Velocity distribution function and transport coefficients of electron swarms in gases: Spherical-harmonics decomposition of Boltzmann's equation

R. E. Robson and K. F. Ness*

Physics Department, James Cook University of North Queensland, Townsville, Queensland 4811, Australia

(Received 15 July 1985)

The multiterm spherical-harmonic representation of the velocity distribution function of "reacting" charged-particle swarms in a gaseous medium is discussed from a general viewpoint, using spherical tensors throughout, in contrast to the traditional mixed spherical-Cartesian notation usually employed in analysis of the hydrodynamic regime. The resulting hierarchy of kinetic equations generated from the Boltzmann equation has a universal validity, applicable to all experimental arrangements, as do the associated transport and reaction-rate coefficients. The structure of these equations and the nature of the eigenvalue problem associated with them are discussed generally, independently of any numerical technique adopted for their solution, of which the moment method of Lin, Robson, and Mason [J. Chem. Phys. 71, 3483 (1979)] is just one possibility.

I. INTRODUCTION

Low-order truncation of the spherical-harmonics representation of the velocity distribution function $f(\mathbf{r},\mathbf{c},t)$ of a swarm of electrons in a neutral gas generally reflects the belief (or the hope) that f is nearly isotropic in $\mathbf{c}$ space or at least that it has this property over the range of velocities $\mathbf{c}$ which controls the transport coefficients of the swarm. The physical basis for this can be seen from elementary mechanics: An electron of mass m and a neutral molecule of mass m_0 exchange a fraction $\sim 2m/m_0 \ll 1$ of their energy in an *elastic* collision and thus, even if the swarm is driven through the gas by a strong electric field, energy and momentum gained from the field are efficiently distributed in all directions through the agency of such collisions, which have the effect of randomizing directions of electron velocity vectors $\mathbf{c}$, without significantly altering their magnitude. The same cannot be said for an ion swarm because of the generally comparable masses of an ion and a neutral molecule and the associated large fractional energy exchange. Neither is it generally true for electron swarms in which *inelastic* collisions play a significant role. Whereas the anisotropy of f for ions has long been recognized, and various methods developed over the years for solving Boltzmann's equation, mostly within the framework of the conventional kinetic theory of gases, the importance of an anisotropic electron distribution function has only attracted serious attention in recent years. The physics of charged-particle swarms has been recently reviewed by Kumar et al.[1] and Kumar[2] and the reader is directed to these for further references and for a general overview. The theory of electron transport in gases has tended to evolve quite separately from ions and, indeed, almost in a conventional kinetic theory vacuum, this in spite of the fact that the spherical-harmonics representation

$$f(\mathbf{r},\mathbf{c},t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_m^{(l)}(\mathbf{r},c,t) Y_m^{[l]}(\hat{\mathbf{c}}) \tag{1}$$

usually forms an integral part of both electron and ion

transport theories, although in the latter case only implicitly so. For practical purposes, it is necessary to make either the truncated representation

$$f(\mathbf{r},\mathbf{c},t) = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} f_m^{(l)}(\mathbf{r},c,t) Y_m^{[l]}(\hat{\mathbf{c}}) , \tag{2}$$

that is, to assume $f_m^{(l)} = 0$ if $l > l_{\max}$, or to assume some other property of these higher-order expansion coefficients. For electrons, it has been traditional[3] to set $l_{\max} = 1$, the so-called two-term or P_1 approximation. With this approximation, the Boltzmann equation

$$(\partial_t + \mathbf{c}\cdot\nabla + \mathbf{a}\cdot\partial_\mathbf{c})f = -J(f) , \tag{3}$$

where $J(f)$ denotes the linear charged-particle—neutral-molecule collision operator,[4] can be solved in a relatively straightforward manner, if J is also approximated by a low-order truncation of an expansion in m/m_0. We do not require an explicit expression for J for present purposes. [See, however, Eq. (158), (159), (164), and (175) of Ref. 1.] This procedure is clearly invalid if f departs substantially from spherical symmetry in $\mathbf{c}$ space, and then one has to systematically investigate solutions of (3) by successively incrementing $l_{\max}$ until some convergence criterion is met. The complexity of the problem is therefore then similar to ions, except that the simplifying approximation of J is still possible. Much effort has been devoted in recent times towards obtaining "multiterm" solutions (i.e., $l_{\max} \geq 2$) of Boltzmann's equation, and this is discussed below. The first accurate systematic multiterm solution, valid for arbitrary cross sections and electric fields and furnishing *all* measured transport coefficients, was given by Lin, Robson, and Mason[5] (LRM), who extended previous ideas of Robson and Kumar[6] for electrons and ions and the then recently developed theory of Viehland and Mason[7] for ions, to provide a comprehensive treatment involving a conjunction of ideas from the two historically different approaches. Since then, LRM, as Ref. 5 has become known, has been used in a wide variety of circumstances,[8] including cases of anisotropic

differential cross sections and negative differential conductivity. Kleban and Davis[9] had earlier developed an iterative technique for solving Boltzmann's equations, but this, unfortunately, is of questionable accuracy.[9-11] Other methods have been proposed.[12-20] Extension of LRM to include nonconservative processes is discussed in detail in a subsequent paper (referred to as II). In this paper we indicate formally how the spherical-harmonics decomposition should be done when such processes are operative. This is necessary, because there is a fundamental change in the structure of the hierarchy of equations and the expressions for transport coefficients themselves, as indicated by Kumar, Skullerud, and Robson.[1]

Before doing this, however, we wish to offer some observations on the work represented in Refs. 12—20 and to respond to criticism and misunderstanding[10,14,21] of LRM. In Ref. 5 the tensor coefficients $f_m^{(l)}$ were further expanded in a set of basis functions $\xi_{vl}(c)$ spanning c space,

$$f_m^{(l)}(c) = \sum_{v=0}^{\infty} F_m^{(vl)} \xi_{vl}(c) , \qquad (4)$$

these functions being essentially products of a Maxwellian function of arbitrary temperature and a Sonine (Laguerre) polynomial of degree v. Explicit expressions are given in II but are not needed here. Equations (1) and (4) combine to give the well-known Burnett-function expansion[1] and when substituted in (3) furnish a doubly infinite set of equations for $F_m^{(vl)}$ which in turn are related to moments of $f(c)$. For practical purposes, truncation of these moment equations in both l and v indices is required, through specification of l_{max} and v_{max}, respectively. Convergence in these two indices can generally be treated independently.[1] Our comments on LRM and other work are, then, as follows.

(i) While the choice of basis functions $\xi_{vl}(c)$ is of crucial importance for determining the best representation of $f_m^{(l)}(c)$ and therefore the most efficient computational algorithm, it is questionable whether many of the various methods are really fundamentally all that different, since this choice is essentially the *only* difference in most cases. The designation "theory" should certainly be avoided.[5,21]

Thus, $\{\xi_{vl}(c)\}$ could be a set of cubic splines,[14,17] each spline being nonzero only in a specified interval $c_v \leq c \leq c_{v+1}$ ($v = 0, 1, 2, \ldots$), or they could be a set of constant, but different, values in these intervals, as in the usual finite element technique. Approximation of $f_m^{(l)}$ by restricting the number of these intervals to a finite value (say v_{max}) is not much different, at least in principle, from truncation of an expansion in orthogonal functions, which span the *entire* range of c, to a finite number, as was the case in LRM. The latter approach may not be favored in "conventional" approaches[20] to solution of the differential equations characterizing electron transport, but it is quite common in many other problems in kinetic theory.[22] In any case, there is a common mathematical basis, as discussed above. The remarks of McMahon[18] are interesting in this regard, especially taken in the context of his own very promising iterative procedure for solving Boltzmann's equation.

