

*This research was supported by the U. S. Air Force Office of Scientific Research and the Graduate School of the University of Minnesota.

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Inelastic Boltzmann Equation for Slightly Ionized Gases

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(Received 16 September 1968)

By expanding in a Taylor series the inelastic scattering probability in the collision term of the Boltzmann transport equation, an approximate form of the Boltzmann equation for slightly ionized gases in the presence of a time-dependent electric field, which takes into account elastic and inelastic electron-molecule collisions, is obtained in a rigorous fashion. The inelastic collision term is obtained for arbitrary collision frequency, and it is shown how this expression can be simplified under the assumption of a low inelastic (in comparison with the elastic) collision frequency, or low molecular excitation energy in comparison with the average kinetic energy of the electrons, or both. Making both these assumptions and further assuming a low inelastic energy transfer, a formal solution of this equation is effected by an iterative procedure. This solution indicates explicitly that inelastic collisions are responsible for a small correction term to the distribution which is obtained if one considers only elastic collisions.

I. INTRODUCTION

In many investigations into ionospheric and gas-discharge phenomena, one is frequently confronted with the problem of determining the electron-velocity distribution for a slightly ionized gas in the presence of a relatively weak time-dependent electric field. The Boltzmann equation for the electron-distribution function, $f(\vec{v}, t)$, in this situation is (assuming spatial homogeneity and the external electric field \vec{E} to be in the x direction)

$$\partial f / \partial t + (eE/m) \partial f / \partial v_x = (\partial f / \partial t)_c, \quad (1)$$

where e and m are the charge and mass of the electron, respectively, and $(\partial f / \partial t)_c$ is the rate of change of the distribution function due to collisions. To solve this equation one often makes the following, quite reasonable assumptions:

(a) $f(\vec{v}, t)$ is isotropic except for a time varying perturbation in the x direction caused by the electric field, i. e.,

$$f(\vec{v}, t) = f_0(v) + v_x g(v, t). \quad (2)$$

(b) Since the gas is only slightly ionized, we can neglect electron-electron and electron-ion collisions and consider only electron-molecule collisions in evaluating $(\partial f/\partial t)_c$.

(c) The distribution function for the molecules is essentially the equilibrium distribution at a temperature T_0 .

Making these assumptions and further assuming only elastic electron-molecule encounters, Chapman, and Cowling¹ have derived expressions for the separate collisions terms $(\partial f_0/\partial t)_c$ and $[\partial(v_x g)/\partial t]_c$ whenever $m \ll M$, M being the molecular mass. Their results are

$$\begin{aligned} \left(\frac{\partial f_0}{\partial t}\right)_c &= \frac{m}{Mv^2} \frac{d}{dv} [v^3 \tilde{\nu}(v) f_0(v)] \\ &+ \frac{kT_0}{Mv^2} \frac{d}{dv} \left(v^2 \tilde{\nu}(v) \frac{df_0}{dv} \right), \end{aligned} \quad (3)$$

$$[\partial(v_x g)/\partial t]_c = -\tilde{\nu}(v) v_x g(v, t). \quad (4)$$

In these expressions $\tilde{\nu}(v)$ is the elastic collision frequency for momentum transfer and is given by

$$\tilde{\nu}(v) = Nv\tilde{q}(v) = Nv \int (1 - \cos\theta) q(v, \theta) d\Omega, \quad (5)$$

where N is the molecular density and $q(v, \theta)$ is the differential cross section for elastic scattering into the solid angle $d\Omega = 2\pi \sin\theta d\theta$.

Equation (1) together with Eqs. (3) and (4) is the starting point for many investigations into the microscopic behavior of ionized gases. If one knows $\tilde{\nu}(v)$, one can in principle solve the differential equation and obtain the distribution function for the electrons. As mentioned, however, this result is valid only for elastic encounters. Holstein,² investigating the distribution of electrons in high-frequency gas discharges, appears to have been the first author to have considered the effects of inelastic collisions in obtaining the approximate collision term. His derivation, however, relies heavily upon geometri-

cal and physical arguments which may have obscured important details. For example, the role of inverse collisions (microscopic reversibility) is not clearly brought out. Thus, he only considers collisions of the first kind, in which electrons lose energy by exciting the internal degrees of freedom of the molecule. Bowe³ gives a derivation of this term similar to Holstein's for the constant-field case, but only considers the possibility of one level being excited. Frost and Phelps⁴ extend Holstein's result to include collisions of the second kind in which electrons gain energy through molecular de-excitation, but only state their results without giving the derivation. Altshuler⁵ gives the same extension, but neglects elastic collisions and molecular recoil during inelastic collisions. A precise mathematical derivation of the inelastic collision term which is practically free of intuitive geometric and physical arguments, and which carefully elucidates the major assumptions necessary to obtain the final results, appears to be lacking in the literature; and it is this deficiency which the present paper attempts to remedy. In this paper, then, we derive an expression for the approximate collision term which is quite general in the sense that it includes on an equal footing, *ab initio*, elastic collisions and inelastic collisions of both the first and the second kind in which the molecules may have any number of levels. Our efforts will extend and incorporate the work of the above mentioned authors and, it is hoped, clearly indicate what assumptions are necessary to obtain their results.

