

## MOBILITY AND DIFFUSION

### I. BOLTZMANN EQUATION TREATMENT FOR CHARGED PARTICLES IN A NEUTRAL GAS

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#### *Abstract*

The conditions that usually prevail in drift tube experiments for the measurement of mobility and diffusion of electron and ion swarms are appropriate for the application of a linearized Boltzmann equation. Starting from such an equation, formulae for mobility and (anisotropic) diffusion coefficients are derived for the case where only elastic collisions are important. No restriction is placed on the masses of particles or on the nature of interaction potential. Results of earlier theories are shown to be special cases of the formulae obtained here. The intended application of the equations is mainly to the case of alkali metal ions in neutral rare gases, where numerical evaluation of the formulae is necessary. The main features of some of the numerical procedures are discussed.

Before presenting the applied aspect of this work, an outline of the general theory is given. This includes a scheme for calculating transport coefficients of higher tensorial rank and a rough estimate of their effect. The role of the continuity equation in this connection is discussed. An attempt is made to place the theory in the general context of kinetic theory. In particular, the close similarity between the present theory and that of sound propagation in rarified gases is pointed out. Some experimental and theoretical implications of this comparison are discussed.

#### I. INTRODUCTION

Recently the results of experiments on the drift and diffusion of electron swarms through neutral gases have been the subject of extensive critical reviews (Phelps 1968, 1969; Crompton 1969; Bederson and Kieffer 1971; Golden *et al.* 1971). It seems beyond doubt that these experiments now make possible some of the most accurate determinations of the electron-atom scattering cross sections in the low energy region. A much greater variety of interactions can occur in ion swarms and experiments of comparable or greater accuracy are possible (McDaniel 1964; Elford 1971), but uncertainties in the theoretical analysis and the interpretation of experimental data in this case have prevented an equally reliable determination of ion-atom interactions. Many experimental possibilities remain unexplored because of the discouragement from this source.

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The analysis of electron data is based upon an approximation which makes essential use of the smallness of electron mass (Lorentz 1916; Davydov 1935; Morse *et al.* 1935; Margenau 1946; Allis 1956; Ginzburg and Gurevich 1960). This approximation is built into the equations at an early stage, and it so alters their form that it has been difficult to see some fairly important physical consequences. Usually there is no estimate of errors caused by the approximation. Thus, although the phenomena are closely related, the theory of electron transport in its usual form offers no guidance for the treatment of ion transport. The theory for the latter has developed almost independently and is dominated by the fact that for the inverse fifth power force (Maxwellian or polarization force law) the equations are exactly solvable, and the approximations are built around this model case (Kihara 1952, 1953; Wannier 1953). Their limited successes and unsuitability for more extensive work are to be traced to this starting point.

The rather specialized treatment of the problems has also obscured the fact that these phenomena are described by the linearized Boltzmann equation. They have as much basic interest as the sound propagation experiments of Greenspan (1956), which have received so much theoretical attention (Pekeris *et al.* 1962; Uhlenbeck and Ford 1963; Sirovich and Thurber 1965; de Boer and Uhlenbeck 1970; Foch and Losa 1972). In fact the swarm experiments seem to have many advantages over the sound experiments. Since the former are concerned with the movement of charged particles, a variety of experimental techniques become possible and properties of many different types of ions and gases can be studied. Although it is not easy to compare these two phenomena, it would appear that greater accuracy and control should be possible with the measurement of electrical movements involved in swarm experiments.

The theories mentioned above and the one investigated in the present work are based on the Boltzmann equation, but in principle it should be possible to extract information by considering the underlying random processes. Attempts at developing a theory of the latter type for swarm experiments have been made by Fahr and Müller (1967), Cavalleri and Sesta (1968, 1969), Cavalleri (1969), and Braglia (1970). It is of interest to note that there exist experiments in which the motion of individual charged particles is observed (Hurst *et al.* 1963). At the present time the tendency is to emphasize their equivalence with the swarm experiments, and thus vast numbers of events are accumulated and fluctuations are disregarded. However, it is possible that further development of different approaches may indicate some significance in the differences that must exist (e.g. fluctuations), presumably in connection with more adequately formulated random process theories.

The preceding remarks indicate the extraordinary scope and interest of this subject and the need for an adequate development of theory. In the present work we wish to make a beginning in that direction by further developing the Boltzmann equation approach, especially to improve the theory for ion swarms. It has been found that the most effective way to formulate the theory is also the most general. In Section II we indicate the place of this theory in the general context of kinetic theory, not for the sake of generality but to indicate, through comparison with the theory of sound propagation, the direction in which further improvements may be

sought. It will involve special approximations as well as investigation of spectral properties of operators that occur in the equations.

Starting from the linearized Boltzmann equation for the charged particles, it has been shown, albeit only in outline (Section II), that the coefficients in a polynomial expansion of the distribution function can be obtained as elements of a matrix for a wide class of problems. The lowest of these coefficients are related to the transport coefficients measured in experiment, namely mobility and diffusion. Detailed formulae are then obtained for these coefficients for the case in which collisions are assumed elastic but no restriction is placed on masses or on the type of interaction potential (Section III). Special approximations are left to Section IV so that they do not obscure the features common to various cases; they are indicated briefly to show how most of the earlier special theories on the subject, starting from Langevin's (1905) theory, are contained in the formulae derived here. These formulae have also proved useful for the electron case where we were able to estimate the errors caused by the usual two-term approximation (Robson and Kumar 1971; see also Section IV(c) below).

In beginning the discussion in Section II we pay some attention to the continuity equation. This equation is the link between the Boltzmann level of description and the experimental measurements. Transport coefficients occur as constants in this equation and are determined by fitting experimental data to appropriate solutions. To go beyond the first-order diffusion approximation (Section II(c)) is to consider transport coefficients of tensorial order higher than two. Recently there has been some interest in such coefficients in view of the possibility of experimentally observing the pear-shaped components in diffusing swarms (R. W. Crompton, personal communication). Our discussion serves to indicate their place in the approximation scheme and provides some rough estimate of qualitative features.

In concluding the introduction we may say that this paper is concerned with the derivation of formulae for mobility and diffusion, their theoretical antecedents, and some broad features of the process of evaluating them; they are limited to the case of elastic collisions so that the most appropriate applications will be to alkali metal ions in neutral rare gases. The dependence of transport coefficients upon experimental parameters is sensitive to the shape of the ion-neutral interaction potential. A detailed study of the physical consequences of varying the potential parameters (and hence determining these parameters from experimental data) is made in Part II (Robson and Kumar 1973, present issue pp. 187-201).

## II. OUTLINE OF BASIC THEORY AND ITS PLACE IN GENERAL CONTEXT OF KINETIC THEORY

### (a) *Boltzmann Equation and Continuity Equation*

The theory of electron mobility and diffusion, in a form adequate for obtaining anisotropic diffusion effects, has been considered by several authors (Parker and Lowke 1969; Lowke and Parker 1969; Skullerud 1969; Huxley 1972). They have confined themselves to the well-known two-term approximation of the distribution function which is sufficient for their purpose. Within this limitation Parker and

Lowke developed a one-dimensional treatment using Fourier transforms of the Boltzmann equation and outlined a three-dimensional treatment along the same lines. In an equivalent treatment Huxley emphasized the importance of the continuity equation for clarifying the physical basis of the experiments. These elements may be combined in the presentation of a general theory. In this section we suppress details and give only the essential definitions in order to bring out the basic structure of the theory.

The starting point is the linearized Boltzmann equation

$$(\partial_t + \mathbf{c} \cdot \partial_r + \mathbf{a} \cdot \partial_c + J)f(\mathbf{r}, \mathbf{c}, t) = 0, \quad (1)$$

where  $\mathbf{a}$  is the acceleration suffered by the particles due to the application of an external field and  $J$  is the collision operator whose only property needed for the time being is that it acts on any function of  $\mathbf{c}$  as a linear operator. This form of the equation is applicable when the density of charged particles is very small compared with the density of the neutrals so that mutual interactions among charged particles, which have to be described by a nonlinear operator, can be neglected.

Assume now that the space-time dependence of  $f$  can be expressed in terms of a Fourier transform with a  $\mathbf{k}$ -dependent  $\omega$ , as

$$f(\mathbf{r}, \mathbf{c}, t) = (2\pi)^{-3} \int d\mathbf{k} \hat{f}(\mathbf{k}, \mathbf{c}) \exp\{i\mathbf{k} \cdot \mathbf{r} - \omega(\mathbf{k})t\}. \quad (2)$$

The equation satisfied by  $\hat{f}$  is obtained from (1) as

$$(-\omega + i\mathbf{c} \cdot \mathbf{k} + \mathbf{a} \cdot \partial_c + J)\hat{f}(\mathbf{k}, \mathbf{c}) = 0. \quad (3)$$

In terms of the distribution function  $f$ , the density  $n$  and the convective velocity\*  $\bar{\mathbf{W}}$  of the charged particles are given by

$$n(\mathbf{r}, t) = \int d\mathbf{c} f(\mathbf{r}, \mathbf{c}, t) \quad (4)$$

and

$$\bar{\mathbf{W}}(\mathbf{r}, t) = (1/n) \int d\mathbf{c} \mathbf{c} f(\mathbf{r}, \mathbf{c}, t). \quad (5)$$

They are related through the continuity equation

$$\partial_t n + \partial_r \cdot (n\bar{\mathbf{W}}) = 0, \quad (6)$$

which is obtained by integrating equation (1) with respect to  $\mathbf{c}$ . Introducing the analogues of (4) and (5)

$$\hat{n}(\mathbf{k}) = \int d\mathbf{c} \hat{f}(\mathbf{k}, \mathbf{c}) \quad (7)$$

\* The convective velocity  $\bar{\mathbf{W}}$  represents the mean velocity including the effects of the electric field as well as density gradients. Sometimes it is also called the drift velocity, a name we shall reserve here for its part  $\mathbf{W}$  which is proportional to the vector  $\mathbf{a}$ , that is, for  $\mathbf{W}$  in equation (15) below.



and

$$V(\mathbf{k}) = (1/\hat{n}(\mathbf{k})) \int d\mathbf{c} \, c \, \hat{f}(\mathbf{k}, c), \quad (8)$$

the continuity equation in  $\mathbf{k}$  space becomes

$$-\omega(\mathbf{k}) + i\mathbf{k} \cdot V(\mathbf{k}) = 0. \quad (9)$$

We have

$$\hat{n}(\mathbf{0}) \neq 0, \quad V(\mathbf{0}) \neq \infty, \quad \text{and} \quad \omega(\mathbf{0}) \equiv 0. \quad (10)$$

It is evident that  $\mathbf{k}$  is a measure of inhomogeneity. In particular, if the gradients of density are small then  $\hat{n}(\mathbf{k})$  is concentrated close to the origin and the average value of  $\mathbf{k}$  is small. One may then expand as

$$\omega(\mathbf{k}) = i\mathbf{k} \cdot \boldsymbol{\omega}_1 + \mathbf{k}\mathbf{k} : \boldsymbol{\omega}_2 + \dots, \quad (11)$$

$$V(\mathbf{k}) = W - i\mathbf{k} \cdot \mathcal{D} + \dots, \quad (12)$$

where subscripts represent the ranks of the constant tensors. If  $\boldsymbol{\omega}_2$  can be diagonalized by an orthogonal transformation the integral

$$P(\mathbf{r}, t) = (2\pi)^{-3} \int d\mathbf{k} \exp\{i\mathbf{k} \cdot (\mathbf{r} - \boldsymbol{\omega}_1 t) - (\mathbf{k}\mathbf{k} : \boldsymbol{\omega}_2)t\} \quad (13)$$

represents a Gaussian pulse whose centre travels with the velocity  $\boldsymbol{\omega}_1$  and which diffuses in the shape of a spheroid, in general anisotropic, determined by  $\boldsymbol{\omega}_2$ .