(ii) It is obvious that knowledge of the expansion coeffi-

cients $F_m^{(vl)}$ is equivalent to knowing $f_m^{(l)}$ and thus f itself. Thus, the moment theory of LRM *is* capable of furnishing the electron distribution function, if so desired. It is evident that remarks of LRM in this context were quite misleading.[14] The rationale of applying a convergence criterion to the distribution function itself or merely to a few low-order experimentally measured moments, as was done in LRM, is another question entirely. We have generated distribution functions for several cases of current interest using Eq. (17) of LRM and the results[23] are generally in agreement with Pitchford *et al.*[14,17]

(iii) Several apparently different forms of collision operator J are used in some of the works,[9,12,14,19,20] without any attempt to relate them to the original Boltzmann operator or to one another. Although the overall picture is somewhat confusing, large discrepancies probably arise for quite different reasons.[9-11]

In LRM the original Boltzmann collision term[22] was used for elastic collisions plus the Wang-Chang and Uhlenbeck term[24] to represent inelastic processes. Matrix elements with respect to Burnett functions are found which are subsequently approximated by using the smallness of m/m_0. This is known to be consistent[1] with the standard Frost-Phelps, differential—finite-difference form[25] of J, but contrary to the impression which could easily be gained,[14] LRM did *not* start with a differential form, which essentially involves only leading terms in an expansion of J in powers of m/m_0. Equations (35) and (41) of LRM indicate the general decomposition of the matrix elements of J as a power series in m/m_0.

(iv) There appears to be some misunderstanding[14] of basic physical properties of swarms and even definitions of transport coefficients.[12] We feel that Ref. 1 portrays the situation accurately. *Axial symmetry* exists in velocity space *only* if the electric field **E** and density gradient ∇n are collinear, and *only* then is it permissible to use an expansion in *Legendre polynomials* $P_l(\cos\theta)$, where $\cos\theta = \hat{c} \cdot \hat{E}$, in place of (1). If the density gradient has a component transverse to **E**, the distribution function depends upon the azimuthal angle ϕ, as well as θ, and there is *no axial symmetry*—the spherical-harmonics expansion must be used. An expansion in associated Legendre polynomials[14] is not adequate. It is important to distinguish between this and the symmetry which exists in configuration space, as evidenced by a single diffusion coefficient in directions transverse to **E**. Indiscriminate interchange of spherical harmonics and Legendre polynomials is particularly undesirable in the far more complicated case in which nonconservative processes occur, where *second-order* terms in the density of gradient expansion must be retained (Sec. 4 of Ref. 1).

Another point of confusion has arisen[12] in connection with identification of transport coefficients in the presence of non-particle-conserving collisions (ionization, attachment, reactions). Drift velocity and diffusion coefficients are defined[1] as coefficients of ∇n and $\nabla \nabla n$, respectively, in the equation of continuity (25). For a given value of field and for a specified neutral gas, these coefficients are *independent* of the particular experimental arrangement. The latter are accounted for entirely by boundary and/or initial conditions imposed in solution of the

equation of continuity. To assign different drift velocities and diffusion coefficients to time-of-flight, pulsed and steady-state Townsend experiments is misleading.[12] The same can be said regarding ionization or attachment rate coefficients.

Likewise, the kinetic equations for $f_m^{(l)}$ and related quantities have a universal validity. Equations (47)—(53) below, which generalize the particle-conserving equations (184), (186), and (189) of Ref. 1, determine distribution functions and transport coefficients under all circumstances where a hydrodynamic description is valid. It is not necessary to rederive them in connection with any particular experiment or new method by making a ∇n expansion and, as has already been pointed out in (i) above, it is arguable whether different numerical algorithms really constitute different physical "theories" as such.

(v) The aim of a multiterm theory must be to provide accurate values for experimentally determined quantities by successively incrementing l_{max} in Eq. (2) until satisfactory convergence is achieved. Sometimes this means taking $l_{max} = 7$ or higher. Any procedure which does not have this flexibility is of limited value. Likewise, a contender for serious consideration must be capable of handling all types of cross sections, including those for which scattering is anisotropic. At the time of writing, the choice is rather limited within these constraints, with only Refs. 5, 14, and 17—19 being developed to such a sophisticated level.

(vi) The recent work of Phelps and Pitchford[17] also addresses the problem of "reacting" electron swarms and deserved special comment. They neglect certain terms in the expressions for transport coefficients (effectively the second integrals on the right-hand sides of our equations [(53b)—(53d)] below), and while this greatly simplifies the mathematics and the computational effort, it is our experience[23] that this procedure will often involve significant error. The need for a general discussion, as reported in the present paper, remains.

(vii) Braglia[21] correctly points out that the original computer code of LRM was inadequate under some circumstances, but his has been remedied.[23] This, of course, does not impinge in any way upon the theoretical work of LRM, which remains intact. We cannot agree, however, with the labeling of LRM as "less conventional" by Braglia et al.[20] If anything, the opposite is true, when viewed in the context of traditional kinetic theory.[22] We feel that (i) above is the best way to consider all these apparently different approaches.

It is with these remarks as background that we have written the present paper. In Sec. II we give a formal discussion of the spherical-harmonics and density-gradient expansions of the distribution function of electron swarms in which particle number is not conserved, e.g., through ionization or attachment processes. The equations developed are quite general and can be used in connection with any representation (4) in c space. In II we specialize to the Sonine polynomial representation and thus generalize the results of LRM.

Finally, we note that Monte Carlo simulation continues to play an important role in electron-swarm theory, both in its own right and as a means of resolution of discrepancies between the results of other work. For an up-to-date discussion on the state of the art, the reader is referred to Ref. 21.

II. SPHERICAL-HARMONICS EXPANSION, DENSITY-GRADIENT EXPANSION, AND NONCONSERVATIVE PROCESSES

A. Spherical tensor properties

It is now widely recognized that nonconservative processes such as ionization and attachment alter the fundamental structure of the kinetic equation hierarchy and the expressions for transport coefficients (Ref. 1, Sec. 4). The overriding consideration is that second-order terms in the density-gradient expansion

$$f(\mathbf{r},\mathbf{c},t) = n(\mathbf{r},t)f(0) + \mathbf{f}(1)\cdot\nabla n + \underline{f}(2){:}\nabla\nabla n + \cdots \tag{5}$$

must be retained in order for diffusion to be correctly represented. The use of spherical notation in Eq. (1) on the one hand and Cartesian notation in (5) on the other is not satisfactory, and we employ spherical tensors exclusively in what follows, following the conventions of Kumar[26] and Fano and Racah.[27] This is not merely a matter of elegance. Cartesian tensors become extremely cumbersome in the higher orders and the motivation for use of spherical tensors derives from considerations of practicality. Some general tensor properties are discussed before we embark upon the rather lengthy procedure of decomposition of Boltzmann's equation.