Desloge and Matthysse^{6,7} have given a derivation of the approximate collision term for elastic collisions using elastic scattering probabilities. Their derivation, which employs an expansion of the scattering probability in powers of the ratio of the electronic to the molecular mass, is rigorous and eliminates recourse to somewhat questionable intuitive arguments. Our derivation will parallel theirs employing instead an expansion of the inelastic scattering probability discussed in the next section.

II. APPROXIMATE FORM OF THE COLLISION TERM

Let $F_i(\vec{V})d\vec{V}$ be the number of molecules per unit volume in the velocity range $d\vec{V}$ at \vec{V} and in the internal state characterized by i . Considering one of these molecules and an electron of velocity \vec{v} in a container of unit volume, let $W_{ij}(\vec{v}, \vec{V}; \vec{v}', \vec{V}')d\vec{v}'d\vec{V}'$ be the probability per unit time that they will undergo a collision in such a way that the electron ends up with its velocity between \vec{v}' and $\vec{v}'+d\vec{v}'$, while the molecule ends up in the state j with its velocity between \vec{V}' and $\vec{V}'+d\vec{V}'$. It follows that the collision term of Eq. (1) is⁸

$$\left(\frac{\partial f}{\partial t}\right)_c = \int W(\vec{v}', \vec{v}) f(\vec{v}') d\vec{v}' - \int W(\vec{v}, \vec{v}') f(\vec{v}) d\vec{v}', \quad (6)$$

$$\text{where } W(\vec{v}, \vec{v}') = \sum_{ij} \int W_{ij}(\vec{v}, \vec{V}; \vec{v}', \vec{V}') F_i(\vec{V}) d\vec{V} d\vec{V}'. \quad (7)$$

In terms of relative and center-of-mass velocities defined by

$$\bar{u} = \bar{v} - \bar{V}, \quad \bar{w} = (m\bar{v} + M\bar{V})/(m+M), \quad \bar{u}' = \bar{v}' - \bar{V}', \quad \bar{w}' = (m\bar{v}' + M\bar{V}')/(m+M), \quad (8)$$

where m is the electronic mass and M is the molecular mass, the scattering probability can be written in the form⁸

$$W_{ij}(\bar{v}, \bar{V}; \bar{v}', \bar{V}') = S_{ij}(\bar{u}, \bar{u}') \delta(\bar{w} - \bar{w}'). \quad (9)$$

In this expression S_{ij} is given by

$$S_{ij}(\bar{u}, \bar{u}') = (u/u'^2) q_{ij}(u, \theta) \delta(u' - u_{ij}), \quad (10)$$

where $q_{ij}(u, \theta)$ is the inelastic differential cross section for scattering into the solid angle $d\Omega = 2\pi \sin\theta d\theta$ and for the molecule making transitions from the state i to the state j ,

$$u_{ij} = [u^2 + (2/\mu)\epsilon_{ij}]^{1/2}, \quad \epsilon_{ij} = \mathcal{E}_i - \mathcal{E}_j,$$

\mathcal{E}_i is the internal energy of the state i , and $\mu = mM/(m+M)$ is the reduced mass.

On substituting Eq. (9) into (7), transforming from the variable \bar{V}' to \bar{w}' through the use of Eqs. (8), noting that the Jacobian $J(\bar{V}'/\bar{w}') = (m/\mu)^3$, and integrating over \bar{w}' , we obtain

$$W(\bar{v}, \bar{v}') = (m/\mu)^3 \sum_{ij} \int S_{ij}(\bar{v} - \bar{V}, \bar{v}' - \bar{V}') F_i(\bar{V}) d\bar{V}, \quad (11)$$

$$\text{where now } \bar{V}' = \bar{V} + (m/M)(\bar{v} - \bar{v}'). \quad (12)$$

If the average kinetic energy of the electrons does not differ too much from that of the molecules, then⁷ $\langle V \rangle / \langle v \rangle \sim (m/M)^{1/2}$. Since $m \ll M$ we can set $(m/\mu)^3 \approx 1$ in (11), expand $S_{ij}(\bar{v} - \bar{V}, \bar{v}' - \bar{V}')$ in a Taylor series about \bar{v} and \bar{v}' , retain only the first few terms, and obtain

$$\begin{aligned} S_{ij}(\bar{v} - \bar{V}, \bar{v}' - \bar{V}') &= S_{ij}(\bar{v}, \bar{v}') - \sum_r \frac{\partial S_{ij}}{\partial v_r} V_r - \sum_r \frac{\partial S_{ij}}{\partial v_r'} V_r' \\ &+ \frac{1}{2} \sum_{rs} \left(V_r V_s \frac{\partial^2}{\partial v_r \partial v_s} + 2V_r V_s' \frac{\partial^2}{\partial v_r \partial v_s'} + V_r' V_s' \frac{\partial^2}{\partial v_r' \partial v_s'} \right) S_{ij}(\bar{v}, \bar{v}'). \end{aligned} \quad (13)$$