Substituting equations (11) and (12) in (9) we have

$$\boldsymbol{\omega}_1 = W, \quad \boldsymbol{\omega}_2 = \mathcal{D}. \quad (14)$$

These are of the nature of compatibility relations. They must be satisfied if we want to use the Boltzmann equation to determine the constants  $\boldsymbol{\omega}_1$  and  $\boldsymbol{\omega}_2$ , which are respectively the drift velocity and diffusion tensor. In this case from equations (5), (8), and (12), with  $\partial = \partial_r$ ,

$$\bar{W} = W - \mathcal{D} \cdot n^{-1} \partial n, \quad (15)$$

and the continuity equation (6) takes the form

$$(\partial_t + \boldsymbol{\omega}_1 \cdot \partial - \boldsymbol{\omega}_2 : \partial \partial) n(\mathbf{r}, t) = 0. \quad (16)$$

The solution is given by

$$n(\mathbf{r}, t) = (2\pi)^{-3} \int d\mathbf{k} \, \hat{n}(\mathbf{k}) \exp\{i\mathbf{k} \cdot \mathbf{r} - \omega(\mathbf{k})t\} = \hat{n}(-i\partial)P(\mathbf{r}, t), \quad (17a)$$

where the function  $\hat{n}(\mathbf{k})$  is determined by the shape of the pulse at time  $t = 0$ ,

$$\hat{n}(\mathbf{k}) = (2\pi)^{-3} \int d\mathbf{r} \, n(\mathbf{r}, 0) \exp(-i\mathbf{k} \cdot \mathbf{r}). \quad (17b)$$

The function  $\hat{n}$  is usually determined as a power series in  $\mathbf{k}$  or  $\partial$  along with the coefficients  $\omega_1$  and  $\omega_2$  from the Boltzmann equation. The solutions obtained by Parker and Lowke (1969) and Huxley (1972) are of this type. It will be noted that no matter what its initial shape, the pulse will eventually take the form of the function  $P(\mathbf{r}, t)$  since the term  $\omega(\mathbf{k})t$  must at some value of  $t$  dominate the initial shape-dependent contribution  $\log \hat{n}(\mathbf{k})$ ; a delta function shape for  $n(\mathbf{r}, 0)$  corresponds to  $\hat{n}(\mathbf{k}) = 1$  and the resulting pulse  $n(\mathbf{r}, t) = P(\mathbf{r}, t)$ .

It is evident that equations (16) and (17) do not exhaust the content of the continuity equation (6). Equation (16) itself is often called the continuity equation as it is a good approximation to (6) and applies when the usual (i.e. first-order) diffusion approximation (15) holds, a situation that is strictly valid when the density gradients are very small or equivalently when the expansions (11) and (12) are needed only up to the second-order tensor term. The above development is needed to identify the drift velocity ( $\mathbf{W} = \omega_1$ ) and the diffusion tensor ( $\mathcal{D} = \omega_2$ ) in the expansion of  $V$ , which is in turn obtained by solving the Boltzmann equation (3) for  $\hat{f}(\mathbf{k}, c)$ .

(b) *Polynomial Expansion*

Let  $\phi^{[v]}(c)$  be a complete set of functions orthogonal with respect to a weight function  $w(c)$  such that

$$\int dc w(c) \phi^{(v)}(c) \phi^{[v]}(c) = \delta_{vv'}. \quad (18)$$

We may then write

$$\hat{f}(\mathbf{k}, c) = \hat{n}(\mathbf{k}) w(c) \sum_v \phi^{[v]}(c) \mathfrak{G}^{(v)}(\mathbf{k}), \quad (19)$$

where

$$\mathfrak{G}^{(v)}(\mathbf{k}) = (1/\hat{n}(\mathbf{k})) \int dc \hat{f}(\mathbf{k}, c) \phi^{(v)}(c). \quad (20)$$

Here the functions with indices in parentheses are complex conjugates of functions with indices in square brackets. Note that we do not need any detailed properties of this orthonormal system, although we do have a system in mind, which will be specified in Section III(a). It can be arranged to have the first ( $v = 0$ ) of the functions  $\phi^{[v]}$  equal to unity so that with  $\hat{n}(\mathbf{k})$  given by equation (7)

$$\phi^{(0)}(c) = 1, \quad \mathfrak{G}^{(0)}(\mathbf{k}) = 1. \quad (21)$$

In the space of functions  $\phi^{(v)}$  the operators  $c$ ,  $\partial_c$ , and  $J$  induce linear transformations and may therefore be represented by matrices  $\mathbf{C}$ ,  $\mathbf{D}$ , and  $\mathbf{J}$  operating on the column vector  $\mathfrak{G}$  formed from the coefficients  $\mathfrak{G}^{(v)}$ . In other words, using equations (19) and (20) in (3) we get the matrix equation

$$(-\omega(\mathbf{k})\mathbf{I} + i\mathbf{k} \cdot \mathbf{C} + \mathbf{a} \cdot \mathbf{D} + \mathbf{J})\mathfrak{G} = 0. \quad (22)$$

Note that there are three operators each in the symbols  $\mathbf{C}$  and  $\mathbf{D}$  since they are vector operators; the terms involving them in equation (22) are scalar products with ordinary vectors. We shall not elaborate the notation to exhibit this. In going from equations (3) to (22) some constants have to be absorbed in the operators or their coefficients.

Although this makes no difference to the argument of the present section, and is therefore ignored here, it does become important for deriving explicit formulae, as will be seen in the following sections.

Equation (22) is an infinite set of equations for the expansion coefficients  $\mathfrak{G}^{(v)}$ , which are linear combinations of certain moments of the distribution function. Thus (22) is fully equivalent to the moment equations, which continue to play such an important role in these theories. The first of these equations, that corresponding to  $\phi^{(0)}(c) = 1$ , is the continuity equation (9) discussed in subsection (a). This equation needs to be considered separately since (22), which is a homogeneous equation for  $\mathfrak{G}$ , can be solved only if the determinant vanishes. One way of ensuring this is to arrange for the first equation to be satisfied identically, which would mean that the first row of the matrix could be obtained as a linear combination of other rows. This will be true in any polynomial system. With the determinant thus ensured to vanish one can proceed to convert (22) to a set of inhomogeneous equations in the usual way by omitting the first row and using the first column as the inhomogeneous term. Unfortunately the equation so obtained is nonlinear in  $\mathfrak{G}$ . Specifically, we note that without loss of generality three further members of the polynomial system  $\phi^{(v)}$  can be taken to be linear combinations of the three components of the vector  $\mathbf{c}$ , so that from equations (7) and (8) the vector  $\mathbf{V}$  is seen to be one of the vectors in the set  $\mathfrak{G}^{(v)}$ . The nonlinearity arises because according to (9), which is to be satisfied identically,  $\omega(\mathbf{k})$  occurring in the inhomogeneous equation is to be replaced by  $i\mathbf{k} \cdot \mathbf{V}$  where  $\mathbf{V}$  is one of the vectors in  $\mathfrak{G}$ .

The power series expansions (11) and (12) are one way of dealing with the above nonlinearity. For physical reasons  $\mathbf{k}$  may be taken to be small, and it is appropriate to expand as

$$\mathfrak{G} = {}^0\mathfrak{G} + i\mathbf{k} \cdot {}^1\mathfrak{G} + \dots \quad (23)$$

Equation (22) may then be separated into a series of coupled equations according to successive powers of  $\mathbf{k}$ . The lowest approximation  $\mathbf{k} = 0$  gives

$$(\mathbf{a} \cdot \mathbf{D} + \mathbf{J})^0 \mathfrak{G} = 0. \quad (24)$$

The first of these equations takes the form  $0 = 0$ , implying that, independently of the polynomial system, all elements in the first row of the matrix vanish. Hence the determinant vanishes automatically. One sets  ${}^0\mathfrak{G}^{(0)} = 1$  to agree with (21) and converts to an inhomogeneous equation in the usual way. The solution gives the constant term  $W$  of equation (12) or the coefficient of mobility. For the electron problem this equation was discussed by Robson and Kumar (1971).

Collecting linear terms in  $\mathbf{k}$  from equation (22) we get the vector equations (we do not elaborate the notation to indicate the vector nature of various quantities, e.g.  ${}^1\mathfrak{G}$ )

$$(-\omega_1 \mathbf{I} + \mathbf{C})^0 \mathfrak{G} + (\mathbf{a} \cdot \mathbf{D} + \mathbf{J})^1 \mathfrak{G} = 0. \quad (25)$$

In the first equation of this set the second term produces a zero as in (24). In order to be consistent the first term must also produce a zero, i.e. we must have

$$\omega_1 = (\mathbf{C}^0 \mathfrak{G})^{(0)}.$$

This is the implication of using the continuity equation (9) and the expansions (11), (12), and (23). The first equation, which now gives  $0 = 0$ , can thus be omitted. To be consistent with (21) and (23), the disposable  ${}^1\mathfrak{G}^{(0)}$  must now be put equal to zero thus eliminating the need to consider the first column of the matrix in the second term. The reduced matrix is the same as in equation (24) but the inhomogeneous part is given by the first term. The reduced form of (25) is thus similar to the reduced form of (24). Upon solving (25) one obtains the  ${}^1\mathfrak{G}^{(v)}$  which provide the second-order tensor  $\omega_2$  of equation (11), which as we have seen is the diffusion tensor.