1. Basic definitions

The spherical harmonics of Eq. (1) are defined with the phase convention of Fano and Racah:[27]

$$Y_m^{[l]}(\theta,\phi) = i^l(-1)^{(m+|m|)/2}\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2}$$

$$\times P_l^{|m|}(\theta)e^{im\phi}, \tag{6}$$

with

$$P_l^{|m|}(\theta) = \frac{(-1)^l}{2^l l!}(\sin\theta)^{|m|}\frac{d^{l+|m|}}{d\cos\theta^{l+|m|}}(1-\cos^2\theta)^l. \tag{7}$$

In Eq. (1) we have written $Y_m^{[l]}(\hat{c})$ for $Y_m^{[l]}(\theta,\phi)$, where θ,ϕ are the polar angles of c, i.e.,

$$c_x = c\sin\theta\cos\phi, \quad c_y = c\sin\theta\sin\phi, \quad c_z = c\cos\theta.$$

We define

$$c_m^{[1]} = \left[\frac{4\pi}{3}\right]^{1/2}cY_m^{[1]}(\hat{c})$$

so that

$$c_0^{[1]} = ic\cos\theta, \quad c_{\pm 1}^{[1]} = \frac{1}{\sqrt{2}}(\mp ic_x + c_y). \tag{8}$$

A contrastandard, irreducible tensor of rank l is a set of $2l+1$ objects $f_m^{[l]}$ $(m = -l, \ldots, +l)$ which transform

under rotations of the coordinate frame like the spherical harmonics (6). The corresponding standard tensor is simply the complex conjugate and is denoted by a superscript in parentheses:

$$f_m^{(l)} = (f_m^{[l]})^* \ .$$

We may also have *tensor operators*, for example, the gradient operator defined below.

Any two tensors $\underline{f}_{m_1}^{(l_1)}, \underline{g}_{m_2}^{(l_1)}$ may be coupled to form another tensor according to

$$(\underline{f}^{(l_1)}, \underline{g}^{(l_2)})_m^{(l)} = \sum_{m_1, m_2} (l_1 m_1 l_2 m_2 \mid lm) f_{m_1}^{(l_1)} g_{m_2}^{(l_2)} \ , \qquad (9)$$

where $(l_1 m_1 l_2 m_2 \mid lm)$ denotes the Wigner or Clebsch-Gordon coefficient, well known in angular momentum theory.[28] These vanish unless $l_1 + l_2 \geq l \geq \mid l_1 - l_2 \mid$ and $m = m_1 + m_2$ and have the following orthogonality and symmetry properties:

$$\sum_{m_1, m_2} (l_1 m_1 l_2 m_2 \mid lm)(l_1 m_1 l_2 m_2 \mid l'm') = \delta_{l'l} \delta_{m'm} \ ,$$

$$\sum_{l,m} (l_1 m_1 l_2 m_2 \mid lm)(l_1 m_1' l_2 m_2' \mid lm) = \delta_{m_1' m_1} \delta_{m_2' m_2} \ , \qquad (10)$$

$$(l_1 m_1 l_2 m_2 \mid lm) = (-1)^{l_1 + l_2 - l}(l_2 m_2 l_1 m_1 \mid lm)$$

$$= (-1)^{l_1 + l_2 - l}(l_1 - m_1 l_2 - m_2 \mid l - m)$$

$$= (-1)^{l_2 + m_2}(l - m l_2 m_2 \mid l_1 - m_1)$$

$$\times \left[\frac{2l+1}{2l_1+1}\right]^{1/2} \ .$$

Lower-order coefficients are tabulated in Condon and Shortley.[29]

2. The gradient tensor $G_m^{(sl)}$

We often distinguish between tensors of the same rank by insertion of another index in the superscript. Thus in (4) we have $F_m^{(vl)}$ ($v = 0, 1, 2, \ldots$). The gradient tensor defined below also features the additional superscript. We wish to convert the density-gradient expansion (5) into spherical tensor notation and we obviously need the counterpart of ∇ and $\nabla\nabla$ in the appropriate notation. Thus, we define the gradient tensor operator $G_m^{(sl)}$ by

$$G_0^{(00)} = 1 \ , \quad G_m^{(11)} = \nabla_m^{(1)} \quad (m = \pm 1, 0)$$

$$G_m^{(2l)} = (\nabla^{(1)})_m^{(l)} \qquad (11)$$

$$= (G^{(11)}, G^{(11)})_m^{(l)} \quad (m = -l, \ldots +l) \ .$$

We have $G_0^{(10)} = 0$, $G_m^{(21)} = 0$, and, in general, $G_m^{(sl)} = 0$ if $l > s$ or $\mid m \mid > l$.

Higher-order operators with $s \geq 3$ could be defined through suitable coupling of lower-order tensors, but this is not required for the purposes of this paper. Table I shows the relationship between $G_m^{(sl)}$ and Cartesian operators.

TABLE I. Gradient operator of Eq. (11) written in terms of Cartesian operators.

s	l	m	$G_m^{(sl)}$
0	0	0	1
1	1	0	$-i\partial_z$
1	1	± 1	$\frac{1}{\sqrt{2}}(\pm i\partial_x + \partial_y)$
2	0	0	$\frac{1}{\sqrt{3}}\nabla^2$
2	2	0	$(\frac{2}{3})^{1/2}[\frac{1}{2}(\partial_x^2 + \partial_y^2) - \partial_z^2]$
2	2	± 1	$(\pm \partial_x - i\partial_y)\partial_z$
2	2	± 2	$\frac{1}{2}(\pm i\partial_x + \partial_y)^2$

3. Expansion of $f_m^{(l)}$

There are two independent directions defined in any swarm experiment, determined by the electric field **E** and ∇n, respectively. We can form tensors of any rank from these vectors, either individually or by coupling them together. Thus, *any* tensor $f_m^{(l)}$ can be represented quite generally by a sum over all possible couplings of tensors formed from **E** and the gradient operator which produces a tensor of rank l:

$$f_m^{(l)} = \sum_{s=0}^{\infty} \sum_{\lambda=0}^{s} \sum_{\lambda'=0}^{\infty} \bar{f}(l \mid s\lambda\lambda')[\underline{G}^{(s\lambda)}, \underline{Y}^{(\lambda')}(\hat{\mathbf{E}})]_m^{(l)} n \ , \qquad (12)$$

where $\bar{f}(l \mid s\lambda\lambda')$ are scalar coefficients which vanish unless

$$l + \lambda + \lambda' = \text{even} \ ,$$

a result which follows from parity considerations.

It is convenient to choose a system of coordinates in which the z axis lies along the field **E**, for then it can be shown that

$$Y_\mu^{(\lambda')}(\hat{\mathbf{E}}) = (-i)^{\lambda'} \left[\frac{2\lambda'+1}{4\pi}\right]^{1/2} \delta_{\mu'0} \ ,$$

and hence (12) becomes

$$f_m^{(l)} = \sum_{s=0}^{\infty} \sum_{\lambda=0}^{s} f(lm \mid s\lambda) G_m^{(s\lambda)} n \ , \qquad (13)$$

where

$$f(lm \mid s\lambda) = \sum_{\lambda'} \bar{f}(l \mid s\lambda\lambda')(\lambda m \lambda'0 \mid lm)(-i)^{\lambda'}$$

$$\times \left[\frac{2\lambda'+1}{4\pi}\right]^{1/2} \ .$$

The Clebsch-Gordon coefficient here requires that

$$f(l - m \mid s\lambda) = f(lm \mid s\lambda) \qquad (14a)$$

and

$$f(lm \mid s\lambda) = 0 \ , \quad \mid m \mid > \min\{l, \lambda\} \ . \qquad (14b)$$