If we assume a Maxwell-Boltzmann distribution for the molecules, we can write

$$F_i(\bar{V}) = \alpha_i N (M/2\pi k T_0) \exp(-MV^2/2kT_0), \quad \alpha_i = g_i \beta_i, \quad \beta_i = Z^{-1} \exp(-\mathcal{E}_i/kT_0), \quad (14)$$

where N is the number of molecules per unit volume, k is Boltzmann's constant, T_0 is the molecular temperature, Z is the internal partition function, and g_i is the statistical weight (degeneracy) of the i th level.

On substituting Eqs. (13) and (14) into (11), integrating over \bar{V} and neglecting terms of the order $(m/M)^2$, we obtain

$$W(\bar{v}, \bar{v}') = N \sum_{ij} \alpha_i \left[S_{ij}(\bar{v}, \bar{v}') - \frac{m}{M} \sum_r \frac{\partial S_{ij}}{\partial v_r'} (v_r - v_r') + \frac{kT_0}{2M} \sum_r \left(\frac{\partial^2}{\partial v_r^2} + 2 \frac{\partial^2}{\partial v_r \partial v_r'} + \frac{\partial^2}{\partial v_r'^2} \right) S_{ij}(\bar{v}, \bar{v}') \right]. \quad (15)$$

Interchanging \bar{v} and \bar{v}' and invoking microscopic reversibility⁹ (or equivalently the existence of inverse collisions) through the use of the relation¹⁰

$$g_j S_{ji}(\bar{v}', \bar{v}) = g_i S_{ij}(\bar{v}, \bar{v}'), \quad (16)$$

we can write

$$\begin{aligned} W(\bar{v}', \bar{v}) &= N \sum_{ij} \alpha_i \exp(\epsilon_{ij}/kT_0) \\ &\times \left[S_{ij}(\bar{v}, \bar{v}') - \frac{m}{M} \sum_r \frac{\partial S_{ij}}{\partial v_r} (v_r' - v_r) + \frac{kT_0}{2M} \sum_r \left(\frac{\partial^2}{\partial v_r^2} + \frac{\partial^2}{\partial v_r \partial v_r'} + \frac{\partial^2}{\partial v_r'^2} \right) S_{ij}(\bar{v}, \bar{v}') \right]. \end{aligned} \quad (17)$$

Substituting (15) and (17) into (6) we obtain

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_c = N \sum_{ij} \alpha_i \int \left[[f^*(\vec{v}') - f(\vec{v})] S_{ij}(\vec{v}, \vec{v}') - \frac{m}{M} \sum_r (v_r' - v_r) \left(f^*(\vec{v}') \frac{\partial S_{ij}}{\partial v_r} + f(\vec{v}) \frac{\partial S_{ij}}{\partial v_r'} \right) \right. \\ \left. + \frac{kT_0}{2M} [f^*(\vec{v}') - f(\vec{v})] \sum_r \left(\frac{\partial^2}{\partial v_r^2} + 2 \frac{\partial^2}{\partial v_r \partial v_r'} + \frac{\partial^2}{\partial v_r'^2} \right) S_{ij}(\vec{v}, \vec{v}') \right] d\vec{v}', \end{aligned} \quad (18)$$

$$\text{where } f^*(\vec{v}') = \exp(\epsilon_{ij}/kT_0) f(\vec{v}'). \quad (19)$$

This is as far as we can go without specifying $f(\vec{v})$. It is at this point that we assume $f(\vec{v})$ is given by Eq. (2).

