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ELECTRON ENERGY-DISTRIBUTION FUNCTIONS IN GASES

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Knowledge of the electron energy distribution is fundamental to the modeling of electron swarm phenomena and to most aspects of gaseous electronics. The experimentally measured quantities in these areas are properties of the macroscopic behavior of the electron swarm. Since there is no macroscopic theory for electron transport phenomena, it is necessary to go back to the microscopic details of the electron-neutral scattering processes to predict the swarm behavior. The Boltzmann equation provides the connection between the microscopic and the macroscopic domains. Solutions of the Boltzmann equation are energy distribution functions and it is appropriate averages over the distribution functions that yield the measureable parameters.

The solution of the Boltzmann equation can be carried out analytically for only a few very restricted cases, as, for example, in the Maxwellian or Druyvesteyn cases. For most physical situations, solution to the Boltzmann equation must be carried out numerically.

The Boltzmann equation for electrons may be written

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_r f + \vec{a} \cdot \vec{\nabla}_v f = C(f) \qquad (1)$$

where $\vec{a}$ is the acceleration due to the applied electric field $(-\frac{e\vec{E}}{m})$ and C is the collision operator. The electron energy distribution function, f, is related to the electron number density by the relation,

$$\int f(\vec{r},\vec{v},t)\, d^3v = n(\vec{r},t)$$

Here, since f is a function of $\vec{r}$, $\vec{v}$, and t, some assumptions must obviously be made in solving the equation. Fortunately, there are few, if any, experimental situations that demand the detail of a complete solution of $f(\vec{r},\vec{v},t)$. Rather, it is appropriate averages over functions of f that we desire for modeling purposes.

In what follows, we discuss the numerical calculation of the electron energy distribution functions in the regime of drift tube experiments. The discussion is limited to constant applied fields and values of E/N

(ratio of electric field strength to neutral density) low enough that electron growth due to ionization can be neglected. We first present a brief survey of solution methods of the electron Boltzmann equation and then elaborate on the multiterm spherical harmonic expansion solution technique of Pitchford, ONeil and Rumble.[2] Results of the multiterm Boltzmann analysis in the case of N_2 are compared with two-term expansion results. The latter method has been used almost exclusively in the analysis of electron swarm behavior and in the derivation of low-energy electron scattering cross sections from swarm data.[3] It is our intention to indicate regions of validity of the two-term analysis and show the errors introduced by the two-term approximation by comparison with a more general calculational procedure.

Survey of Solution Methods

A. Two-term expansion

By far the most common solution technique in the drift tube regime has been the two-term spherical harmonic expansion solution.[4] In the simplest case one assumes

$$\frac{\partial f}{\partial t} = 0 \tag{2a}$$

and

$$\vec{\nabla}_r f = 0 \tag{2b}$$

to reduce the dependence of f from seven variables to the three velocity variables. At this point the assumption is made that the angular dependence of $f(\vec{v})$ can be approximated by the first two terms of a spherical harmonics expansion,[5,6] or rather a Legendre expansion because of the cylindrical symmetry.

$$f(\vec{v}) = f(\varepsilon,\Theta) = f_0(\varepsilon) + f_1(\varepsilon)\cos\Theta. \tag{2c}$$

The first assumption [Eq. (2a)] is met satisfactorily in the drift tube experiments when field strengths are low enough that there is no appreciable ionization and where there is no attachment. Then the electrons do reach an equilibrium fairly quickly on the time scale of the experiments. While the steady-state assumption simplifies the problem and, is often appropriate, it is not essential to the two-term method. Rockwood and his coworkers[7] developed a solution method for the time-dependent problem subject to assumption (2b) and (2c).

The second assumption [Eq. (2b)] is also fairly accurate in these cases, but in order to calculate diffusion coefficients it is necessary to include the effect of the spatial gradients in some way. Parker and Lowke[8] and Skullerud[9], for example, have proposed methods for doing this from a knowledge of $f(\vec{v})$. Thus the computational problem is that of determination of $f(\vec{v})$ even in these cases.