Combining (1) and (13) gives the counterpart of (5) written entirely in terms of spherical quantities (the upper

limit on the s summation is restricted to 2):

$$f(\mathbf{r},\mathbf{c},t)=n(\mathbf{r},t)\sum_{l=0}^{\infty}f(l0\,|\,00)Y_0^{[l]}(\hat{\mathbf{c}})$$

$$+\sum_{m=-1}^{1}\sum_{l=|m|}^{\infty}f(lm\,11)Y_m^{[l]}(\hat{\mathbf{c}})G_m^{[11]}n(\mathbf{r},t)$$

$$+\sum_{l=0}^{\infty}f(l0\,|\,20)\,|\,Y_0^{[l]}(\hat{\mathbf{c}})G_0^{(20)}n(\mathbf{r},t)$$

$$+\sum_{m=-2}^{2}\sum_{l=|m|}^{\infty}f(lm\,|\,22)Y_m^{[l]}(\hat{\mathbf{c}})G_m^{[22]}n(\mathbf{r},t)\ .$$

(15)

Explicit expressions for the $G_m^{(s\lambda)}n$ could be substituted from Table I, if desired, to enable comparison with Cartesian expansions, but this is not done here. Instead, we concentrate on some of the more general aspects of (15).

It is helpful to write down the following explicit expressions for spherical harmonics:

$$Y_0^{[l]}(\hat{\mathbf{c}})=i^l\left[\frac{2l+1}{4\pi}\right]^{1/2}P_l(\cos\theta)\ ,$$

$$Y_{\pm1}^{[l]}(\hat{\mathbf{c}})=\mp i^l\left[\frac{(2l+1)(l-1)!}{4\pi(l+1)!}\right]^{1/2}P_l^1(\theta)e^{\pm i\phi}\ ,$$

$$Y_{\pm2}^{[l]}(\hat{\mathbf{c}})=i^l\left[\frac{(2l+1)(l-2)!}{4\pi(l+2)!}\right]^{1/2}P_l^2(\theta)e^{\pm2i\phi}\ .$$

These expressions show that the first and third terms on the right-hand side of (15), together with the $m=0$ contributions from the second and fourth summations, depend only upon θ, the angle between $\mathbf{c}$ and $\mathbf{E}$, that is, they represent the axial symmetric parts of the velocity distribution function. All other terms contain a dependence upon the azimuthal angle ϕ and are *not* axially symmetric. Thus, while a density gradient parallel to $\mathbf{E}$, $\partial_z n=iG_0^{(11)}n$, maintains axial symmetry, a transverse gradient $\partial_y n=\frac{1}{2}(G_{+1}^{(11)}+G_{-1}^{(11)})$ destroys it. It is therefore incorrect to try to analyze transverse diffusion through an expansion of f which depends only upon θ.

4. Wigner-Eckhart theorem (Refs. 26—28)

If $A_\mu^{[\lambda]}$ is an irreducible tensor operator which depends only upon $\mathbf{c}$ and $\partial_\mathbf{c}$, then the following expression holds for the matrix elements of the operator:

$$\langle lm\,|\,A_\mu^{[\lambda]}\,|\,l'm'\rangle\equiv\int Y_m^{(l)}(\hat{\mathbf{c}})A_\mu^{[\lambda]}Y_m^{[l']}(\hat{\mathbf{c}})d\hat{\mathbf{c}}$$

$$=(l'm'\lambda\mu\,|\,lm)\langle l||A^{[\lambda]}||l'\rangle\ ,\quad(16)$$

where $\langle l||A^{[\lambda]}||l'\rangle$ is a "reduced matrix element." The significance of the theorem is that it shows that all m dependence is carried by a Clebsch-Gordon coefficient.

B. Decomposition of the Boltzmann equation

1. Matrix elements

Substitution of the expansion (1) into the Boltzmann equation (3) followed by multiplication on the left by $Y_m^{(l)}(\hat{\mathbf{c}})$ and integration over all $\hat{\mathbf{c}}$ yields

$$\sum_{l',m'}\langle lm\,|\,\partial_t+\mathbf{c}\cdot\nabla+\mathbf{a}\cdot\partial_\mathbf{c}\,|\,l'm'\rangle f_{m'}^{(l')}$$

$$=-\sum_{l',m'}\langle lm\,|\,J\,|\,l'm'\rangle f_{m'}^{(l')}\ .\quad(17)$$

The matrix elements may be partially evaluated by appealing to the Wigner-Eckhart theorem (16). Thus, since J is a scalar operator for central forces,

$$\langle lm\,|\,J\,|\,l'm'\rangle=(l'm'00\,|\,lm)\langle l||J||l'\rangle$$

$$=\delta_{l'l}\delta_{m'm}J^l\ ,\quad(18)$$

where we have written J^l for the reduced matrix element $\langle l||J||l\rangle$. Notice that this is still an operator in c space, although we do not require the explicit expression here. Since ∂_t does not depend upon $\mathbf{c}$ we have as a trivial application of (16)

$$\langle lm\,|\,\partial_t\,|\,l'm'\rangle=\delta_{l'l}\delta_{m'm}\partial_t\ .\quad(19)$$

Matrix elements of the gradient and field terms in (17) are

$$\langle lm\,|\,\mathbf{c}\cdot\nabla\,|\,l'm'\rangle=\sum_\mu\langle lm\,|\,c_\mu^{[1]}\,|\,l'm'\rangle G_\mu^{(11)}$$

$$=\sum_\mu(l'm'1\mu\,|\,lm)\langle l||c^{(1)}||l'\rangle G_\mu^{(11)}$$

(20)

$$\langle lm\,|\,\mathbf{a}\cdot\partial_\mathbf{c}\,|\,l'm'\rangle=\sum_\mu a_\mu^{(1)}\langle lm\,|\,\partial_{c_\mu}^{[1]}\,|\,l'm'\rangle$$

$$=\sum_\mu a_\mu^{(1)}(l'm'1\mu\,|\,lm)\langle l||\partial_c^{[1]}||l'\rangle$$

$$=-ia(l'm10\,|\,lm)\langle l||\partial_c^{[1]}||l'\rangle\delta_{m'm}\ ,$$

(21)

respectively, where we have used the fact that the field lies along the z axis and set

$$a_\mu^{(1)}=-ia\delta_{\mu0}\ .$$

Substitution of (18)—(21) into (17) then gives

$$\partial_t f_m^{(l)}+\sum_{l'm'\mu}(l'm'1\mu\,|\,lm)\langle l||c^{[1]}||l'\rangle G_\mu^{(11)}f_{m'}^{(l')}$$

$$-ia\sum_{l'}(l'm10\,|\,lm)\langle l||\partial_c^{[1]}||l'\rangle f_m^{(l')}=-J^lf_m^{(l)}\ .\quad(22)$$

The reduced matrix elements required are

$$\langle l||\partial_c^{[1]}||l-1\rangle=\left[\frac{l}{2l+1}\right]^{1/2}\left[\frac{d}{dc}-\frac{(l-1)}{c}\right]\ ,\quad(23a)$$

$$\langle l||\partial_c^{[1]}||l+1\rangle=\left[\frac{l+1}{2l+1}\right]^{1/2}\left[\frac{d}{dc}+\frac{(l+2)}{c}\right]\ ,\quad(23b)$$

$$\langle l||\partial_c^{[1]}||l'\rangle=0\quad\text{if } l'\neq l\pm1\ ;$$

$$\langle l||c^{[1]}||l-1\rangle=c\left[\frac{l}{2l+1}\right]^{1/2}\ ,\quad(24a)$$

$$\langle l||c^{[1]}||l+1\rangle=c\left[\frac{l+1}{2l+1}\right]^{1/2}\ ,\quad(24b)$$

$$\langle l||c^{[1]}||l'\rangle=0\quad\text{if } l'\neq l\pm1\ .$$

Some simple cases required for later are

$$\langle 0||\partial_c^{[1]}||1\rangle = \frac{d}{dc} + \frac{2}{c} \tag{23c}$$

and

$$\langle 0||c^{[1]}||1\rangle = c \ . \tag{24c}$$

2. Equation of continuity

The equation of continuity[1] provides the link between theory and experiment. In the usual notation it is

$$\partial_t n = -\alpha n - W\partial_z n + D_T(\partial_x^2 + \partial_y^2)n + D_L\partial_z^2 n \ , \tag{25}$$

where α is an attachment rate coefficient, W is the drift velocity, and D_L, D_T denote diffusion along and transverse to the field, respectively. Equation (25) can be solved for a particular experimental arrangement once the boundary and initial conditions are specified. It is *not* necessary in this discussion to assume any symmetry properties for density in configuration space.