In carrying out the integrations over \vec{v}' , we make use of the following relations¹¹:

$$\int h(v') S_{ij}(\vec{v}, \vec{v}') d\vec{v}' = v h(v_{ij}) q_{ij}(v), \quad (20)$$

$$\int v_r' h(v') S_{ij}(\vec{v}, \vec{v}') d\vec{v}' = v_r v_{ij} h(v_{ij}) \bar{q}_{ij}(v), \quad (21)$$

where h is an arbitrary function, and

$$q_{ij}(v) = \int q_{ij}(v, \theta) d\Omega, \quad (22)$$

$$\bar{q}_{ij}(v) = \int q_{ij}(v, \theta) \cos \theta d\Omega. \quad (23)$$

Setting $f = v_x g$ in Eq. (18), integrating over \vec{v}' , and neglecting all but the first term, which makes the largest contribution, we obtain

$$[\partial(v_x g)/\partial t]_c = -v_x \hat{\mu}(v) g(v), \quad (24)$$

where we have suppressed the time dependence of g , and where

$$\hat{\mu}(v) = \sum_{ij} \alpha_i \hat{\nu}_{ij}(v), \quad (25)$$

$$\hat{\nu}_{ij}(v) = Nv \{ q_{ij}(v) - [v_{ij} g^*(v_{ij})/vg(v)] \bar{q}_{ij}(v) \}. \quad (26)$$

If we set $f = f_0$ in Eq. (18), we must consider the contribution from all the terms. The calculations involved in carrying out the integrations over \vec{v}' and grouping all the various derivatives into convenient forms will not be presented here since they differ little from the elastic case discussed in detail in Refs. 6 and 7. The major difference in our treatment is that we make use of Eqs. (20) and (21) instead of the corresponding elastic collision integrals.

Setting $f = f_0$ in Eq. (18), we obtain

$$\begin{aligned} \left(\frac{\partial f_0}{\partial t}\right)_c = \sum_{ij} \alpha_i \left\{ [f_0^*(v_{ij}) - f_0(v)] \nu_{ij}(v) + \frac{m}{Mv^2} \frac{d}{dv} [v^3 \bar{\nu}_{ij}(v) f_0^*(v_{ij})] \right. \\ \left. + \frac{kT_0}{Mv^2} \left[\frac{1}{2} \frac{v}{v_{ij}} \nu_{ij}(v) \frac{d}{dv} \left(\frac{v_{ij}^3}{v} \frac{d}{dv} [f_0^*(v_{ij})] \right) - \frac{d}{dv} \left(v^2 \bar{\nu}_{ij}(v) \frac{d}{dv} [f_0^*(v_{ij})] \right) \right] \right. \\ \left. + \frac{1}{2} \frac{d}{dv} \left(v^2 \frac{d}{dv} [\nu_{ij}(v) f_0^*(v_{ij})] \right) - \frac{1}{2} f_0(v) \frac{d}{dv} \left(v^2 \frac{d\nu_{ij}}{dv} \right) \right\}, \end{aligned} \quad (27)$$

where $\nu_{ij}(v) = Nv q_{ij}(v)$ is the inelastic collision frequency, $\bar{\nu}_{ij}(v) = Nv_{ij} \bar{q}_{ij}(v)$, and $\bar{\nu}_{ij}(v) = \nu_{ij}(v) - \bar{\nu}_{ij}(v)$ is the inelastic collision frequency for momentum transfer.^{5,12}

Equation (27) is general and holds for arbitrary inelastic cross sections and collision frequencies. A very useful simplification of this expression can be achieved if we make the assumption that the collision frequency for inelastic collisions is much smaller than that for elastic collisions. If this be the case, the major inelastic contribution to $(\partial f_0/\partial t)_c$ will come from the first term in (27), and we can neglect inelastic collisions in the remaining terms. We can then write upon combining derivatives

$$\left(\frac{\partial f_0}{\partial t}\right)_c = \sum_{ij} \alpha_i [f_0^*(v_{ij}) - f_0(v)] v_{ij}(v) + \frac{m}{Mv^2} \frac{d}{dv} [v^3 \bar{v}(v) f_0(v)] + \frac{kT_0}{Mv^2} \frac{d}{dv} \left(v^2 \bar{v}(v) \frac{df_0}{dv} \right). \quad (28)$$

In obtaining (28) we have used the result that for elastic collisions $v_{ij} = v$, $f_0^*(v_{ij}) = f_0(v)$, and we have set

$$v = \sum_i \alpha_i v_{ii}, \quad \bar{v} = \sum_i \alpha_i \bar{v}_{ii}, \quad \bar{v} = \sum_i \alpha_i \bar{v}_{ij} = v - \bar{v}.$$

The last two terms of Eq. (28) constitute the purely elastic contribution, and are in agreement with the results obtained by Chapman and Cowling¹ and Desloge and Matthysse.^{6,7} The first term, which contains the purely inelastic contribution, can be arrived at quite readily by retaining only the leading term in the expansion of the scattering probability, Eq. (15). This is equivalent to assuming that for inelastic collisions the molecules may be treated as infinitely massive scatterers at rest.⁶