This completes the basic outline of the theory that is needed for calculations up to the first-order diffusion approximation. To this point we have not needed to say very much about the polynomial system, the only properties of the collision operator used being its linearity and the collisional invariance of the unity. The latter is the property by which the collision integral leaves the continuity equation unaffected, that is to say, no matter what the distribution function there is no change in the total number of particles due to (elastic) collisions.

In order to proceed towards actual calculations one must choose a system of polynomials and consider the representation of the operators in this system. Ideally one would like a system in which the operator matrix elements were easy to calculate and only a few terms sufficed to express the distribution function in (19). These requirements are probably incompatible. At present only the system of polynomials based on a Maxwell distribution as the weight function, i.e. the system of eigenfunctions of the linearized collision operator appropriate to an inverse fifth power intermolecular force, is well enough developed to enable the operators to be constructed. The problems that this presents in representing the function  $f$  for high values of the external fields will be discussed in Section IV.

Equations (22), (24), and (25) can be simplified by a proper choice of coordinate systems for  $\mathbf{a}$  and  $\mathbf{k}$  or by use of the algebra of the three-dimensional rotation group. This may be looked upon as part of the problem of specifying the representation of the operators and is discussed in Section III(b). We continue here with some further points of general theory.

### (c) *Beyond First-order Diffusion Approximation*

In the second order in  $\mathbf{k}$ , equation (22) yields the tensor equation for the unknown  ${}^2\mathfrak{G}$

$$(\omega_2 \mathbf{I})^0 \mathfrak{G} + (-\omega_1 \mathbf{I} + \mathbf{C})^1 \mathfrak{G} + (\mathbf{a} \cdot \mathbf{D} + \mathbf{J})^2 \mathfrak{G} = 0. \quad (26)$$

The discussion is similar to that for equation (25). The inhomogeneous term comes entirely from the first two terms, when  ${}^2\mathfrak{G}^{(0)}$  is taken to vanish in accordance with (21). In general there is no reason to suppose that the solution vanishes identically. It will lead to the third-order tensor term  $\omega_3$  in the expansion\*

$$\bar{W}(\mathbf{r}, t) = \omega_1 - \omega_2 \cdot n^{-1} \partial n + \omega_3 : n^{-1} \partial \partial n. \quad (27)$$

\* This can be looked upon as a multipole expansion. It will be appropriate to speak of dipole ( $\omega_1$ ), quadrupole ( $\omega_2$ ), and octupole ( $\omega_3$ ) diffusion coefficients.

The solution of equation (6) in terms of the Fourier transforms is

$$\begin{aligned} n(\mathbf{r}, t) &= (2\pi)^{-3} \int d\mathbf{k} \hat{n}(\mathbf{k}) \exp\{i\mathbf{k} \cdot (\mathbf{r} - \boldsymbol{\omega}_1 t) - t\boldsymbol{\omega}_2 : \mathbf{k}\mathbf{k} - it\boldsymbol{\omega}_3 : \mathbf{k}\mathbf{k}\mathbf{k}\} \\ &\equiv \exp(t\boldsymbol{\omega}_3 : \partial\partial\partial) \hat{n}(-i\partial) P(\mathbf{r}, t). \end{aligned} \quad (28)$$

Without going into too much detail one can form some idea of the process involved by recalling that there is only one vector,  $\mathbf{a}$ , from which the tensors  $\boldsymbol{\omega}_i$  are to be formed. Hence

$$\boldsymbol{\omega}_1 = \kappa \mathbf{a}, \quad (29)$$

$$\boldsymbol{\omega}_2 = \delta_1 \mathbf{1} + \delta_2 \mathbf{a}\mathbf{a}, \quad \boldsymbol{\omega}_2^{-1} = \varepsilon_1 \mathbf{1} + \varepsilon_2 \mathbf{a}\mathbf{a}, \quad (30)$$

$$\boldsymbol{\omega}_3 = \tau_1 \mathbf{1} \mathbf{a} + \tau_2 \mathbf{a}\mathbf{a}\mathbf{a}, \quad (31)$$

where Greek letters represent constants and  $\mathbf{1}$  is the unit tensor. The explicit form of  $P(\mathbf{r}, t)$  is

$$P(\mathbf{r}, t) = (4\pi t)^{-3/2} (\det \boldsymbol{\omega}_2)^{-\frac{1}{2}} \exp(-\boldsymbol{\omega}_2^{-1} : \mathbf{r}'\mathbf{r}')/4t, \quad (32)$$

where

$$\mathbf{r}' = \mathbf{r} - \boldsymbol{\omega}_1 t. \quad (33)$$

Taking  $\hat{n} = 1$  in equation (28) it can be seen that a delta function pulse at  $\mathbf{r} = 0$ ,  $t = 0$  expands into a form which has pear-shaped components. Assuming the exponent to be sufficiently small we can make a rough estimate of the pulse shape. We note, however, that

$$\partial P = -(\boldsymbol{\omega}_2^{-1} : \mathbf{r}')/2t, \quad (34)$$

so that, measuring the distances from the moving centre (33), we have approximately

$$t\boldsymbol{\omega}_3 : \partial\partial\partial \sim t^{-2}, \quad (35)$$

in contrast to the exponent of (32), which is  $\sim t^{-1}$ . Hence the pear-shaped deformation of the pulse may decay faster than the spheroidal deformation. It is difficult to assign a characteristic rate for this relative decay. A crude estimate is probably given by the magnitude of the vector  $(\boldsymbol{\omega}_3 : \boldsymbol{\omega}_2^{-1})$ . These considerations indicate that some delicate calculation may be needed to disentangle the effects of boundary conditions and the tensors  $\boldsymbol{\omega}_2$  and  $\boldsymbol{\omega}_3$ .

#### (d) Theory without Fourier Transform

The essential assumption in the foregoing is that the spatial inhomogeneities are small and that it makes sense to separate the Boltzmann equation into a hierarchy of equations corresponding to different orders of inhomogeneity. Fourier transformation is not essential to the argument, although it leads to a neater expression of it. We now consider an alternative argument which is somewhat more convenient for evaluation of transport coefficients and shows the relationship of the present method to that of Chapman and Enskog.

Let  $\varepsilon$  be a small parameter which is a measure of spatial gradients. In equation (1) the operators  $\mathbf{a} \cdot \partial_c$  and  $J$  are independent of density variation and are therefore of order zero in  $\varepsilon$ . The operator  $\mathbf{c} \cdot \partial_r$  is clearly of first order. The main part of temporal variation comes from the density, and hence  $\partial_t$  mainly produces  $\partial_t n$  and can be of any order in  $\varepsilon$  except the zeroth. Similarly, the distribution function can be of any order in  $\varepsilon$ :

$$\partial_t = \sum_{s=1}^{\infty} \varepsilon^s \partial_t^s, \quad (36)$$

$$f(\mathbf{r}, \mathbf{c}, t) = \sum_{s=0}^{\infty} \varepsilon^s f^s(\mathbf{r}, \mathbf{c}, t). \quad (37)$$

Substituting these expressions into equation (1) and separating terms of different order in  $\varepsilon$  we have the hierarchy

$$(\mathbf{a} \cdot \partial_c + J)^0 f = 0, \quad (38)$$

$$({}^1\partial_t + \mathbf{c} \cdot \partial_r)^0 f + (\mathbf{a} \cdot \partial_c + J)^1 f = 0, \quad (39)$$

$${}^2\partial_t^0 f + ({}^1\partial_t + \mathbf{c} \cdot \partial_r)^1 f + (\mathbf{a} \cdot \partial_c + J)^2 f = 0. \quad (40)$$

The first of these (38) determines only the velocity dependence of  ${}^0f$ . It is sometimes called the equation for the spatially uniform case but strictly speaking that is incorrect, as it makes no reference to the space-time dependence, which can in particular be uniform.

The space-time dependence of  $f$  is determined in successive approximation by the remaining equations (39) and (40). It is necessary to arrange the manner of this determination so as to be consistent with the continuity equation in each order. Without loss of generality one can assume that  ${}^0f$  is proportional to some space- and time-dependent density function  $n(\mathbf{r}, t)$  and

$$\int {}^0f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = n(\mathbf{r}, t), \quad (41)$$

$$\int {}^s f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = 0. \quad (42)$$

The zeroth moment of (39) provides the first (approximate) equation for  $n$ , namely

$$(\partial_t + \mathbf{W} \cdot \partial) n = 0, \quad \mathbf{W} = n^{-1} \int d\mathbf{c} \mathbf{c} {}^0f. \quad (43a)$$

With the help of (43a)  $\partial_t n$  is then eliminated from the remaining moment equations of (39). There is no arbitrariness in the space-time dependence of  ${}^1f$  determined from these equations except for the presence of  $n$ . It is proportional to  $(\mathbf{c} - \mathbf{W}) \cdot \partial n$ .

In the zeroth moment of equation (40) the term  ${}^1\partial_t^1 f$  does not contribute because of (42). The  $\mathbf{c} \cdot \partial$  term provides a second-order tensor, so that

$$({}^2\partial_t - \mathcal{D} \cdot \partial \partial) n = 0, \quad (43b)$$

where  $\mathcal{D}$  is defined in terms of  ${}^1f$ . Combining this with (43a) and recalling that to this order  $\partial_t = \varepsilon {}^1\partial_t + \varepsilon^2 {}^2\partial_t$ , one gets the appropriate continuity equation (16).

In these equations a transport coefficient, e.g.  $K$  or  $\mathcal{D}$ , is determined at one level of the hierarchy but finds its interpretation from the continuity equation of the next level. This argument and the use of  $\varepsilon$  is similar to that used in the Chapman-Enskog method (see Chapman and Cowling 1970).

On carrying out the polynomial expansion, equation (38) gives equation (24) so that  ${}^0\mathfrak{F}$ , the column vector corresponding to  ${}^0f$  is the same as  ${}^0\mathfrak{G}$ . The matrix equation corresponding to (39) is

$$(-\omega_1 \mathbf{I} + \mathbf{C}) \cdot \partial n {}^0\mathfrak{F} + (\mathbf{a} \cdot \mathbf{D} + \mathbf{J}) {}^1\mathfrak{F} = 0. \quad (44)$$

It follows that  ${}^1\mathfrak{F}$  is of order  $\partial n$  and if this is factored out equation (25) will result. Similarly, (40) yields (26). In Section III we will solve equations (24) and (44) to obtain the mobility and diffusion.