Equation (13) applies to any tensor, in particular to a scalar:

$$f_0^{(0)} = \sum_{s=0}^{\infty} \sum_{\lambda=0}^{s} f(00|s\lambda)G_0^{(s\lambda)}n \ .$$

Since $\partial_t n$ is a scalar, we can express it in this way:

$$\partial_t n = \sum_{s=0}^{\infty} \sum_{\lambda=0}^{s} \omega(s\lambda)G_0^{(s\lambda)}n \tag{26a}$$

$$= \omega(00)n - i\omega(11)\partial_z n + \frac{1}{\sqrt{3}}\omega(20)\nabla^2 n$$

$$+ (\tfrac{2}{3})^{1/2}\omega(22)[\tfrac{1}{2}(\partial_x^2 + \partial_y^2) - \partial_z^2]n + \cdots \ , \tag{26b}$$

where we have used the explicit expressions for $G_0^{(sl)}$ shown in Table I. Comparison of (25) and (26b) allows us to make the following identification of the quantities $\omega(s\lambda)$:

$$\omega(00) = -\alpha \ ,$$

$$\omega(11) = -iW \ ,$$

$$\omega(22) = (\tfrac{2}{3})^{1/2}(D_T - D_L) \ ,$$

$$\omega(20) = \frac{1}{\sqrt{3}}(2D_T + D_L) \ ,$$

or equivalently,

$$\alpha = -\omega(00) \ , \quad W = i\omega(11) \ ,$$

$$D_L = \frac{1}{\sqrt{3}}[\omega(20) - \sqrt{2}\omega(22)] \ , \tag{27}$$

$$D_T = \frac{1}{\sqrt{3}}\left[\omega(20) + \frac{1}{\sqrt{2}}\omega(22)\right] \ .$$

In what follows we shall explain how to obtain the $\omega(s\lambda)$ from Boltzmann's equation. The procedure is formally equivalent to Sec. 4 of Ref. 1 but the results are expressed entirely in terms of spherical tensors rather than the mixed spherical-Cartesian notation.

3. The hierarchy of equations

We substitute the expansion (13) into the Boltzmann equation (22) and equate the coefficients of $G_m^{(s\lambda)}$, thereby generating a hierarchy of coupled equations for $f(lm|s\lambda)$. The time-derivative term in (22) also requires the use of the equation of continuity (26). After some algebra we find the following:

$s = \lambda = 0$

$$[J^l + \omega(00)]f(l0|00) - ia\sum_{l'}(l'010|l0)\langle l||\partial_c^{[1]}||l'\rangle f(l'0|00) = 0 \ ; \tag{28}$$

$s = \lambda = 1$

$$[J^l + \omega(00)]f(lm|11) - ia\sum_{l'}(l'm10|lm)\langle l||\partial_c^{[1]}||l'\rangle f(l'm|11)$$

$$= -\delta_{m0}f(l0|00)\omega(11) - \sum_{l'}(l'01m|lm)\langle l||c^{[1]}||l'\rangle f(l'0|00) \quad (m=0,\pm1) \ ; \tag{29}$$

$s = 2, \lambda = 0$

$$[J^l + \omega(00)]f(l0|20) - ia\sum_{l'}(l'010|l0)\langle l||\partial_c^{[1]}||l'\rangle f(l'0|20)$$

$$= -f(l0|00)\omega(20) - \frac{1}{\sqrt{3}}f(l0|11)\omega(11) - \frac{1}{\sqrt{3}}\sum_{l'}\langle l||c^{[1]}||l'\rangle[-(l'010|l0)f(l'0|11) + 2(l'11-1|l0)f(l'1|11)] \ ; \tag{30}$$

$s = 2, \lambda = 2$

$$[J^l + \omega(00)]f(lm|22) - ia\sum_{l'}(l'm10|lm)\langle l||\partial_c^{[1]}||l'\rangle f(l'm|22)$$

$$= -\delta_{m0}f(l0|00)\omega(22) - f(lm|11)\omega(11)(1m10|2m)$$

$$- \sum_{l'}\langle l||c^{[1]}||l'\rangle\{f(l'0|11)(l'01m|lm)(1m10|2m) + f(l'1|11)[(l'11m-1|lm)(1m-111|2m)$$

$$+ (l'-11m+1|lm)(1m+11-1|2m)\} \quad (m=0,\pm1,\pm2) \ . \tag{31}$$

The first equation of the chain, i.e., (28), is an eigenvalue equation, with $\omega(00)$ as eigenvalue. The remainder, (29)–(31), are inhomogeneous equations, with material on the rhs obtained by solving the previous equation of the chain, although the $\omega(s\lambda)$ with $(s,\lambda)\neq(0,0)$ have to be found in a self-consistent manner, as explained below. For each eigenvalue of (28), $\omega_j(00)$, there will be a uniquely determined solution of this hierarchy which we write as $f_j(\lambda m \mid s\lambda), \omega_j(s\lambda)$, with $j=1,2,\ldots$, and the most general solution will be a linear superposition of these "modes." The solution of the equation of continuity (26) can be written formally as

$$n(\mathbf{r},t)=\sum_j e^{\omega_j(00)t}\bar{n}_j(\mathbf{r},t) \tag{32}$$

and the solution (13) of the Boltzmann equation will be of the form

$$f_m^{(l)}=\sum_j\sum_s\sum_\lambda f_j(lm \mid s\lambda)e^{\omega_j(00)t}G_m^{(s\lambda)}\bar{n}_j(\mathbf{r},t) , \tag{33}$$

where $\bar{n}_j(\mathbf{r},t)$ is given by the solution of

$$\partial_t\bar{n}_j+\sum_{s,\lambda}{}'\omega_j(s\lambda)G_0^{(s\lambda)}\bar{n}_j=0 \quad (j=1,2,\ldots) , \tag{34}$$

where the prime indicates no $s=0=\lambda$ term. One is normally interested in the asymptotic time regime $t\to\infty$, in which case there will usually be one dominant term in each of (32) and (33), provided that the spectrum of eigenvalues $\omega_j(00)$ has certain discreteness properties as explained below.

For *attachment*, $\omega_j(00)$ will be negative and then the dominant term in (32) and (33) will be that corresponding to the eigenvalue with the *smallest* magnitude. (For *ionization*, the *largest* positive eigenvalue controls the asymptotic behavior.) These remarks apply only if the smallest, or, for ionization, largest, eigenvalue, $\omega_1(00)$, is distinct from the rest of the spectrum, which may or may not be discrete.