When one cannot assume a low inelastic collision frequency, another very useful simplification of Eq. (27) can be obtained by assuming that the average kinetic energy of the electrons is much greater than the internal energy difference of the molecules for allowed transitions, i. e.,

$$\langle \frac{1}{2} mv^2 \rangle \gg \epsilon_{ij}. \quad (29)$$

If this be the case, we can reasonably approximate v_{ij} and $f_0^*(v_{ij})$ in (27) by the first few terms of their Taylor series. Thus we take

$$v_{ij}^n \approx v^n (1 + n\epsilon_{ij}/mv^2), \quad f_0^*(v_{ij}) \approx f_0(v) + \epsilon_{ij} f_1(v), \quad (30)$$

$$\text{where } f_1(v) = f_0(v)/kT_0 + (1/mv)(d/dv)f_0(v). \quad (31)$$

Substituting (30) and (31) into (27), we obtain upon neglecting the quadratic terms in ϵ_{ij} and grouping derivatives

$$\begin{aligned} \left(\frac{\partial f_0}{\partial t}\right)_c &= f_1(v)\epsilon(v) + \frac{m}{Mv^2} \frac{d}{dv} [v^3(\bar{\mu}f_0 + \bar{\epsilon}f_1)] \\ &+ \frac{kT_0}{Mv^2} \left\{ \frac{d}{dv} \left[v^2 \left(\bar{\mu} \frac{df_0}{dv} + \bar{\epsilon} \frac{df_1}{dv} \right) \right] + \frac{v\epsilon}{m} \frac{d}{dv} \left(\frac{1}{v} \frac{df_0}{dv} \right) + \frac{f_1}{2} \frac{d}{dv} \left(v^2 \frac{d\epsilon}{dv} \right) \right\}, \end{aligned} \quad (32)$$

$$\text{where } \bar{\mu} = \sum_{ij} \alpha_i \bar{v}_{ij}, \quad \epsilon = \sum_{ij} \alpha_i \epsilon_{ij} v_{ij}, \quad \bar{\epsilon} = \sum_{ij} \alpha_i \epsilon_{ij} \bar{v}_{ij}.$$

III. THE BOLTZMANN EQUATION

Combining Eqs. (1) and (2) we have

$$\begin{aligned} v_x \frac{\partial g}{\partial t} + \frac{eE}{m} \left(\frac{v_x}{v} + \frac{df_0}{dv} + \frac{v_x^2}{v} \frac{\partial g}{\partial v} + g \right) \\ = \left(\frac{\partial f_0}{\partial t} \right)_c + \left(\frac{\partial}{\partial t} (v_x g) \right)_c. \end{aligned} \quad (33)$$

Replacing v_x by $-v_x$ in (33) and alternately adding and subtracting the result equation from (33), we obtain the separate equations^{6,13,14}

$$\frac{eE}{m} \left(\frac{v_x^2}{v} \frac{\partial g}{\partial v} + g \right) = \left(\frac{\partial f_0}{\partial t} \right)_c, \quad (34)$$

$$\frac{\partial g}{\partial t} + \frac{eE}{m} \frac{df_0}{dv} = \frac{1}{v_x} \left(\frac{\partial}{\partial t} (v_x g) \right)_c. \quad (35)$$

Assuming $E = E_0 \cos \omega t$ and combining (24) with (35), we obtain

$$\frac{\partial g}{\partial t} + \hat{\mu}(v)g = -\frac{\gamma}{v} \frac{df_0}{dv} \cos \omega t, \quad (36)$$

where $\gamma = eE_0/m$.

It would appear at first glance that we immediately could integrate (36) to obtain g in terms of f_0 . This would be possible if we were considering only elastic collisions. The introduction of inelastic collisions, however, introduces a further complication through the term $\hat{\mu}(v)$. From Eqs. (25) and (26) we see that $\hat{\mu}(v)$ is dependent upon the functional form of g . Consequently, (36) cannot be integrated in the obvious manner without some further assumptions concerning inelastic collision processes. Fortunately, the two assumptions which we can make to render $\hat{\mu}$ independent of g are the same assumptions which were employed above to simplify the expression for $(\partial f_0/\partial t)_c$, that is, to obtain Eqs. (28) and (32). In the first case, then, we assume the inelastic collision frequency is much smaller than the frequency for elastic encounters, i. e., $q_{ij}(v, \theta) \ll q_{ii}(v, \theta)$ for $i \neq j$. For elastic collisions we have from (26)

$$\hat{v}_{ii}(v) = Nv[q_{ii}(v) - \bar{q}_{ii}(v)] = \bar{v}_{ii}(v). \quad (37)$$