The third assumption [Eq. (2c)] is the "two-term" approximation. In order for the two-term assumption to be valid, the inelastic cross sections[6] must be small compared to the elastic cross sections, i.e., on the average the electrons must lose only a small fraction of their initial energy upon colliding with the neutral gas atoms or molecules. This is not always the case, especially for molecules. Implicit in the two-term approximation, but not usually stated, is the idea that the elastic electron-neutral cross sections are no more anisotropic than $\cos\theta$, and that the inelastic cross sections are isotropic. In other words, if the cross sections were also expanded in spherical harmonics it would only be the first two terms of the elastic and the first term of the inelastic that would enter into the calculation.

Computer codes have been described by Luft[10], Morgan[11], and Rockwood[8], Green[7], to name a few, to solve the Boltzmann equation subject to these assumptions and have been widely circulated throughout the gaseous electronics community.

B. Multiterm expansion

At the cost of computational complexity, one may of course retain higher terms in the Legendre expansion. The extension to three terms has been investigated by Ferrari[12], Wilhelm and Winkler,[13] and more recently by Makabe and Mori.[14] As expected, the results of these workers suggest that in cases where the ratio of inelastic to elastic cross sections is large, the two-term approximation begins to break down, and it remains uncertain whether the addition of one more Legendre component is sufficient.

Recently two more general multiterm solution techniques have appeared in the literature. Lin, Robson, and Mason[15] have presented a general moment method for calculating transport coefficients from the Boltzmann equation in which a multiterm Legendre expansion is employed. In this approach, it is the velocity moments of the distribution function rather than the function itself that are calculated as the moments relate directly to the transport coefficients. Pitchford, ONeil and Rumble[2] have developed a second multiterm method using a Galerkin method in which the distribution function is calculated directly. Transport and rate coefficients are then calculated as integrals over functions of the distribution function. In a later section we will discuss this method and show applications in the case of N_2. This calculation provides a straightforward comparison with the two-term results and gives an indication of the severity of the two-term approximation for a case of practical interest.

C. Direct Solution Methods

All the methods mentioned above convert the Boltzmann partial differential equation (PDE) into a set of coupled ordinary differential equations (ODE), one such equation for each term retained in the Legendre expansion. Alternately, one might make a more direct attack, avoiding the Legendre expansion entirely and employing the techniques available for the solution of partial differential equations. This has been carried out in the work of Kleban and Davis[16], and Kitamori et al.[17] The drawback to this latter approach is that the state of the art of PDE's is not nearly as advanced as that for ODE's, so that while a direct solution of the Boltzmann equation as a PDE is an interesting and promising alternative, it is currently not computationally competitive.

This list of direct methods is not meant to be comprehensive, but rather illustrative of recent efforts.

D. Monte Carlo

In the Boltzmann equation, the electron ensemble in a swarm experiment is described by a probability distribution which reflects the statistical nature of the macroscopic behavior of the electrons due to a large number of individual interactions. An alternate approach, perhaps closer in spirit to the actual experiment, would be to calculate a series of electron trajectories through a gas, with the exact outcome of the collisions modeled by a random variable for each process considered.[18] Although a single such trajectory is simply evaluated, these Monte Carlo procedures are generally inefficient since they require a vast number of trajectories to achieve an accuracy comparable to that available from a Boltzmann treatment. Such methods do, however, offer a means for verifying a solution independently derived from a given set of cross sections.