#### (e) Relation to Sound Propagation Problem

The theory for the sound problem has been reviewed at length by de Boer and Uhlenbeck (1970). Other important papers are by Pekeris *et al.* (1962) and Sirovich and Thurber (1965). One considers a simple gas and sets

$$f = f^{(0)}(1+h) \quad (45)$$

in the Boltzmann collision integral. The terms linear in  $h$  define the operator  $J$  of the governing equation of the sound problem,

$$(-\omega(\mathbf{k}) + i\mathbf{c} \cdot \mathbf{k} + J)\hat{h}(\mathbf{k}, \mathbf{c}) = 0. \quad (46)$$

This has the same form as equation (3) with  $\mathbf{a} = 0$ . The main difference comes from the operator  $J$ . For the swarm experiments  $J$  is linear in the distribution function because the principal effect arises from the collisions with unlike neutral particles. The operator  $J$  in the sound problem (equation (46) above) has five collisional invariants, 1,  $\mathbf{c}$ , and  $c^2$ , corresponding to the conservation of number, momentum, and energy. Symmetry about the direction of  $\mathbf{k}$  permits one to consider only three invariants and they lead to the first three values of  $\omega$  for which the system can be solved. One of these is zero and the other two are imaginary, representing the modes of heat conduction and sound propagation respectively. The solvability condition for equation (46) is that the infinite determinant should vanish. As this is a polynomial of infinite degree in  $\omega$  there is an infinity of zeros and hence an infinity of propagation modes (e.g. Sirovich and Thurber 1969; Foch and Ford 1970). It has been suggested that these modes are highly damped and hence unimportant or spurious, but they do play an important part in the theory.

By contrast in the swarm problem the operator  $J$  has only one collisional invariant, namely 1. The only mode considered in this paper is the one which corresponds to  $\omega = 0$  in the lowest approximation; this mode represents a damped

motion in higher approximation. We have not studied other modes of this problem—presumably they do exist and represent less important phenomena.

The perturbation method of treating the sound problem (Foch and Ford 1970; Foch and Losa 1972) is very close to the method described above for the present problem. In the zeroth order the operator  $J$  of the sound problem is replaced by the operator  $(\mathbf{a} \cdot \partial_c + J)$  in the present one. It follows that for a complete elucidation of the problem a full discussion of the spectrum of this operator is needed. However, as is often the case, one can extract information of physical interest without going into such an investigation, by treating the operators as if there were no pathologies. This is the attitude we have adopted. In the following work, questions about spectral properties will be ignored and the operators will be treated as matrices.

At the level of constructing the polynomial system and the matrices and in solving the equations, there are also some useful comparisons with studies of the sound problem and these will be pointed out at appropriate places.

Model kinetic equations have been used to study the mobility problem by Bakshi and Gross (1968). Their main interest was to look at some special forms of singular behaviour of the distribution function. It is not clear how much practical importance this will have in the three-dimensional problem with an ordinary non-separable collision term. Our method ignores and does not encounter such singular behaviour. There is considerable literature on model equations (Bhatnagar *et al.* 1954; Gross and Jackson 1959; Sirovich 1962; Cercignani 1969) and they have been used extensively for the sound problem (Sirovich and Thurber 1965; Foch and Ford 1970). In view of the connection discussed here, similar investigation into the mobility-diffusion problem may be useful. We return to one aspect of it in Section III(b)(iii).

### III. REPRESENTATION AND SOLUTION OF EQUATIONS: FORMULAE FOR MOBILITY AND DIFFUSION

In the rest of this paper we assume collisions between the charged particles and neutral molecules to be elastic and neglect phenomena such as charge transfer, clustering, and ion-molecule reactions. Some of these phenomena may be described by a linear collision operator and may therefore be treated by the general theory of the previous section. As the following treatment is confined to elastic collisions, it is, strictly speaking, valid only for monatomic gases in which the excitation energies and ionization potentials of the atoms are sufficiently high so that the internal structures of the colliding particles are not changed at the energies appropriate to swarm experiments ( $\lesssim 1$  eV). Alkali ions in noble gases most closely satisfy these criteria.

In deriving the formulae for mobility and diffusion we place no restriction on the actual form of the potential except that it lead to an elastic collision. The masses of particles are similarly unrestricted. The formulae contain contributions from all the terms in the spherical harmonic expansion of the velocity distribution function. The final results of the derivation are given in subsections (c) and (d) below, equations (117) and (136) in particular.



(a) *Notation and Polynomial System*

We consider particles of charge  $e$  and mass  $m$  subject to an electric field  $E$ . Thus in equation (1) the acceleration is given by

$$\mathbf{a} = e\mathbf{E}/m. \quad (47)$$

The distribution function  $f(\mathbf{r}, \mathbf{c}, t)$  for the charged particles was introduced in Section II(a) and the density  $n$  and convective velocity  $\bar{\mathbf{W}}$  were defined by equations (4) and (5) respectively. The temperature  $T$  of the charged particles may be defined via their average kinetic energy as

$$3kT(\mathbf{r}, t) = (1/n(\mathbf{r}, t)) \int m(\mathbf{c} - \bar{\mathbf{W}})^2 f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = m\{\langle c^2 \rangle - \bar{\mathbf{W}}^2\}. \quad (48)$$

These particles move through a neutral gas for which the corresponding quantities are  $m_0$ ,  $\mathbf{c}_0$ ,  $f_0 \equiv f_0(\mathbf{r}, \mathbf{c}_0, t)$ ,  $n_0$ ,  $\bar{\mathbf{W}}_0 \equiv 0$ , and  $T_0$ .

For the motion of the charged particles only their interaction with the neutrals is important. The interaction is assumed to be isotropic and described by the scattering cross section  $\sigma(g, \chi)$  where  $g = |\mathbf{c}_0 - \mathbf{c}|$  is the relative velocity and  $\chi$  is the scattering angle. We shall need the expansion of  $\sigma$  in Legendre polynomials:

$$\sigma_l(g) = 2\pi \int \sigma(g, \chi) P_l(\cos \chi) d(\cos \chi). \quad (49)$$

The polynomial system is characterized by a set  $\mathbf{v}$  of three discrete indices  $v$ ,  $l$ , and  $m$  where  $v = 0, 1, 2, \dots$ ,  $l = 0, 1, 2, \dots$ , and  $m = -l, -l+1, \dots, l-1, l$  for each  $l$ . The polynomials are written as

$$\phi^{[v]}(\alpha \mathbf{c}) \equiv \phi^{[v]}_m(\alpha \mathbf{c}) = \phi^{(v)l*}_m(\alpha \mathbf{c}), \quad (50)$$

where the asterisk represents complex conjugation. This equation serves to define the abbreviation of indices and the relation between parentheses and square brackets enclosing them. Their usage is necessitated by requirements of the tensor algebra (see Kumar 1966, 1967). The polynomials are orthogonal with respect to the weight function

$$\bar{w}(\alpha, c) = (\alpha^2/2\pi)^{3/2} \exp(-\frac{1}{2}\alpha^2 c^2), \quad (51)$$

with

$$\alpha^2 = m/kT_0. \quad (52)$$

This signifies an expansion about the absolute equilibrium at the temperature  $T_0$  of the neutral gas. The polynomials which require special mention are

$$\phi^{[00]}_0 = 1, \quad (53)$$

$$\phi^{[01]}_m(\alpha \mathbf{c}) = \alpha c^{[1]}_m, \quad (54)$$

$$\phi^{[10]}_0(\alpha \mathbf{c}) = (3 - \alpha^2 c^2)/\sqrt{6}. \quad (55)$$

In general,

$$\phi_m^{[v]l}(c) = R_{vl}(c) \mathfrak{Y}_m^{(l)}(c), \quad (56)$$

where

$$R_{vl}(c) = N_{vl}(c/\sqrt{2})^l S_{l+\frac{1}{2}}^v(\frac{1}{2}c^2), \quad (57)$$

$$N_{vl}^2 = 2\pi^{3/2} v! / \Gamma(v + l + \frac{3}{2}), \quad (58)$$

and the  $S_{l+\frac{1}{2}}^v$  are the usual Sonine polynomials.

The distribution function is expanded in terms of  $\phi^{[v]}$  as

$$f(\mathbf{r}, \mathbf{c}, t) = n(\mathbf{r}, t) \bar{w}(\alpha, c) \sum_v \phi^{[v]}(\alpha c) \mathfrak{F}^{(v)}(\mathbf{r}, t), \quad (59)$$

with

$$\mathfrak{F}^{(v)}(\mathbf{r}, t) = n^{-1} \int \phi^{(v)}(\alpha c) f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c} = \langle \phi^{(v)}(\alpha c) \rangle, \quad (60)$$

$$\mathfrak{F}_0^{(00)}(\mathbf{r}, t) = 1. \quad (61)$$

The same expansion can be used for any other function of  $\mathbf{c}$ . In particular, the functions  $f(\mathbf{r}, \mathbf{c}, t)$  of equation (42) are expressed in terms of the coefficients

$${}^s \mathfrak{F}^{(v)}(\mathbf{r}, t) = n^{-1} \int {}^s f(\mathbf{r}, \mathbf{c}, t) \phi^{(v)}(\alpha c) d\mathbf{c}, \quad (62)$$

so that, from equations (41), (42), and (59),

$$\left. \begin{aligned} {}^s \mathfrak{F}^{(0)}(\mathbf{r}, t) &= 0, & s &\geq 1, \\ &= 1, & s &= 0. \end{aligned} \right\} \quad (63)$$

No expansion is needed for the neutral gas which is in equilibrium, and

$$f_0(\mathbf{r}, \mathbf{c}_0, t) = f_0(\mathbf{c}_0) = n_0 \bar{w}(\alpha_0, c_0), \quad (64)$$

with

$$\alpha_0^2 = m_0/kT_0. \quad (65)$$

However, the expansion in terms of  $\phi^{(v)}(\alpha_0 c_0)$  is still meaningful. The coefficients of the expansion for the neutral gas, calculated according to equation (60) are

$$\mathfrak{F}_0^{(v)} = \delta_{v0} \delta_{l0} \delta_{m0}. \quad (66)$$

With these coefficients one can directly use the general expressions derived by Kumar (1967, equation (173) in particular).

Under rotations, the polynomial  $\phi_m^{(v)l}$  and the expansion coefficient  $\mathfrak{F}_m^{(v)l}$  both transform like the spherical harmonic  $\mathfrak{Y}_m^{(l)}$ . In this notation any vector  $\mathbf{x}$  corresponds to a tensor  $x_m^{(1)}$ , where

$$x_m^{(1)} = (4\pi/3)^{\frac{1}{2}} x \mathfrak{Y}_m^{(1)}(\hat{\mathbf{x}}). \quad (67)$$

Here  $\hat{\mathbf{x}}$  is the unit vector in the direction  $\mathbf{x}$  and represents the spherical polar angles  $\theta$  and  $\phi$  in the argument of  $\mathfrak{Y}_m^{(1)}$ . These tensors are irreducible and any two may be

combined to produce a third of rank  $j$  according to the formula for the tensor product (coupling rule)

$$[a^{(j_1)} \times b^{(j_2)}]_m^{(j)} = \sum_{m_1, m_2} (j_1 m_1 j_2 m_2 | jm) a_{m_1}^{(j_1)} b_{m_2}^{(j_2)}. \quad (68)$$

The coefficients on the right-hand side are the so-called Clebsch–Gordan or Wigner coefficients.