Thus, neglecting inelastic collisions, we obtain

$$\hat{\mu}(v) = \sum_i \alpha_i \tilde{v}_{ij}(v) = \tilde{v}(v). \quad (38)$$

Putting (38) into (36) and solving for g gives^{6,13,14}

$$g(v, t) = \gamma h_\nu(v) \cos \omega t + \gamma k_\nu(v) \sin \omega t, \quad (39)$$

$$\text{where } h_\nu(v) = -\frac{1}{v} \frac{df_0}{dv} \frac{\tilde{v}}{\omega^2 + \tilde{v}^2}, \quad (40)$$

$$k_\nu(v) = -\frac{1}{v} \frac{df_0}{dv} \frac{\omega}{\omega^2 + \tilde{v}^2}. \quad (41)$$

If the inelastic collision frequency is not small in comparison with the elastic, we can, under certain conditions, employ fruitfully the approximations which are valid when $\langle \frac{1}{2} m v^2 \rangle \gg \epsilon_{ij}$. If this is true, then similar to Eqs. (30) and (31), we have

$$g^*(v_{ij})/g(v) = 1 + \epsilon_{ij} g_1(v)/g(v), \quad (42)$$

$$\text{where } \frac{g_1(v)}{g(v)} = \frac{1}{kT_0} \left(1 + \frac{kT_0}{mvg(v)} \frac{\partial g}{\partial v} \right). \quad (43)$$

If we assume further that

$$\epsilon_{ij} g_1(v)/g(v) \ll 1, \quad (44)$$

then we have from (26)

$$\begin{aligned} \hat{v}_{ij}(v) &\approx Nv \int \left(1 - \frac{v_{ij}}{v} \cos \theta \right) q_{ij}(v) d\Omega \\ &= \tilde{v}_{ij}(v), \end{aligned} \quad (45)$$

$$\text{and } \hat{\mu}(v) = \sum_{ij} \alpha_i \tilde{v}_{ij}(v) = \tilde{\mu}(v). \quad (46)$$

Substituting (46) into (36) and integrating, we obtain

$$g(v, t) = \gamma h_\mu(v) \cos \omega t + \gamma k_\mu(v) \sin \omega t, \quad (47)$$

$$\text{where } h_\mu(v) = -\frac{1}{v} \frac{df_0}{dv} \frac{\tilde{\mu}}{\omega^2 + \tilde{\mu}^2}, \quad (48)$$

$$k_\mu(v) = -\frac{1}{v} \frac{df_0}{dv} \frac{\omega}{\omega^2 + \tilde{\mu}^2}. \quad (49)$$

In order to verify if our result (47) is consistent with the assumption of Eq. (44), we look at the constant-field case. Setting $\omega = 0$ in (47), (48), and (49), and setting $\tilde{\mu} = v/p$ in (48), where p is the mean free path of the electrons (for simplicity assumed constant), we obtain

$$g(v) = -(\gamma p/v^2) df_0/dv. \quad (50)$$

If we assume $f_0(v)$ is a Maxwellian with temperature T , compute $g(v)$ from (50), and substitute the result into (43), we obtain

$$\frac{g_1(v)}{g(v)} = \frac{1}{kT_0} \left[1 - \left(\frac{T_0}{T} + \frac{kT_0}{mv^2} \right) \right]. \quad (51)$$

Thus, except for the low-energy tail of the distribution, we have from (51)

$$\epsilon_{ij} g_1(v)/g(v) \sim \epsilon_{ij}/kT_0 \ll 1. \quad (52)$$

If $f_0(v)$ is a Druyvesteyn distribution, i. e., if

$$f_0(v) = A \exp(-\alpha v^4), \quad (52)$$

where $\alpha = 3m/2M\gamma^2 p^2$, we obtain

$$\frac{g_1(v)}{g(v)} = \frac{1}{kT_0} \left(1 + \frac{kT_0}{mv^2} (1 - 4\alpha v^4) \right). \quad (53)$$

For a Druyvesteyn distribution $\langle v^2 \rangle \sim \alpha^{-1/2}$, so that except for the high- and low-energy tails of the distribution we again obtain

$$\epsilon_{ij} g_1(v)/g(v) \sim \epsilon_{ij}/kT_0 \ll 1.$$

Therefore, our result Eq. (47) is consistent with the approximation used to derive it if $f_0(v)$ is either Maxwellian or Druyvesteyn and if we ignore the divergencies which appear in the ratio $g_1(v)/g(v)$ at the low- and high-energy tails of the distribution.