Outline of Multiterm Formulation

Since the details of the multiterm formulation of Reference 2 have been described in detail in that reference, we give only a brief outline here. The density gradient expansion as formulated by Skullerud[9] is used to transform the Boltzmann equation for $f(\vec{r},\vec{v},t)$ into a series of equations relating the velocity dependent coefficients of the powers of the gradient of the density. Thus, the expansion,

$$f(\vec{r},\vec{v},t) = f^{(0)}(\vec{v})\, n(\vec{r},t) - \vec{f}^{(1)}(\vec{v})\cdot\vec{\nabla} n(\vec{r},t) + \ldots \qquad (3)$$

together with the electron continuity equation,

$$\frac{\partial n}{\partial t} = \omega^{(0)}\, n(\vec{r},t) - \vec{\omega}^{(1)}\cdot\vec{\nabla} n(\vec{r},t) + \underline{\omega}^{(2)} : \vec{\nabla}\vec{\nabla} n(\vec{r},t) + \ldots \qquad (4)$$

where the $\omega^{(i)}$'s are the transport coefficients (ionization growth frequency, drift velocity and diffusion tensor, in that order), leads to equations for $f^{(0)}(\vec{v})$ and $\vec{f}^{(1)}(\vec{v})$. The forms of these equations are independent of the number of term in Eqs. (3) or (4). $\omega^{(0)}$ and $\vec{\omega}^{(1)}$ are defined as integrals over functions of $f^{(0)}$ and $\underline{\omega}^{(2)}$ can be found from $\vec{f}^{(1)}(\vec{v})$.[9] Once $f^{(0)}(\vec{v})$ is determined, the same techniques may be employed to determine $\vec{f}^{(1)}(\vec{v})$. In what follows we discuss only $f^{(0)}(\vec{v})$. The Legendre expansion is now employed for $f^{(0)}(\vec{v})$,

$$f^{(0)}(\vec{v}) \equiv f(\varepsilon,\theta) = \sum_{\substack{l=0 \\ i=0}}^{n-1} f_i(\varepsilon)\, P_i(\cos\theta) \qquad (5)$$

In reference 2 details of the Galerkin solution method for the $f_i(\varepsilon)$'s are presented. The definitions of the transport coefficients in the multiterm formulation reduce to the usual two-term definitions[1] when (a) $f_i = 0$ for $i > 1$ and (b) inelastic scattering is negligible or isotropic.

Comparison of Two-Term and Multiterm Results

In order to investigate the error introduced in the two-term approximation in a typical example we have performed calculations in N_2 for values of E/N from 1 to 200 Td as a function of the number of terms in the Legendre expansion of f.[19] At these values of E/N ionization may be treated as an energy loss only. For these calculations we used a set of cross sections derived from previous swarm experiments by Tachibana and Phelps.[20] This cross section set includes a single level approximation to the rotational excitation,[21] excitation from the ground state to seven vibrational and eleven electronic levels, and ionization

Since the computational problem is the determination of the Legendre expansion coefficients, the f_i's, we will first look at those. The normalized $f_i(\epsilon)$'s in N_2 at an E/N of 100 Td (where the average energy of the electrons in the swarm is 2.2 eV) are shown in Fig. 1 as a function of energy. The results shown are the first four coefficients in a six-term expansion. The isotropic component, f_0, is the largest at all energies. The higher order coefficients are are smaller but still significant in comparison to f_0. This is especially true in the 2 eV region where the vibrational cross sections are large. The considerable structure in the 2 eV region and again around 7-8 eV seems to reflect the onset of important inelastic cross sections at those energies.

Only the first few coefficients enter into the calculation of the measurable parameters of interest in most swarm applications and not the total distribution function. For the calculation of those measurables, it is really not important to have the full distribution function. The important thing here is to determine how well we have calculated the first few coefficients. Due to the coupling in the equations, the solution obtained for f_0, for example, will depend on the number of terms in the expansion.