An ordinary product of two spherical harmonics of the same argument may be expanded as

$$\mathfrak{Y}_{m_1}^{(l_1)} \mathfrak{Y}_{m_2}^{(l_2)} = \sum_l \sigma(l_1 l_2 l) (l_1 m_1 l_2 m_2 | lm) \mathfrak{Y}_m^{(l)}, \quad (69)$$

where

$$\sigma(l_1 l_2 l) = i^{l_1 + l_2 - l} \left( \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l + 1)} \right)^{\frac{1}{2}} (l_1 0 l_2 0 | l 0). \quad (70)$$

Further description of the polynomial system and the method of calculation with spherical tensors will not be considered here, as these details together with the motivation for their use and their relation to previous literature are given by Kumar (1966, 1967). It remains to note that in terms of the expansion coefficients  $\mathfrak{F}^{(v)}$  of equation (60) the convective velocity  $\bar{W}$  in spherical components is given by (equations (54) and (60))

$$\bar{W}_m^{(1)} = \langle c_m^{(1)} \rangle = \alpha^{-1} \mathfrak{F}_m^{(01)}. \quad (71)$$

From equations (48) and (55) the temperature  $T$  of the charged particles is given by

$$T/T_0 = 1 - \sqrt{\frac{2}{3}} \mathfrak{F}_0^{(10)} - \frac{1}{3} (\mathfrak{F}_0^{(01)})^2. \quad (72)$$

It is convenient to define an “effective temperature”  $T^{\text{eff}}$  by

$$T^{\text{eff}}/T_0 = 1 - \sqrt{\frac{2}{3}} \mathfrak{F}_0^{(10)} = m \langle c^2 \rangle / 3kT_0. \quad (73)$$

### (b) Representation of Operators

The polynomial system provides a basis for representing operators as matrices. Since any operator may be expressed in terms of irreducible tensor operators, it is sufficient to give the definition for one of these. Matrix elements of an irreducible tensor operator  $\mathcal{T}_\mu^{(\lambda)}$ , which may involve differential operators, are given by

$$(\mathbf{v} | \mathcal{T}_\mu^{[\lambda]} | \mathbf{v}') = (v | m | \mathcal{T}_\mu^{[\lambda]} | v' l' m') \quad (74a)$$

$$= \int \bar{w}(\alpha, \mathbf{c}) \phi^{(v l)}_m(\alpha \mathbf{c}) \mathcal{T}_\mu^{[\lambda]}(\mathbf{c}, \partial_c) \phi^{[v' l']}_{m'}(\alpha \mathbf{c}) d\mathbf{c} \quad (74b)$$

$$= (l m | \lambda \mu l' m') (v l || \mathcal{T}^{[\lambda]} || v' l'). \quad (74c)$$

The integral in (74b) is the quantity which can be calculated. The actual value and sign of this quantity depends on the definition and the order in which the factors in the integrand are arranged; hence the importance of the details in this matter. In equation (74c) the first factor is the Wigner coefficient (cf. equation (68)) and the second factor, called the reduced matrix element, is defined by this relation. The

equation is an expression of the Wigner-Eckart theorem, which shows that the  $m$ -dependence of the integral can be factored out in this way. The motivation behind the definition is discussed by Kumar (1967).

(i) *Collision Operator*

The Boltzmann collision integral which describes elastic interactions is a scalar operator and hence bears no indices ( $\lambda = \mu = 0$ ). In the usual notation of kinetic theory for equation (1) we have

$$J(f) = \int (ff_0 - f'f'_0) g \sigma(g, \chi) d\Omega d\mathbf{c}_0. \quad (75)$$

Using the polynomial expansion for  $f$  given by equations (59) and (60), the matrix elements of  $J$  are defined by the integral

$$\int \phi^{(\mathbf{v})}(\alpha\mathbf{c}) J(f) d\mathbf{c} = \sum_{\mathbf{v}'} n n_0(\mathbf{v} | J | \mathbf{v}') \mathfrak{F}^{(\mathbf{v}')} \quad (76)$$

Since  $J$  is a scalar operator, by the Wigner-Eckart theorem (74c) we have

$$(\mathbf{v} | J | \mathbf{v}') = J_{\mathbf{v}\mathbf{v}'}^l \delta_{ll'} \delta_{mm'}. \quad (77)$$

In terms of quantities defined in the paper by Kumar (1967)

$$\begin{aligned} (\mathbf{v}_1 | J | \mathbf{v}_2) &= (\alpha\mathbf{v}_1 | J | \alpha\mathbf{v}_2, \alpha_0 \mathbf{0}) \\ &= \sum_{N, \mathbf{v}, \mathbf{v}'} T(\Gamma N, \gamma \mathbf{v} | \alpha\mathbf{v}_1, \alpha_0 \mathbf{0}) T(\Gamma N, \gamma \mathbf{v}' | \alpha\mathbf{v}_2, \alpha_0 \mathbf{0}) V_{\mathbf{v}\mathbf{v}'}^l, \end{aligned} \quad (78)$$

or, using the formulae for  $T$  from Appendix I of Kumar (1967) we find, for  $v_1 \leq v_2$ ,

$$\begin{aligned} J_{\mathbf{v}_1 \mathbf{v}_2}^{l_1} &= \sum_{v=0}^{v_1} \sum_{v'=0}^{v_2} \sum_{l=0}^{l_1+v_1-v} X(l_1 v_1 v_2 | l v v') \\ &\quad \times \left( \frac{m}{m+m_0} \right)^{2(v_1-v)+l_1-l} \left( \frac{m_0}{m+m_0} \right)^{l+v+v'} V_{\mathbf{v}\mathbf{v}'}^l, \end{aligned} \quad (79)$$

with

$$V_{\mathbf{v}\mathbf{v}'}^l = \int_0^\infty \bar{w}(\gamma, g) R_{v,l}(\gamma g) R_{v',l}(\gamma g) (\sigma_0 - \sigma_l) g^3 dg, \quad (80)$$

$$\gamma = \alpha\alpha_0/\Gamma, \quad \Gamma^2 = \alpha^2 + \alpha_0^2, \quad (81)$$

and other symbols as defined in equations (49), (51), (52), and (57). Also

$$X(l_1 v_1 v_2 | l v v') = \frac{\bar{N}_{v,l} \bar{N}_{v',l}}{\bar{N}_{v_1 l_1} \bar{N}_{v_2 l_1}} \left( \sum_{NL} \{ \bar{N}_{NL} \sigma(l L l_1) \}^2 \delta_{p+p, p_1} \right) \delta_{v', v+v_2-v_1}, \quad (82)$$

with

$$\bar{N}_{v,l} = N_{v,l}/v!, \quad p = 2v+l, \quad \text{etc.}, \quad (83)$$

and  $N_{v,l}$  and  $\sigma(l L l_1)$  as defined in equations (58) and (70) respectively.

Equations (79)–(83) fully define the matrix  $J_{vv'}^l$ , which can be constructed from them. The basic input required is the scattering cross section  $\sigma(g, \chi)$ , although this information could also be supplied in the form of partial cross sections  $\sigma_0 - \sigma_l$ . Usually, however, one assumes an interaction potential and calculates  $\sigma(g, \chi)$  from it by the methods of classical mechanics. Use of quantum mechanics is also possible. The operator does not distinguish between the types of dynamics, as it depends only on the cross section  $\sigma(g, \chi)$  used in constructing  $V_{vv'}^l$ . (For the same potential shape, classical and quantum cross sections can be different, especially at the lowest energies, and this may produce a detectable difference in transport coefficients.) Only one of the partial cross sections, namely the momentum transfer cross section

$$q_m = 2\pi \int \sigma(g, \chi) (1 - \cos \chi) d(\cos \chi) = \sigma_0 - \sigma_1, \quad (84)$$

enters into the equations for the electrons, and the energy dependence of this quantity can be determined from a comparison with experiments without assuming any particular potential. In the case of ions a number of partial cross sections  $\sigma_0 - \sigma_l$  are significant and it is more convenient to start from an assumed potential whose parameters are then determined by comparison with experiment.

For any  $l$  the diagonal elements  $V_{vv}^l$  and  $J_{vv}^l$  are always positive. They are also usually large compared with non-diagonal elements. To supplement equation (79) we have

$$J_{v_1 v_2}^l = J_{v_2 v_1}^l. \quad (85)$$

From (79) we also have

$$J_{00}^1 = \{m_0/(m+m_0)\} V_{00}^1, \quad (86)$$

$$J_{01}^1 = J_{10}^1 = \{m_0/(m+m_0)\}^2 V_{10}^1, \quad (87)$$

and most significantly

$$J_{0v}^0 = J_{v0}^0 = 0. \quad (88)$$

The collision matrix is diagonal in  $l$  and symmetric in  $v$ . Its first row and column vanish identically, as a consequence of the conservation of the number of particles in a collision. This is also why the collision term does not occur in the continuity equation. In case of like molecules there are two more relations of this type and two more rows and columns vanish, but the symmetry property which makes it possible is no longer available in the case of unlike molecules (cf. Section II(d) (i) and (ii) in Kumar 1967).