Thus, we have asymptotically

$$n(\mathbf{r},t)=e^{\omega_1(00)t}\bar{n}_1(\mathbf{r},t) , \tag{35}$$

$$f_m^{(l)}(\mathbf{r},c,t)=\sum_{s,\lambda}f_1(lm \mid s\lambda)e^{\omega_1(00)t}G_m^{(s\lambda)}\bar{n}_1(\mathbf{r},t) , \tag{36}$$

where $\bar{n}_1$ is the solution of (34) with $j=1$. It is to be henceforth understood when making the identification of transport coefficients, as in (27), that $\omega_1(s\lambda)$ is implied.

Restriction to the asymptotic regime greatly simplifies the problem, for then only one eigenvalue and eigensolution need to be obtained from (28). It will be assumed here that the required eigenvalue separates from the rest of the spectrum, but we do not attempt to establish general conditions for which this will be true. Instead, in subsequent numerical calculations in II we verify for the particular cases studied that the spectrum has the required property.

C. Determination of transport coefficients

1. Normalization considerations

By definition, the number density is given by

$$n(\mathbf{r},t)=\int f(\mathbf{r},c,t)d^3c$$
$$=\sqrt{4\pi}\int_0^\infty f_0^{(0)}c^2\,dc$$
$$=\sqrt{4\pi}\sum_{s,\lambda}G_0^{(s\lambda)}n\int_0^\infty f(00 \mid s\lambda)c^2\,dc ,$$

where we have substituted expansions (1) and (13) and made use of the orthogonality of spherical harmonics and the fact that $Y_0^{[0]}=1/\sqrt{4\pi}$. Since $G_0^{(00)}n=n$, it then follows that

$$\sqrt{4\pi}\int_0^\infty f(00 \mid 00)c^2\,dc=1 , \tag{37a}$$

$$\int_0^\infty f(00 \mid s\lambda)c^2\,dc=0 \quad (s,\lambda)\neq(0,0) . \tag{37b}$$

Another property we shall need below follows from (23c). For any well-behaved function of c, say $\phi(c)$,

$$\int_0^\infty\langle0||\partial_c^{[1]}||1\rangle\phi(c)c^2\,dc=\int_0^\infty c^2\left[\frac{d}{dc}+\frac{2}{c}\right]\phi(c)dc$$

$$=\int_0^\infty\frac{d}{dc}[c^2\phi(c)]dc$$

$$=0 . \tag{38}$$

2. Determination of the $\omega(s\lambda)$

If we integrate the $l=0$ member of (28) with c^2 and make use of (37a) and (38), it follows that

$$\omega(00)=-\sqrt{4\pi}\int_0^\infty J_R^0[f(00 \mid 00)]c^2\,dc , \tag{39}$$

where J_R denotes the nonconservative or "reactive" part of the collision operator. Equation (39) does not determine $\omega(00)$, since $f(00 \mid 00)$ is unknown. The correct way to treat (28) is as an eigenvalue problem and to select the eigenvalue $\omega(00)$ which is appropriate to the physics of the problem as explained in Sec. II B 3 above. [It is implied in what follows that $\omega(00)$ and $f(l0 \mid 00)$ are the appropriate eigenvalue and eigensolution, respectively—a subscript "1" is not then needed.] Equation (39) merely serves to emphasize that $\omega(00)\neq0$ if and only if reactions take place. It is interesting to note, however, that in discussions of *ion-molecule reactions*,[30] *for which this theory is still applicable*, Eq. (39) *is* used to determine $\omega(00)$, the $f(00 \mid 00)$ on the rhs being approximated by the solution of (28) with all reactive effects omitted. This amounts to treating reactions as a small perturbation on the ion velocity distribution function. No such approximation can generally be made for electrons—the electron velocity distribution is often substantially perturbed, leading to effects such as "attachment cooling."[31]

To find $\omega(11)$, we integrate the $l=m=0$ member of (29) with c^2 over all speeds and obtain

$$\omega(11)=\left[\frac{4\pi}{3}\right]^{1/2}\int_0^\infty c^3f(10 \mid 00)dc$$

$$-\sqrt{4\pi}\int_0^\infty c^2J_R^0[f(00 \mid 11)]dc , \tag{40}$$

where we have made use of (24c) and (38). The second term on the rhs of (40) contains the unknown function $f(00 \mid 11)$ which is to be found from solving (29), which in turn contains the unknown quantity $\omega(11)$. Thus Eqs. (29) and (40) have to be solved self-consistently for $f(10 \mid 11)$ and $\omega(11)$, bearing in mind the constraint (37b). Equation (29) is not an eigenvalue equation, at least, not in the same sense as (28). Integration of c^2 times the $l = 0$ members of (30) and (31) similarly yields

$$\omega(20) = -\frac{\sqrt{4\pi}}{3} \int_0^\infty c^3 [2f(11 \mid 11) + f(10 \mid 11)]dc$$

$$-\sqrt{4\pi} \int_0^\infty c^2 J_R^0 [f(00 \mid 20)]dc \qquad (41)$$

and

$$\omega(22) = -\frac{\sqrt{8\pi}}{3} \int_0^\infty c^3 [f(11 \mid 11) - f(10 \mid 11)]dc$$

$$-\sqrt{4\pi} \int_0^\infty c^2 J_R^0 [f(00 \mid 22)]dc \,, \qquad (42)$$

respectively. Again, the ω's and f's have to be obtained through a self-consistent procedure. Notice that only the $m = 0$ equation of the set (31) needs be solved to obtain $\omega(22)$.

3. Transport coefficients

It follows directly from (27) and (40)—(42) that

$$W = i \left[\frac{4\pi}{3} \right]^{1/2} \int_0^\infty c^3 f(10 \mid 00)dc$$

$$- i\sqrt{4\pi} \int_0^\infty c^2 J_R^0 [f(00 \mid 11)]dc \,, \qquad (43)$$

$$D_T = -\left[\frac{4\pi}{3} \right]^{1/2} \left[\int_0^\infty c^3 f(11 \mid 11)dc \right.$$

$$+ \int_0^\infty c^2 J_R^0 \left| f(00 \mid 20) \right.$$

$$\left. + \frac{1}{\sqrt{2}} f(00 \mid 22) \right| dc \left. \right] \,, \qquad (44)$$

$$D_L = -\left[\frac{4\pi}{3} \right]^{1/2} \left[\int_0^\infty c^3 f(10 \mid 11) \right.$$

$$+ \int_0^\infty c^2 J_R^0 [f(00 \mid 20)$$

$$\left. -\sqrt{2} f(00 \mid 22)]dc \right] \qquad (45)$$

are the transport coefficients as defined in Sec. II B 2 in terms of the coefficients in the equation of continuity. The first member on the rhs of (43) represents the average velocity in the absence of spatial gradients, as can readily be verified by evaluation,

$$\langle c_z \rangle = \frac{1}{n} \int c_z f \, d^3 c \,,$$

and substituting from (1) and (13). The quantity (43) could therefore perhaps be referred to as the "apparent drift velocity" as measured by a macroscopic observer whose only information comes from the equation of continuity. We prefer just "drift velocity." The second member on the rhs of (43) has the effect of providing an apparent drift motion through selective "chemical" production or annihilation of charged particles with different energies. [If the reactive operator were not energy selective, that is, $J_R = \text{const}$, then the second member of each of (43), (44), and (45) would vanish identically by virtue of (37).] It should be noted that the solution of only *five* equations is needed: Eqs. (28) and (29) with $m = 0$ and $m = +1$ or -1 and Eqs. (30) and (31) with $m = 0$ only.