The convergence of the transport coefficients and rate coefficients is connected very closely to the convergence of f_0. Figure 2 shows the convergence of the transport coefficients, drift velocity (v_d), transverse and parallel diffusion (D_T and D_p) coefficients and the $A^3\Sigma$ electronic excitation rate in the case of nitrogen at 100 Td as a function of the order of the solution or the number of spherical harmonic components used in the calculation. From the figure it can be seen that the two-term values of the drift velocity and the transverse diffusion coefficient are higher than the higher-order calculations. Conversely, the values of the A-state excitation rate, illustrative of electronic excitation in general, and the parallel diffusion coefficient are lower in the two-term than in the higher-order calculations. The calculated values are seen to converge as the order of the calculation is increased. Beyond four terms, there is very little change in the values. Monte Carlo calculations performed using a code due to Reid[22] are shown on the right for comparison.

Calculations similar to the one above for values of E/N from 1 to 200 Td reveal that the largest error in the two-term values of transport and rate parameters over the range investigated appears at 70 Td, the value of E/N at which the electrons are "seeing" the largest ratio of inelastic to elastic cross sections. The errors at 70 Td are small (~1%) for the drift velocity, larger for the diffusion coefficients (~5%) and up to 30% for some of the excitation rate coefficients. Convergence of the transport and excitation coefficients with the number of terms in the expansion to within a few percent was achieved by four terms in all cases.

Conclusion

Convergence of the transport and rate coefficients is seen empirically to be achieved independently of convergence of the distribution function at these field strengths. As seen in Fig. 1, the higher order Legendre expansion coefficients at 100 Td in N_2 are not negligible with respect to the isotropic component. However, the isotropic component changes very little between the calculations performed using four and six terms. Thus, it seems that calculations of electron transport and rate parameters using four to six terms in the multi-term Boltzmann solutions are as accurate as required for the iterative extraction of of cross sections from swarm experiments over a wide range of E/N values.

Calculations similar to the ones above have been reported for a model atom and for CH_4[2]. In general, the effect of adding more terms in the spherical harmonic expansion is to raise the tail of the distribution at the expense of the low energy or bulk portion. This, then, has the effect of lowering the drift velocity, and raising excitation rates for processes with cross sections large in the tail region. The division between the bulk and the tail region occurs at higher energies as E/N is increased. Thus, vibrational rates in N_2, for example, are higher in the six-term calculation than in the two-term at low E/N but lower than the two-term at high E/N. The largest differences between the two-term and converged results occur at values of E/N where the average electron energy is such that the electrons "see" a large ratio of inelastic to elastic cross sections. In CH_4 at E/N = 2. 42 Td, the average energy swarm passes into the Ramsauer minimum and most of the electron collisions are inelastic. The two-term error in this case is 34% for D_TN and 6.4% for v_d. For purposes of cross section determination from swarm experiments, the two-term assumption can introduce intolerably large error[13] depending on the neutral species.[23] It is important to note, however, that two-term derived cross sections used in two-term codes will reproduce the swarm data in a single component neutral gas.