(ii) *Operator  $\mathbf{a} \cdot \partial_c$*

From equation (59)

$$\mathbf{a} \cdot \partial_c f = \mathbf{a} \cdot \partial_c \left( \sum_v n \bar{w} \phi^{[v]} \mathfrak{F}^{(v)} \right) = n \bar{w} \alpha \mathbf{a} \cdot \mathbf{K} \left( \sum_v \phi^{[v]} \mathfrak{F}^{(v)} \right), \quad (89)$$

where

$$\mathbf{K} = \alpha \mathbf{c} - \alpha^{-1} \partial_c. \quad (90)$$

Hence the matrix element of interest is

$$(\mathbf{v} | \mathbf{a} \cdot \mathbf{K} | \mathbf{v}') = \sum_{\mu} a_{\mu}^{(1)} (lm | 1\mu l' m') (vl || K^{[1]} || v'l'), \quad (91)$$

where (Kumar 1967, equation (A43))

$$(vl || K^{[1]} || v'l') = (-)^{v'+v} \bar{\sigma}(l'1l) \sqrt{2} \delta_{p'+1,p} \bar{N}_{v'l'} / \bar{N}_{vl} \quad (92)$$

with

$$\bar{\sigma}(l'1l) = (l'010 | l0) i^{l'-l+3}. \quad (93)$$

If the electric field is along the  $z$  axis, the operator  $\mathbf{a} \cdot \mathbf{K}$  is diagonal in  $m$ , for then

$$a_{\mu}^{(1)} = -ia\delta_{\mu 0} \quad (94)$$

and

$$(\mathbf{v} | \mathbf{a} \cdot \mathbf{K} | \mathbf{v}') = -ia(lm | 10l'm) (vl || K^{[1]} || v'l') \delta_{mm'}. \quad (95)$$

Acting on a spherical harmonic it produces one of another rank by virtue of the relation (69),

$$\sum_{l'm'} (\mathbf{v} | \mathbf{a} \cdot \mathbf{K} | \mathbf{v}') \mathfrak{Y}_m^{(l)}(\hat{\mathbf{a}}) = a \mathfrak{Y}_m^{(l)}(\hat{\mathbf{a}}) D_{vl,v'l'}, \quad (96)$$

where

$$D_{vl,v'l'} = \bar{\sigma}(l'1l) (vl || K^{[1]} || v'l') \equiv d_{+vv'}^l \delta_{l',l+1} + d_{-vv'}^l \delta_{l',l-1}, \quad (97)$$

with

$$d_{+vv'}^l = (2v)^{\frac{1}{2}} \{(l+1)/(2l+1)\} \delta_{v',v-1}, \quad (98)$$

$$d_{-vv'}^l = -(2v+2l+1)^{\frac{1}{2}} \{l/(2l+1)\} \delta_{v',v}. \quad (99)$$

The matrix  $\mathbf{D}$  above and the coefficient of  $\delta_{mm'}$  in equation (95) may be looked upon as matrices in two indices  $v$  and  $l$ . In contrast to  $\mathbf{J}$  they have no diagonal elements in  $l$ . Off-diagonal nonzero elements of  $\mathbf{D}$  occur in the blocks  $d_{\pm}^l$  labelled by  $v$ . If the matrices are labelled by  $p = 2v+l$  and  $l$  instead of  $v$  and  $l$ , all elements of these matrices lie below the diagonal. An interesting consequence is that no matter what the value of the parameter  $a$

$$\det(a\mathbf{D} + \mathbf{I}) = 1, \quad (100)$$

where  $\mathbf{I}$  is the unit matrix.

In the mobility problem one has to invert the matrix of  $(\mathbf{a} \cdot \partial_c + \mathbf{J})$ , omitting the first row and column. In practice this is done by truncating the matrix and then inverting the finite truncated matrix. When  $\mathbf{J}$  is diagonal, i.e. for the Maxwellian force law, the determinant and the inverse are very simple to calculate, essentially because one has a triangular matrix. (By considering the matrix  $(a\mathbf{D} + \mathbf{I})$  it can be verified that, on enlarging the matrix, new elements are introduced in the new rows and columns of the inverse matrix but the elements already calculated from the smaller matrix remain unchanged.) For a non-diagonal  $\mathbf{J}$  there is an  $a$ -dependence even in the diagonal elements of the inverse matrix, and enlarging the matrix now has large effects upon the inverse elements. This is at the root of the difficulties in perturbation treatments as well as in other treatments based upon these matrices. These difficulties are inherent in the particular representation, i.e. the polynomial

system chosen here. We have not investigated other systems in much detail but it seems that the calculation of the collision operator would be more difficult than in the present system. The truncation problem and special models are considered further in Section IV.

(iii) *Operator  $\mathbf{k} \cdot \mathbf{c}$*

In this case the matrix element is given by

$$(\mathbf{v} | \mathbf{k} \cdot \mathbf{c} | \mathbf{v}') = \sum_{\mu, \mu'} k_{\mu}^{(1)} (lm | 1\mu l'm') (vl | \alpha c^{[1]} | v'l'), \quad (101)$$

where (Kumar 1967, equation (A44))

$$(vl | \alpha c^{[1]} | v'l') = (-)^{v'+v} \bar{\sigma}(l'1l) \sqrt{2} \left( \delta_{p'+1,p} \frac{\bar{N}_{v'l'}}{\bar{N}_{vl}} + \delta_{p'-1,p} \frac{\bar{N}_{vl}}{\bar{N}_{v'l'}} \right). \quad (102)$$

Since the operator  $\mathbf{k} \cdot \mathbf{c}$  occurs only in the inhomogeneous part of the diffusion equation there is no need to invert it in the present calculations. On the other hand, in the sound problem one wants the determinant of  $(\mathbf{k} \cdot \mathbf{c} + \mathbf{J})$  and  $\mathbf{k}$  can be large. This is related to the problem of inversion, and it appears as such in other approaches. This operator differs from that in subsection (ii) above in that it is not triangular in the  $p, l$  (or  $v, l$ ) representation even for a diagonal  $\mathbf{J}$ . The determinant depends sensitively on the magnitude of  $\mathbf{k}$ . The situation is somewhat comparable to inverting  $(\mathbf{a} \cdot \partial_c + \mathbf{J})$  for a non-diagonal  $\mathbf{J}$ . In other words, there is not much qualitative difference whether the operator  $\mathbf{J}$  in  $(\mathbf{k} \cdot \mathbf{c} + \mathbf{J})$  is diagonal or not.

It has been pointed out by Sirovich and Thurber (1965) that an approximation suitable over the whole range of  $k$  can be obtained if the equations are arranged so that  $k$  occurs only in the operator  $(\mathbf{k} \cdot \mathbf{c} + 1)^{-1}$ . One obtains elements of this operator without truncating the matrix of  $(\mathbf{k} \cdot \mathbf{c} + 1)$ , and then truncates all the remaining matrices, at which stage fairly small matrices seem to suffice. In view of the comparison with  $(\mathbf{a} \cdot \partial_c + \mathbf{J})$  for non-diagonal  $\mathbf{J}$ , it would appear that if the matrix elements of  $(\mathbf{k} \cdot \mathbf{c} + 1)^{-1}$  were obtained by inverting a truncated matrix of  $(\mathbf{k} \cdot \mathbf{c} + 1)$  then very large matrices would be needed to get suitable approximations. The success of the Sirovich and Thurber procedure therefore suggests that the function of large matrices in sound problem calculations is to provide a good approximation to  $(\mathbf{k} \cdot \mathbf{c} + 1)^{-1}$ , which carries most of the information.

There is no scope in using the Sirovich-Thurber (1965) type of approximation in the mobility problem since most elements of the operator  $(\mathbf{a} \cdot \partial_c + 1)^{-1}$  are exactly determined for any given truncation of the matrix  $(\mathbf{a} \cdot \partial_c + 1)$ . The difference in the two problems is that  $(\mathbf{k} \cdot \mathbf{c} + 1)^{-1}$  is qualitatively similar to the operator  $(\mathbf{k} \cdot \mathbf{c} + \mathbf{J})^{-1}$  and can be used to extract most of the physical effects, while  $(\mathbf{a} \cdot \partial_c + 1)^{-1}$  is qualitatively very different from  $(\mathbf{a} \cdot \partial_c + \mathbf{J})^{-1}$  and does not contain certain significant information that is contained in the latter for non-diagonal  $\mathbf{J}$ .

If one makes a Fourier transform on the  $\mathbf{c}$  variables the role of the operators are changed, and it may then be possible to use an approximation of the above type. Thus, if  $s$  is the conjugate variable to  $\mathbf{c}$ , equation (1) becomes

$$\{\omega(\mathbf{k}) - i\mathbf{k} \cdot \partial_s - i\mathbf{a} \cdot \mathbf{s} + J'\} f' = 0. \quad (103)$$

This can be converted to a matrix equation as before, using the same polynomial system in the  $s$  variables but with a different constant in place of  $\alpha$ . The matrix elements of  $\mathbf{a} \cdot \mathbf{s}$  are therefore essentially the same as those of  $\mathbf{k} \cdot \mathbf{c}$  in the earlier equation. The matrix elements of  $\mathbf{J}'$  are related to those of  $\mathbf{J}$  by a similarity transformation  $\mathbf{J}' = \mathbf{R}\mathbf{J}\mathbf{R}^{-1}$ , where  $\mathbf{R}$  is again diagonal in  $l$  and  $m$  indices. It may be possible to apply a Sirovich-Thurber (1965) type of approximation to the resulting equations. This will probably lead to a sizeable investigation of its own, which we do not attempt here. Perhaps, it is of even greater interest that in some such way the theory of mobility can be related to the various model and spectral theories which are being discussed in other contexts (e.g. Sirovich and Thurber 1969; Cercignani 1969).

(c) *Equation for Mobility and its Solution*

It was shown in Section II(d) that the mobility is obtained from the solution of equation (38), which may be expressed as

$$\{(e/m)\mathbf{E} \cdot \partial_c + J\}^0 f = 0.$$

Using the polynomial expansion (59) and the representation of operators discussed in subsection (b), and equations (76), (77), (89), (91), together with equations (68) and (101), we obtain the matrix equation

$$-(\alpha e/m) \sum_{v_2 l_2} (v_1 l_1 || K^{[1]} || v_2 l_2) [E^{(1)} \times {}^0\mathcal{F}^{(v_2 l_2)}]_{m_1}^{(l_1)} = -n_0 \sum_{v_2} J_{v_1 v_2}^{l_1} {}^0\mathcal{F}_{m_1}^{(v_2 l_1)}. \quad (104)$$

The first row of the matrix has only zeros in it and can be omitted. The first column then provides the inhomogeneous term, leading to the equations

$$\sum_{v_2 \neq 0} M_{\mathbf{v}_1 \mathbf{v}_2} {}^0\mathcal{F}^{(\mathbf{v}_2)} = {}^0b^{(\mathbf{v}_1)}, \quad \mathbf{v}_1 \neq 0, \quad (105)$$

where

$$\begin{aligned} M_{\mathbf{v}_1 \mathbf{v}_2} &= M_{v_1 l_1 m_1, v_2 l_2 m_2} \\ &= J_{v_1 v_2}^{l_1} \delta_{l_1 l_2} \delta_{m_1 m_2} \\ &\quad - (\alpha e/m n_0) (v_1 l_1 || K^{[1]} || v_2 l_2) \sum_{\mu} (l_1 m_1 | 1 \mu l_2 m_2) E_{\mu}^{(1)} \end{aligned} \quad (106)$$

and

$${}^0b_{m_1}^{(v_1 l_1)} = (\alpha e/m n_0) E_{m_1}^{(1)} \delta_{v_1 0} \delta_{l_1 1}. \quad (107)$$