III. DISCUSSION

We have reviewed existing approaches to electron transport and have outlined the formal aspects of the problem when nonconservative collisions take place. The equations to be solved are (28)—(31), the solutions of which then provide the transport coefficients through (43)—(45). Depending upon whether particles are created or annihilated in collisions, the largest or smallest eigenvalue of (28) is to be found. The discussion applies, in fact, to ions, as well as to electrons. It also applies to positron transport.[32] In II we represent the $f_m^{(l)}$ [or, equivalently, the $f(lm \mid s\lambda)$] in terms of Sonine polynomials. This may be looked upon as an extension of the LRM analysis to account for nonconservative collisions. Other methods involving finite difference techniques differ from this insofar as the $f_m^{(l)}$ are represented by low-order polynomials in discrete intervals of c. In principle, however, the difference is small as explained in Sec. I. Transport coefficients *and* the distribution function are obtainable from the LRM procedure, as well as these other methods. All methods can (and should) start from the same set of equations.

We can rewrite our Eqs. (28)—(31) in a form more amenable to computation and more suitable for comparison with any previous results by defining

$$F_l \equiv i^l \left[\frac{2l+1}{4\pi} \right]^{1/2} f(l0 \mid 00) \,, \qquad (46a)$$

$$F_l^{(L)} \equiv i^{l+1} \left[\frac{2l+1}{4\pi} \right]^{1/2} f(l0 \mid 11) \,, \qquad (46b)$$

$$F_l^{(T)} \equiv i^{l+1} \left[\frac{2(2l+1)}{4\pi l(l+1)} \right]^{1/2} f(l1 \mid 11) \,, \qquad (46c)$$

$$F_l^{(2T)} \equiv i^{l+1} \left[\frac{2l+1}{4\pi} \right]^{1/2} f(l0 \mid 20) \,, \qquad (46d)$$

$$F_l^{(2L)} \equiv i^{l+1} \left[\frac{2l+1}{4\pi} \right]^{1/2} f(l0 \mid 22) \qquad (46e)$$

and

$$\omega_0 = \omega(00) = -\alpha \,, \qquad (47a)$$

$$\omega_1 = i\omega(11) = W \,, \qquad (47b)$$

$$\omega_2 = \omega(20) = 1/\sqrt{3}(2D_T + D_L) \,, \qquad (47c)$$

$$\bar{\omega}_2 = \omega(22) = (\tfrac{2}{3})^{1/2}(D_T - D_L) . \tag{47d}$$

Thus, it can be shown that F_l, $F_l^{(L)}$, $F_l^{(2T)}$, and $F_l^{(2L)}$ all obey equations of the form

$$(J^l + \omega_0)\phi_l + \frac{l+1}{2l+3}a\left[\frac{d}{dc} + \frac{l+2}{c}\right]\phi_{l+1}$$
$$+ \frac{l}{2l-1}a\left[\frac{d}{dc} - \frac{l-1}{c}\right]\phi_{l-1} = h_l , \tag{48}$$

where h_l assumes the expressions

$$0 , \tag{49a}$$

$$c\left[\frac{l+1}{2l+3}F_{l+1} + \frac{l}{2l-1}F_{l-1}\right] - \omega_1 F_l , \tag{49b}$$

$$\frac{c}{\sqrt{3}}\left[\frac{l+1}{2l+3}\left[F_{l+1}^{(L)} + (l+2)F_{l+1}^{(T)}\right]\right.$$
$$\left. + \frac{l}{2l-1}\left[F_{l-1}^{(L)} - (l-1)F_{l-1}^{(T)}\right]\right] - \omega_2 F_l - \frac{1}{\sqrt{3}}F_l^{(L)} , \tag{49c}$$

and

$$-\left[\frac{2}{3}\right]^{1/2}c\left[\frac{l+1}{2l+3}\left[F_{l+1}^{(L)} - \frac{(l+2)}{2}F_{l+1}^{(T)}\right]\right.$$
$$\left. + \frac{l}{2l-1}\left[F_{l-1}^{(L)} + \frac{(l-1)}{2}F_{l-1}^{(T)}\right]\right]$$
$$-\bar{\omega}_2 F_l + \left[\frac{2}{3}\right]^{1/2}\omega_1 F_l^{(L)} , \tag{49d}$$

respectively, while

$$(J^l + \omega_0)F_l^{(T)} + \frac{l+2}{2l+3}a\left[\frac{d}{dc} + \frac{l+2}{c}\right]F_{l+1}^{(T)}$$
$$+ \frac{l-1}{2l-1}a\left[\frac{d}{dc} + \frac{l-1}{c}\right]F_{l-1}^{(T)}$$
$$= c\left[\frac{F_{l-1}}{2l-1} - \frac{F_{l+1}}{2l+3}\right] . \tag{50}$$

The normalization is

$$4\pi\int_0^\infty F_0 c^2 \, dc = 1 ,$$
$$\tag{51}$$
$$\int_0^\infty F_0^{(L)} c^2 \, dc = \int_0^\infty F_0^{(T)} c^2 \, dc$$
$$= \int_0^\infty F_0^{(2L)} c^2 \, dc = \int_0^\infty F_0^{(2T)} c^2 \, dc = 0 ,$$

and by (39), (40), (41), and (42),

$$\omega_0 = -4\pi\int_0^\infty J_R^0(F_0)c^2 \, dc , \tag{52a}$$

$$\omega_1 = \frac{4\pi}{3}\int_0^\infty c^3 F_1 \, dc - 4\pi\int_0^\infty c^2 J_R^0(F_0^{(L)})dc , \tag{52b}$$

$$\omega_2 = \frac{4\pi}{3\sqrt{3}}\int_0^\infty c^3(F_1^{(L)} + 2F_1^{(T)})dc$$
$$- 4\pi\int_0^\infty c^2 J_R^0(F_0^{(2T)})dc , \tag{52c}$$

$$\bar{\omega}_2 = -\frac{4\pi}{3}\left[\frac{2}{3}\right]^{1/2}\int_0^\infty c^3(F_1^{(L)} - F_1^{(T)})dc$$
$$- 4\pi\int_0^\infty c^2 J_R^0(F_0^{(2L)})dc , \tag{52d}$$

respectively. Thus, we have by (47a)–(47d) and the above that

$$\alpha = 4\pi\int_0^\infty J_R^{(0)}(F_0)c^2 \, dc , \tag{53a}$$

$$W = \frac{4\pi}{3}\int_0^\infty c^3 F_1 \, dc - 4\pi\int_0^\infty c^2 J_R^0(F_0^{(L)})dc , \tag{53b}$$

$$D_T = \frac{4\pi}{3}\int_0^\infty c^3 F_1^{(T)} dc$$
$$- \frac{4\pi}{\sqrt{3}}\int_0^\infty J_R^0\left[F_0^{(2T)} + \frac{1}{\sqrt{2}}F_0^{(2L)}\right]c^2 \, dc , \tag{53c}$$

$$D_L = \frac{4\pi}{3}\int_0^\infty c^3 F_1^{(L)} dc$$
$$- \frac{4\pi}{\sqrt{3}}\int_0^\infty J_R^0(F_0^{(2T)} - \sqrt{2}F_0^{(2L)})c^2 \, dc . \tag{53d}$$

Equation (53a) is consistent with results derived on the basis of the two-term approximation—see, for example, Eq. (26) of Ref. 31, with boundary effects removed. After insertion of appropriate expressions for J^l [see Ref. 1, Eqs. (158a), (159), and (175)], the above equations can be solved for F_l, $F_l^{(L)}$, $F_l^{(T)}$, $F_l^{(2T)}$, and $F_l^{(2L)}$. In the absence of reactive effects, the equations for F_l, $F_l^{(L)}$, and $F_l^{(T)}$ reduce to well-known forms, as do the expressions for W, D_T, and D_L. [See Ref. 1, Eqs. (184), (186), and (189), but note that a factor 4π is required in (184c), (184d), (186d), and (189d).]