An approximately valid differential equation for f_0 can be realized by proceeding in a manner similar to the elastic collision case.^{6,13,14} Thus, substituting either (39) or (47) into (34) and averaging over all directions of \tilde{v} and over one cycle of the external field, we obtain

$$\frac{1}{6} \gamma^2 \frac{d(v^3 h_\xi)}{dv} = v^2 \left(\frac{\partial f_0}{\partial t} \right)_c, \quad (54)$$

where $\xi = \nu$ or μ depending upon which form of g we use, Eq. (39) or (47). If we can assume a low inelastic collision frequency, then $\xi = \nu$ and the $(\partial f_0/\partial t)_c$ term in Eq. (54) will be given by Eq. (28). Therefore, substituting Eqs. (28) and (40) into (54), we obtain

$$\begin{aligned} &\frac{\gamma^2}{6} \frac{d}{dv} \left(v^2 \frac{df_0}{dv} \frac{\tilde{v}}{\omega^2 + \tilde{v}^2} \right) + \frac{m}{M} \frac{d}{dv} (v^3 \tilde{v} f_0) \\ &+ \frac{kT_0}{M} \frac{d}{dv} \left(v^2 \tilde{v} \frac{df_0}{dv} \right) \\ &+ v^2 \sum_{ij} \alpha_i [f_0^*(v_{ij}) - f_0(v)] v_{ij}(v) = 0. \end{aligned} \quad (55)$$

If we had not assumed microscopic reversibility back in Eq. (17), the last term in (55) would read instead

$$\sum_{ij} [\alpha_j v_{ij}^2 f_0(v_{ij}) v_{ji}(v_{ij}) - \alpha_i v^2 f_0(v) v_{ij}(v)].$$

Equation (55) with $\omega = 0$ (dc case), when applied to electron- N_2 collisions in which j is either $i-2$ or $i+2$, is essentially the fundamental equation for f_0 employed by Frost and Phelps.⁴ It is based, as we have seen, upon the neglect in inelastic collisions of molecular motion or recoil. Methods of solution of Eq. (55) for various physical situations are described in detail by Frost and Phelps⁴ and by Sherman,¹⁵ and for a similar expression by Carleton and McGill.¹⁶

If we cannot assume a low inelastic collision frequency but can assume $\langle \frac{1}{2}mv^2 \rangle \gg \epsilon_{ij}$, then in Eq. (54) $\xi = \mu$, and $(\partial f_0 / \partial t)_C$ will be given by (32). Combining (32) with (48) and (54), we obtain

$$\begin{aligned} & \frac{\gamma^2}{6} \frac{d}{dv} \left(v^2 \frac{df_0}{dv} \frac{\tilde{\mu}}{\omega^2 + \tilde{\mu}^2} \right) + \frac{m}{M} \frac{d}{dv} [v^3 (f_0 \tilde{\mu} + f_1 \tilde{\epsilon})] \\ & + \frac{kT_0}{M} \frac{d}{dv} \left[v^2 \left(\tilde{\mu} \frac{df_0}{dv} + \tilde{\epsilon} \frac{df_1}{dv} \right) \right] \\ & + \frac{kT_0}{M} \left[\frac{v\epsilon}{m} \frac{d}{dv} \left(\frac{1}{v} \frac{df_0}{dv} \right) + \frac{f_1}{2} \frac{d}{dv} \left(v^2 \frac{d\epsilon}{dv} \right) \right] \\ & + v^2 f_1(v) \epsilon(v) = 0. \end{aligned} \quad (56)$$

As far as this author knows, an expression along the lines of Eq. (56) has not appeared previously in the literature. The reason for this probably lies in the fact that most authors content themselves to use somewhat simpler expressions analogous to (55). Equation (56), however, can be used as the starting point for many investigations into the properties of ionized gases when the assumptions involved in the derivation of Eq. (55) are no longer valid.

A third useful differential equation for f_0 may be obtained by assuming both a low inelastic collision frequency and the condition $\langle \frac{1}{2}mv^2 \rangle \gg \epsilon_{ij}$. If we do this, we can use Eq. (34) to rewrite the fourth term in Eq. (55) as

$$\begin{aligned} & v^2 \sum_i \alpha_i [f_0^*(v_{ij}) - f_0(v)] v_{ij}(v) \\ & \approx v^2 f_1(v) \epsilon(v). \end{aligned} \quad (57)$$

Substituting (57) into (55) we have

$$\begin{aligned} & \frac{d}{dv} \left\{ v^2 \tilde{\nu} \left[\left(kT_0 + \frac{M\gamma^2}{6} \frac{1}{\omega^2 + \tilde{\nu}^2} \right) \frac{df_0}{dv} + mvf_0 \right] \right\} \\ & = -Mv^2 f_1(v) \epsilon(v), \end{aligned} \quad (58)$$

which can be integrated formally to yield

$$\begin{aligned} f_0(v) &= A \exp \left[- \int_0^v P(v') dv' \right] + \exp \left[- \int_0^v P(v') dv' \right] \\ & \times \int Q(v) \exp \left[\int_0^v P(v') dv' \right] dv, \end{aligned} \quad (59)$$

where A is a normalization constant, and

$$P(v) = mv \left(kT_0 + \frac{M\gamma^2}{6(\omega^2 + \tilde{\nu}^2)} \right)^{-1}, \quad (60)$$

$$\begin{aligned} Q(v) &= - \frac{M}{v^2 \tilde{\nu}} \left(kT_0 + \frac{M\gamma^2}{6(\omega^2 + \tilde{\nu}^2)} \right)^{-1} \\ & \times \int_0^v \left(f_0(v') + \frac{kT_0}{mv'} \frac{df_0}{dv'} \right) v'^2 \epsilon(v') dv'. \end{aligned} \quad (61)$$