The  $m$ -dependence of these equations can be eliminated by making use of the fact that all tensors  ${}^0\mathcal{F}^{(\mathbf{v})}$  must be constructed from the vector  $\mathbf{E}$  which is the only vector occurring in these equations. If we set

$${}^0\mathcal{F}_m^{(\mathbf{v} l)}(\mathbf{E}) = {}^0f^{v l}(\mathbf{E}) \mathfrak{Y}_m^{(l)}(\hat{\mathbf{E}}) \quad (108)$$

and use equations (61) and (68) in (105), we obtain the following coordinate-independent equations for  ${}^0f$ ,

$$\sum_{v_2 l_2 \neq 00} M_{v_1 l_1, v_2 l_2} {}^0f^{v_2 l_2} = (4\pi/3)^{\frac{1}{2}} \mathcal{E} \delta_{v,0} \delta_{l,1}, \quad (109)$$



where

$$M_{v_1 l_1, v_2 l_2} = J_{v_1 v_2}^{l_1} \delta_{l_2 l_1} + \mathcal{E} D_{v_1 l_1, v_2 l_2} \quad (110)$$

and

$$\mathcal{E} = \alpha e E / n_0 m. \quad (111)$$

Equation (109) is essentially the same as Kihara's (1953) equation (43) with the correspondences

$$J_{vv'}^l = \{v! \Gamma(v' + l + \frac{3}{2}) / v'! \Gamma(v + l + \frac{3}{2})\}^{\frac{1}{2}} a_{vv'}(l), \quad (112)$$

$${}^0 f^{vl} = \{2\pi^{3/2} v! / \Gamma(v + l + \frac{3}{2})\} \langle \psi_l^{(v)} \rangle, \quad (113)$$

and

$$\mathcal{E} = \sqrt{2} \mathcal{E}(\text{Kihara}). \quad (114)$$

The formal solution of equation (109) can be written in terms of the inverse of the matrix  $\mathbf{M}$

$${}^0 f^{vl} = (4\pi/3)^{\frac{1}{2}} \mathcal{E} (M^{-1})_{vl, 01}. \quad (115)$$

From the definition of the drift velocity (71), (15), and (43a) and equation (108)

$$\begin{aligned} W_m^{(1)} &= (4\pi/3)^{\frac{1}{2}} \alpha^{-1} \mathcal{E} (M^{-1})_{01, 01} \mathfrak{Y}_m^{(1)}(\hat{E}) \\ &= (e/n_0 m) (M^{-1})_{01, 01} E_m^{(1)}, \end{aligned} \quad (116)$$

so that the *mobility*  $K$  is given by

$$K = (e/n_0 m) (M^{-1})_{01, 01}. \quad (117)$$

Experimental results are often expressed in terms of the *reduced mobility*  $\mathcal{K}$ ,

$$\mathcal{K} = (n_0/n_s) K, \quad (118)$$

where  $n_s = 2.69 \times 10^{19} \text{ cm}^{-3}$  is Loschmidt's number (i.e. the gas density under standard conditions of temperature and pressure). Another quantity of physical interest that is accessible in this approximation is the effective temperature of the charged particles defined by their average kinetic energy, equation (73):

$$T^{\text{eff}}/T_0 = 1 - \frac{1}{3} \sqrt{2} \mathcal{E} (M^{-1})_{10, 01}. \quad (119)$$

As a function of  $c$  the distribution function in this approximation is given by (from equations (56), (59), and (108))

$${}^0 f(c) = n \bar{w}(\alpha, c) \sum_{v=0} \sum_{l=0} \{(2l+1)/4\pi\} {}^0 f^{vl} R_v(\alpha c) P_l(\hat{c} \cdot \hat{E}). \quad (120)$$

The mobility and effective temperature given above depend only on the parameter  $\mathcal{E}^2$ , as can be seen, for instance, by introducing a matrix

$$\bar{M}_{v_1 l_1, v_2 l_2} = J_{v_1 v_2}^{l_1} \mathcal{E}^{2(v_2 - v_1)} \delta_{l_1 l_2} + D_{v_1 l_1, v_2 l_2}. \quad (121)$$

In terms of this matrix

$$(M^{-1})_{vl,01} = \mathcal{E}^{2v+l-1} (\bar{M}^{-1})_{vl,01}, \quad (122)$$

$${}^0f^{vl} = (4\pi/3)^{\frac{1}{2}} \mathcal{E}^{2v+l} (\bar{M}^{-1})_{vl,01}, \quad (123)$$

$$K = (e/mn_0) (\bar{M}^{-1})_{01,01}, \quad (124)$$

$$T^{\text{eff}}/T_0 = 1 - \frac{1}{3}\sqrt{2} \mathcal{E}^2 (\bar{M}^{-1})_{10,01}. \quad (125)$$

The advantage of using  $\bar{\mathbf{M}}$  is that it is independent of  $\mathcal{E}$  when  $\mathbf{J}$  is diagonal.

It is convenient to visualize the matrix  $\mathbf{M}$  as partitioned into blocks labelled by  $l$  indices, the elements within each block being labelled by  $v$  indices, as indicated below.

$$\begin{array}{c|ccccc}
 & l_2 = 0 & 1 & 2 & \cdot & \cdot \\
 \hline
 l_1 = 0 & \mathbf{J}^0 & \mathcal{E} \mathbf{d}_+^0 & 0 & 0 & 0 \\
 1 & \mathcal{E} \mathbf{d}_-^1 & \mathbf{J}^1 & \mathcal{E} \mathbf{d}_+^1 & 0 & 0 \\
 2 & 0 & \mathcal{E} \mathbf{d}_-^2 & \mathbf{J}^2 & \cdot & 0 \\
 \cdot & 0 & 0 & \cdot & \cdot & \cdot \\
 \cdot & 0 & 0 & 0 & \cdot & \cdot
 \end{array}$$

The blocks along the diagonal are the matrices  $\mathbf{J}^l$  (with elements  $J_{vv}^l$ , given by equation (79)) which contain all the information about the interaction, while the field dependence is carried in the off-diagonal blocks of the matrix  $\mathbf{D}$  (represented by  $d_{\pm vv}^l$ , equations (98) and (99)). It is evident that for sufficiently strong fields the off-diagonal terms become very large, and this leads to difficulties in inverting the matrix.

The above arrangement of the elements is by no means the only possible one (see e.g. the arrangement according to  $p, l$  indicated in subsection (b)(ii) above). In numerical calculations the matrices and blocks are truncated and it is clear that truncated versions of different arrangements will lead to different approximations.

#### (d) Equation for Diffusion and its Solution

The matrix equation corresponding to (39) is obtained by introducing the expansion as in subsection (c) above,

$$\begin{aligned}
 (n^{-1} \partial_t n) {}^0\mathfrak{F}^{(v_1 l_1)}_{m_1} + \alpha^{-1} \sum_{v_2 l_2} (v_1 l_1 \| \alpha c^{[1]} \| v_2 l_2) [n^{-1} \partial n^{(1)} \times {}^0\mathfrak{F}^{(v_2 l_2)}]_{m_1}^{(l_1)} \\
 - (\alpha e/m) \sum_{v_2 l_2} (v_1 l_1 \| K^{[1]} \| v_2 l_2) [E^{(1)} \times {}^1\mathfrak{F}^{(v_2 l_2)}]_{m_1}^{(l_1)} = -n_0 \sum_{v_2} J_{v_1 v_2}^{l_1} {}^1\mathfrak{F}^{(v_2 l_1)}_{m_1}. \quad (126)
 \end{aligned}$$

The procedure for eliminating the time derivative and for removing the redundant part was explained in Section II(d). It leads to the equations

$$\sum_{v_2 \neq 0} M_{v_1 v_2} {}^1\mathfrak{F}^{(v_2)} = {}^1b^{(v_1)}, \quad v_1 \neq 0, \quad (127)$$

where

$${}^1b_{m_1}^{(v_1l_1)} = (n_0\alpha)^{-1} \left( \sqrt{3} {}^0\mathcal{F}_{m_1}^{(v_1l_1)} [n^{-1} \partial n^{(1)} \times {}^0\mathcal{F}_0^{(01)}]_0^{(0)} - \sum_{v_2l_2} (v_1l_1 || \alpha c^{[11]} || v_2l_2) [n^{-1} \partial n^{(1)} \times {}^0\mathcal{F}_{m_1}^{(v_2l_2)}]_{m_1}^{(l_1)} \right). \quad (128)$$

In the inhomogeneous term the zero-order solution is assumed to be known from the solution of (105). Equation (127) may also be converted into a coordinate-independent form, but it is somewhat more convenient to choose the  $z$  axis to lie along the electric field. Using equations (94) and (95) we have

$$\sum_{v_2l_2 \neq 00} P(m)_{v_1l_1, v_2l_2} {}^1\mathcal{F}_m^{(v_2l_2)} = -(n_0\alpha)^{-1} k(m)^{v_1l_1}, \quad (129)$$

where

$$P(m)_{v_1l_1, v_2l_2} = J_{v_1v_2}^{l_1} \delta_{l_1l_2} + i\mathcal{E}(l_1m | 10l_2m) (v_1l_1 || K^{[11]} || v_2l_2) \quad (130)$$

and

$$k(m)^{v_1l_1} = {}^0\mathcal{F}_0^{(v_1l_1)} {}^0\mathcal{F}_0^{(01)} \delta_{m0} + \sum_{v_2l_2} (l_1m | 1m l_2 0) (v_1l_1 || \alpha c^{[11]} || v_2l_2) {}^0\mathcal{F}_0^{(v_2l_2)}. \quad (131)$$

The formal solution is

$${}^1\mathcal{F}_m^{(v_l)} = -(n_0\alpha)^{-1} \left( \sum_{v'l'} [P(m)]_{v_l, v'l'}^{-1} k(m)^{v'l'} \right) n^{-1} \partial n_m^{(1)}. \quad (132)$$

In the coordinate system used here the tensor  $\mathcal{D}$  ( $= \omega_2$  of equation (30)) has the form

$$\mathcal{D} = \begin{bmatrix} \mathcal{D}_T & 0 & 0 \\ 0 & \mathcal{D}_T & 0 \\ 0 & 0 & \mathcal{D}_L \end{bmatrix}, \quad (133)$$

where rows and columns are labelled by  $x$ ,  $y$ , and  $z$  axes. This identifies the transverse ( $\mathcal{D}_T$ ) and longitudinal ( $\mathcal{D}_L$ ) diffusion constants. Defining the symbol  $\mathcal{D}_\mu$  ( $\mu = 0, \pm 1$ ) by

$$\mathcal{D}_{\pm 1} = \mathcal{D}_T, \quad \mathcal{D}_0 = \mathcal{D}_L, \quad (134)$$

we observe that the diffusion contribution to the convective velocity (see equations (15) and (43b)) is given by

$$\delta \bar{W}_\mu^{(1)} \equiv -(\omega_2 \cdot n^{-1} \partial n)_\mu^{(1)} = \mathcal{D}_\mu (n^{-1} \partial n)_\mu^{(1)} = \alpha^{-1} {}^1\mathcal{F}_\mu^{(01)}. \quad (135)$$

Thus from equation (132)

$$\mathcal{D}_m = (n_0\alpha^2)^{-1} \sum_{v'l'} [P(m)]_{01, v'l'}^{-1} k(m)^{v'l'}. \quad (136)$$

For a given  $m$ , the matrix  $\mathbf{P}(m)$ , defined by equation (130), has an analogous structure to that of  $\mathbf{M}$  in subsection (c) so that the procedure of inversion is similar and no new questions of principle arise.

