-transfer-collision frequency with characteristic energy near 1 eV when the resonance spike begins to reduce average energies more rapidly than can be accounted for in the Fokker-Planck

FIG. 14. Calculated avalanche rates in  $N_2$ . Open circles are from Eq. (4.3). Open diamonds are the CSDA. Small data points are representative of those compiled by Dutton [32].





approximation.

The avalanche rate, Fig. 14, is computed to be too large at small  $E/N_0$ , similar to O<sub>2</sub>. Bracketing by the CSDA and the  $L, \mathcal{M}$  approximations is again evident.

As was the case for  $O_2$ , energy loss is sufficiently small over wide energy intervals for the Fokker-Planck approximation to reproduce transport coefficients to generally excellent accuracy.

## X. CONCLUSIONS

The Fokker-Planck, or  $L,\mathcal{M}$ , approximation reduces the integro-differential Boltzmann equation to differential form. It is accurate when quantum transition energies are small and average energy loss is small compared with the spectrum width. This condition appears to be true over wide energy intervals in O<sub>2</sub> and N<sub>2</sub>, corresponding to more than four orders of magnitude in  $E/N_0$ , and would undoubtedly be true in many other diatomic or polyatomic gases as well.

At most values of  $E/N_0$  the steady-state spectrum is

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computed with sufficient accuracy that swarm parameters are in excellent agreement with data. These results lend credence and utility to the time-dependent equation (4.2). Exceptions occur when the Fokker-Planck smallenergy-loss condition is stressed, such as in  $N_2$  when the distribution function straddles the 2.5-eV resonance, or when the large first electronic excitation plays a significant role.

The  $L, \mathcal{M}$  approximation enables the energy spectrum to be understood from a simple physical perspective. If in some gases L and  $\mathcal{M}$  could be fit by integrable functions, then the quadratures could be performed, and Fcould be expressed fully in closed form.

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