We note that the first term in (59) represents the contribution to f_0 from elastic collisions.¹³ Margenau¹³ has investigated the functional form of this term in the constant mean-free-path approximation. The second term in (59) is the correction due to inelastic collisions, and we see from (61) that it is dependent upon the functional form of f_0 . We can eliminate this dependence by assuming the inelastic contribution is much smaller than the elastic, obtain the first iterative form of (59), and neglect terms quadratic in ϵ . Doing this we obtain

$$\begin{aligned} f_0(v) &= A \exp \left[- \int_0^v P(v') dv' \right] \\ & \times \left\{ 1 + \int R(v) \exp \left[\int_0^v P(v') dv' \right] dv \right\}, \end{aligned}$$

where

$$\begin{aligned} R(v) &= - \frac{M}{kT_0 v^2 \tilde{\nu}} \left(kT_0 + \frac{M\gamma^2}{6(\omega^2 + \tilde{\nu}^2)} \right)^{-1} \\ & \times \int_0^v \exp \left[- \int_0^{v'} P(v'') dv'' \right] \\ & \times \left(1 - \frac{kT_0}{mv'} P(v') \right) v'^2 \epsilon(v') dv'. \end{aligned}$$

Following Margenau¹³ we can, in the constant mean-free-path approximation, evaluate further the integrals in (62) and (63) for two important special cases. In the first case (high-frequency ac field) $\omega \gg \nu$ and we obtain

$$\begin{aligned} f_0(v) &= A e^{-\lambda v^2} \left(1 - \frac{M^2 \gamma^2 p}{6k^3 T^2 T_0 \omega^2} \int \left[\int_0^v v'^2 \right. \right. \\ & \left. \left. \times \epsilon(v') e^{-\lambda v'^2} dv' \right] v^{-3} e^{\lambda v^2} dv \right), \end{aligned}$$

where $p = v/\nu$ is the constant mean-free-path of the electrons, and

$$\lambda = m/2k(T_0 + m\gamma^2/6k\omega^2) = m/2kT.$$

In the second case (strong dc field) we assume $M\gamma^2 p^2/6v^2 \gg kT_0$ and obtain

$$\begin{aligned} f_0(v) &= A e^{-\alpha v^4} \left(1 - \frac{6}{kT_0 \gamma^2 p} \int \left[\int_0^v v'^2 \right. \right. \\ & \left. \left. \times \epsilon(v') e^{-\alpha v'^4} dv' \right] v^{-1} e^{\alpha v^4} dv \right). \end{aligned} \quad (65)$$

Thus, in both cases considered here the effect of inelastic collisions on the isotropic part of the electron distribution is, within the limitations of our assumptions, to add a small correction term to the well known Maxwellian and Druyvesteyn distributions which arise when only elastic collisions are considered.

IV. SUMMARY AND CONCLUSION

By expanding in a Taylor series the inelastic scattering probability in the collision term of the Boltzmann transport equation, an approximate form of the Boltzmann equation for slightly ionized gases in the presence of a time-dependent electric field, which takes into account elastic and inelastic electron-molecule collisions, has been obtained in a rigorous fashion. The inelastic collision term was obtained for arbitrary collision

frequency, and it was shown how this expression could be simplified under the assumption of a low inelastic (in comparison with the elastic) collision frequency, or low molecular excitation energy in comparison with the average kinetic energy of the electrons, or both. Making both these assumptions and further assuming a low inelastic energy transfer, a formal solution of this equation was effected by an iterative procedure. This solution indicated explicitly that inelastic collisions are responsible for a small correction term to the distribution function which would be obtained if one considered only elastic collisions.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation and the Research Council of the University of North Carolina at Greensboro.

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(16) is a valid generalization. An equivalent expression in terms of cross section is $g_j v_{ij}^2 q_{ji}(v_{ij}) = g_i v^2 q_{ij}(v)$, which is obtained by substituting Eq. (10) into (16) and integrating over \vec{v}' . This equation is satisfied by the theoretical cross sections for rotational excitation of N_2 derived by E. Gerjuoy and S. Stein, *Phys. Rev.* **97**, 1671 (1955), and of CO derived by K. Takayanagi, *J. Phys. Soc. Japan* **21**, 507 (1966).

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