To make contact with other expansions, we use Eq. (15) and the explicit expressions for $Y_m^{[l]}$, together with the definitions (46a)–(46e) and Table I, to find

$$f(\mathbf{r},\mathbf{c},t) = n\sum_{l=0}^\infty F_l(c)P_l(\cos\theta) - \sum_{l=0}^\infty F_l^{(L)}(c)P_l(\cos\theta)\partial_z n - \sum_{l=1}^\infty F_l^{(T)}(c)P_l^1(\theta)(\cos\phi\,\partial_x n + \sin\phi\,\partial_y n)$$
$$+ \frac{1}{\sqrt{3}}\sum_{l=0}^\infty \{F_l^{(2T)}(c)\nabla^2 n + \sqrt{2}F_l^{(2L)}(c)[\tfrac{1}{2}(\partial_x^2 + \partial_y^2) - \partial_z^2]n\}P_l(\cos\theta)$$
$$+ \sum_{m=\pm 1,\pm 2}\sum_{l=|m|}^\infty f(lm\,|\,22)Y_m^{[l]}(\hat{c})G_m^{(22)}n + \cdots . \tag{54}$$

This is the most general expansion to second order in the density gradient. Note that we do not need $f(lm \mid 22)$ with $m \neq 0$ in order to obtain the conventional transport coefficients.

The first three members of the rhs of (54) correspond to well-known expansions to first-order in the density gradient [Ref. 1, Eqs. (183), (185), (187), and (188)], while the fourth summation, containing second-order density-gradient terms, may be compared with the second-order terms of Eq. (2) of Ref. 17. Note, however, that it is not necessary to make any assumptions about symmetry properties of density n, as is implicitly done in the latter.

This concludes the general discussion on the spherical-harmonics decomposition and it is at this point that the various representations of the F's as functions of c will differ, as will the means of solving (48) and (50). In the subsequent paper (II), we perform a further expansion in Sonine polynomials in order to effect numerical solutions and examine a wide variety of problems in electron-swarm physics.

ACKNOWLEDGMENTS

*Present address: Chemistry Department, University of British Columbia, Vancouver, British Columbia, Canada V6T 1N5.

[1]K. Kumar, H. R. Skullerud, and R. E. Robson, Aust. J. Phys. 33, 343 (1980).

[2]K. Kumar, Phys. Rep. 112, 319 (1984).

[3]L. G. H. Huxley and R. W. Crompton, The Diffusion and Drift of Electrons in Gases (Wiley, New York, 1974).

[4]Charged-particle densities are assumed sufficiently low so that mutual interactions between these particles are negligible. Such conditions are normally achieved in swarm experiments.

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

[6]R. E. Robson and K. Kumar, Aust. J. Phys. 24, 835 (1971).

[7]L. A. Viehland and E. A. Mason, Ann. Phys. (N.Y.) 91, 499 (1975); 110, 287 (1978).

[8]G. N. Haddad and R. W. Crompton, Aust. J. Phys. 33, 975 (1980); G. N. Haddad, S. L. Lin, and R. E. Robson, ibid. 34, 243 (1981); G. N. Haddad and H. B. Milloy, ibid. 36, 473 (1983); G. N. Haddad, ibid. 37, 487 (1984); R. W. Crompton, Z. Lj. Petrovic, and G. N. Haddad, ibid. 37, 23 (1984); R. E. Robson, ibid. 37, 35 (1984); G. N. Haddad, ibid. 38, 677 (1985).

[9]P. Kleban and H. T. Davis, Phys. Rev. Lett. 39, 456 (1977); J. Chem. Phys. 68, 2999 (1978).

[10]P. Kleban, L. Foreman, and H. T. Davis, J. Chem. Phys. 73, 519 (1980).

[11]G. L. Braglia, J. Chem. Phys. 74, 2990 (1981); H. R. Skullerud and S. Kuhn, J. Phys. D 16, 1225 (1983).

[12]H. Tagashira, T. Tanaguchi, K. Kitamori, and Y. Sakai, J. Phys. D 11, L43 (1978); K. Kitamori, H. Tagashira, and Y. Sakai, ibid. 11, 283 (1978); 13, 535 (1980); H. Tagashira, in Proceedings of the Fifteenth International Conference on Phenomena in Ionized Gases, Minsk, U.S.S.R., 1981 (unpublished); H. A. Blevin and J. Fletcher, Aust. J. Phys. 37, 593 (1984).

[13]G. L. Braglia and G. L. Caraffini, Lett. Nuovo Cimento 27, 145 (1980).

[14]L. C. Pitchford, S. V. O'Neil, and J. R. Rumble, Phys. Rev. A 23, 294 (1981); L. C. Pitchford and A. V. Phelps, ibid. 25, 540 (1982).

[15]G. Cavallieri, Aust. J. Phys. 34, 361 (1981).

[16]W. P. Allis, Phys. Rev. A 26, 1704 (1982).

[17]A. V. Phelps and L. C. Pitchford, Phys. Rev. A 31, 2932 (1985).

[18]D. R. A. McMahon, Aust. J. Phys. 36, 163 (1983) and unpublished.

[19]P. Segur, M. C. Bordage, J. P. Balaguer, and M. Yousfi, J. Comput. Phys. 50, 116 (1983); P. Segur, M. Yousfi, and M. C. Bordage, J. Phys. D 17, 2199 (1984).

[20]G. L. Braglia, J. Wilhelm, and R. Winkler, Nuovo Cimento 80, 21 (1984).

[21]G. L. Braglia, Lett. Nuovo Cimento 31, 183 (1981).

[22]S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform Gases, 3rd ed. (Cambridge University Press, Cambridge, England, 1970).

[23]K. F. Ness, Ph.D. thesis, James Cook University of North Queensland, 1985.

[24]C. S. Wang-Chang, G. E. Uhlenbeck, and J. de Boer, in Studies in Statistical Mechanics, edited by J. de Boer and G. E. Uhlenbeck, Vol. II (Wiley, New York, 1964).

[25]L. S. Frost and A. V. Phelps, Phys. Rev. 127, 1621 (1962).

[26]K. Kumar, Aust. J. Phys. 20, 205 (1967).

[27]U. Fano and G. Racah, Irreducible Tensorial Sets (Academic, New York, 1959).

[28]M. E. Rose, Elementary Theory of Angular Momentum (Wiley, New York, 1957).

[29]E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, England, 1953).

[30]L. A. Viehland and E. A. Mason, J. Chem. Phys. 66, 422 (1977).

[31]H. R. Skullerud, Aust. J. Phys. 36, 845 (1983).

[32]R. I. Campeanu and J. W. Humberston, J. Phys. B 10, 239 (1977).