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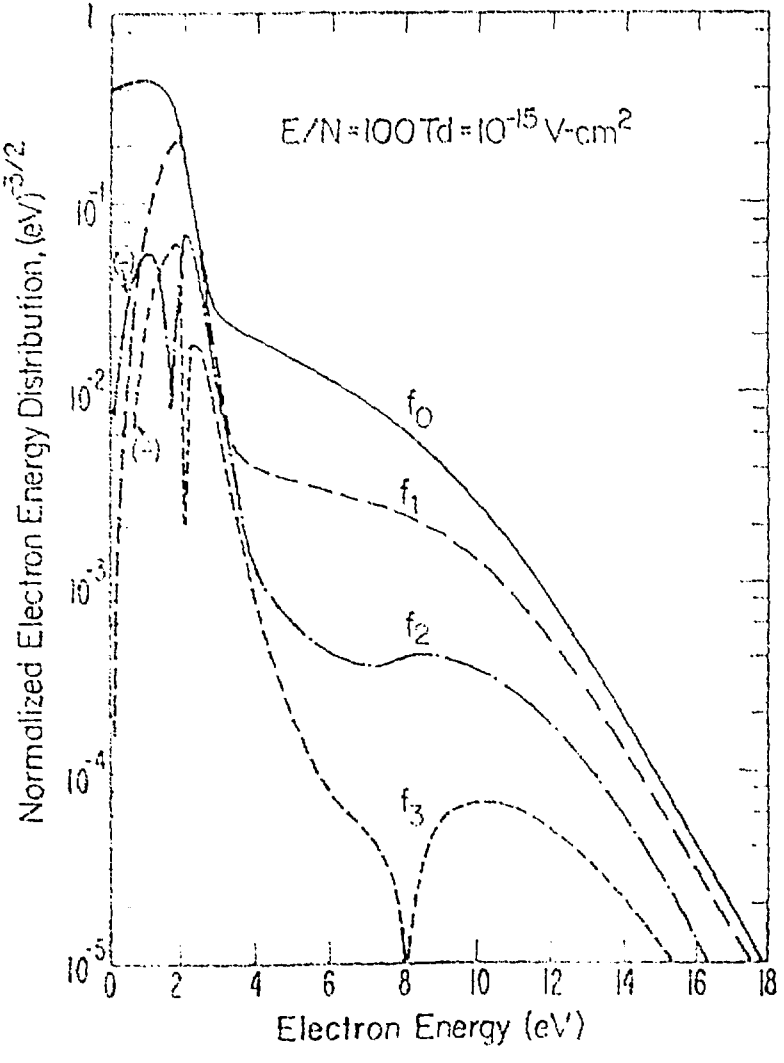
Fig. 1. The first four normalized Legendre coefficients of a six-term solution for the electron energy distribution function in N_2 at 100 Td.



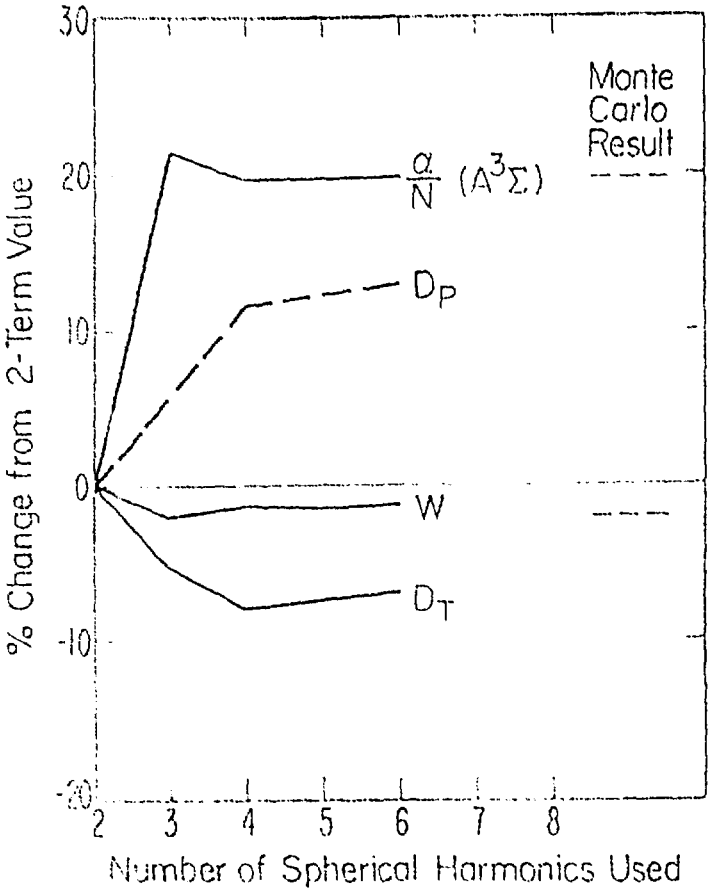


Fig. 2. The percent change from the two-term values in the indicated transport coefficients and the $A^3\Sigma_u^+$ excitation rate coefficient as a function of the number of spherical harmonics used in the calculation. The dashed lines on the right are Monte Carlo results for comparison. These calculations are in N_2 at 100 Td.