## IV. EVALUATION OF FORMULAE: SPECIAL CASES AND NUMERICAL PROCEDURE

In this section some special cases are discussed where the formulae for transport coefficients simplify and the results can be obtained without recourse to numerical calculations. It is shown how the results of earlier investigations in this field appear as special cases of the present, more general treatment. The intended area of application is mainly that of experiments with alkali metal ions in rare gases. The potential needed for reproducing these results is more complicated than the model potentials mentioned below, and it becomes necessary to perform the computations numerically. Furthermore, because the ionic and atomic masses are comparable, many terms are needed in the spherical harmonic expansion of the distribution function. The formulae derived in the previous sections allow a systematic approach to this aspect of the problem by successively increasing the size of the matrix whose inverse gives the transport coefficients. The physical implications of the comparison between experimental and theoretical results are discussed in Part II.

## (a) Zero Field and Weak Fields

The earliest treatment of mobility using the Boltzmann equation was given by Langevin (1905). He assumed the field strength to be infinitesimally small (or, more explicitly, drift energy very much less than thermal energy) and took the distribution function to be

$$f(c) = n(\alpha^2/\pi)^{3/2} \exp\{\frac{1}{2}\alpha^2(c-W)^2\}.$$

With the approximation  $\alpha^2 W^2 \ll 1$ , this reduces to

$$f(c) \approx n \bar{w}(\alpha, c) \{1 + (\alpha c) \cdot (\alpha W)\}. \quad (137)$$

The coefficients in the expansion (59) are therefore

$$\bar{g}^{(v0)}_0 = \delta_{v0}, \quad \bar{g}^{(v1)}_m = \alpha W^{(1)}_m \delta_{v0}, \quad \bar{g}^{(v)} = 0 \quad (\text{all other } v). \quad (138)$$

Langevin (1905) considered the balance equation for momentum, which is the vector equation corresponding to  $v = 0, l = 1, \mu = \pm 1, 0$  in (105),

$$(\alpha e/mn_0)E^{(1)}_\mu = \sum_{v=0}^{\infty} J^{1\ 0}_{0v} \bar{g}^{(v1)}_\mu, \quad (139)$$

or from (138)

$$(\alpha e/mn_0)E^{(1)}_\mu = J^{1\ 0}_{00} \alpha W^{(1)}_\mu. \quad (140)$$

The Langevin relation is usually expressed in terms of the momentum transfer cross section, which enters through  $J^{1\ 0}_{00}$  (see equations (80), (84), and (86)). We thus obtain the Langevin formula  $W = K_L E$ , with

$$K_L = e/mn_0 J^{1\ 0}_{00} = e(m+m_0)/mm_0 n_0 V^{1\ 0}_{00}. \quad (141)$$

On the other hand, from the general expression (117) the zero-field mobility  $K_0$  is given by

$$K_0 = (e/mn_0)(J^1)_{00}^{-1}, \quad (142)$$

where the inversion is with respect to the  $v$  indices only. Off-diagonal elements of  $J_{vv'}^l$  are usually small compared with the diagonal elements and hence the first approximation to  $K_0$  in equation (142) is the Langevin expression (141) for  $K_L$ . For the types of potential encountered in practice  $K_0$  and  $K_L$  usually agree to within 1%.

Kihara (1953) improved upon Langevin's treatment by considering the field to be nonzero, and the theory was further developed by Mason and Schamp (1958). We may regain these expressions by expanding the matrix in equation (117) in powers of the field:

$$\mathbf{M}^{-1} = (\mathbf{J} - \mathcal{E}\mathbf{D})^{-1} = \sum_{j=0}^{\infty} \mathbf{J}^{-1}(-\mathcal{E}\mathbf{D}\mathbf{J}^{-1})^j. \quad (143)$$

It can be verified, for example, from the block structure of the matrix  $\mathbf{M}$  (Section III(c)), that the matrix element  $(M^{-1})_{01,01}$  contains only even powers of  $\mathcal{E}$ . This series in powers of  $\mathcal{E}^2$  will converge only at sufficiently low values of the field. A further approximation (Mason and Schamp 1958) is that only the elements of  $J_{vv'}^l$  at most  $j$  units off the diagonal occur in the coefficient of  $\mathcal{E}^{2j}$  in the above expansion. That is, the  $(j+1)$ th approximation to mobility is a polynomial in  $\mathcal{E}^2$  of degree  $j$  involving only those  $J_{vv'}^l$  for which  $|v' - v| \leq j$ . The first Kihara approximation,  $j = 0$ , is seen to be the same as the Langevin expression (141) above. Higher approximations of this type can be obtained from the expansion (143) as indicated. This is, however, unnecessary since one can deal directly with equation (117), which is more compact and makes no assumptions about the magnitude of the field.

Further properties of  $K_0$  emerge from those of  $V_{00}^1$ . Thus, because of the identity

$$T_0 dV_{00}^1/dT_0 \equiv -\sqrt{\frac{5}{2}} V_{01}^1, \quad (144)$$

which is a special case of the more general identity derivable from the definition of the  $V$ 's, namely

$$T_0 dV_{vv'}^l/dT_0 = (v - v')V_{vv'}^l + \{v'(v' + l + \frac{1}{2})\}^{\frac{1}{2}} V_{v,v'-1}^l - \{(v+1)(v+l+\frac{3}{2})\}^{\frac{1}{2}} V_{v+1,v'}^l, \quad (145)$$

it follows that

$$\frac{dK_0}{dT_0} = \sqrt{\frac{5}{2}} \frac{e}{n_0 T_0} \frac{m+m_0}{mm_0} \frac{V_{10}^1}{(V_{00}^1)^2}. \quad (146)$$

Thus, the sign of  $dK_0/dT_0$  is the same as that of the integral  $V_{10}^1$ . One can calculate the initial slope of the  $K$  versus  $\mathcal{E}$  curve in the second Kihara approximation. It turns out that at a given temperature  $T_0$  the slope is fixed by the sign of  $V_{10}^1$  or  $dK_0/dT_0$  at that temperature. This has interesting implication in those temperature regions where  $K_0$  exhibits an extremum (Kihara 1953, Figs. 4 and 5; Mason and Schamp 1958, Fig. 2).

For a power law potential of the form  $r^{-2N}$  ( $N > 2$ ) the interaction integrals have the properties

$$V_{vv}^1 > 0, \quad V_{vv'}^1 < 0 \quad (v' \neq v), \quad V_{vv'}^1 \sim T^{\frac{1}{2}-1/N}, \quad (147)$$

so that

$$K_0 \sim T_0^{1/N-\frac{1}{2}}. \quad (148)$$

One may expect to observe such a power law dependence at high temperatures where the effects of the hard core in ion-molecular potential dominate, if, as is often assumed, the hard core can be represented by a power law potential.

For the case of diffusion at zero field, we note that

$${}^0\tilde{\mathcal{D}}_{\mu}^{(vl)} = \delta_{v0} \delta_{l0} \delta_{\mu 0}, \quad (149)$$

$$[P(\mu)]_{vl, v'l'}^{-1} = (J^l)_{vv'}^{-1} \delta_{ll'}, \quad (150)$$

and

$$k(\mu)^{vl} = \delta_{v0} \delta_{l1}, \quad (151)$$

so that

$$\mathcal{D}_{\mu} = (kT_0/mn_0)(J^1)_{00}^{-1} = \mathcal{D}_L = \mathcal{D}_T \equiv \mathcal{D}. \quad (152)$$

Using equation (142) one can verify the so-called Einstein relation

$$\mathcal{D}/K_0 = kT_0/e. \quad (153)$$

#### (b) Maxwell Interaction and Heavy Ions in Light Gas

For the Maxwell model of interaction, that is, an  $r^{-5}$  force law, it can be shown (see e.g. Chapman and Cowling 1970, Ch. 10) that  $\sigma_l(g)$  is proportional to  $g^{-1}$ . From the definition of  $V_{vv}^l$  in equation (80) and the orthogonality properties of the polynomials  $R_{vl}$ , it follows that in this case the interaction integrals are diagonal in  $v$  and also independent of temperature. Similar properties hold for the collision matrix  $J_{vv'}^l$ , as may be deduced from equation (79), that is,

$$J_{vv'}^l = J_{vv}^l \delta_{v'v} \quad (154)$$

and  $J_{vv}^l$  is independent of temperature. If  $J_{vv}^l$  is diagonal, then  $\bar{\mathbf{M}}$  is independent of  $\mathcal{E}$  and can be inverted exactly, in particular

$$(\bar{\mathbf{M}}^{-1})_{01,01} = (\mathbf{M}^{-1})_{01,01} = 1/J_{00}^1. \quad (155)$$

The mobility is then independent of field strength, being given by equation (141) again. Note that it is also independent of gas temperature for this model.

On the other hand, for very heavy ions in a light gas ( $m_0/m \ll 1$ ), it can be shown from equation (79) that, to first order in  $m_0/m$ , the collision matrix is diagonal in  $v$  no matter what the form of the interaction. Explicitly, we have

$$J_{vv'}^l = (m_0/m)(2v+l)V_{00}^1 \delta_{v'v} + O(m_0/m)^2, \quad (156)$$

so that equations (155) and (141) hold once again. Hence, for heavy ions, the mobility is independent of the field strength. However, in contrast to the Maxwell model,  $K$  may now be a function of gas temperature, with the nature of this dependence determined by  $V_{00}^1$ .

For a diagonal collision matrix, it can also be shown from equations (125) and (73) that the formula

$$m\langle c^2 \rangle = (m+m_0)W^2 + 3kT_0 \quad (157)$$

holds exactly. This equation has also been deduced by Wannier (1953) for the case of the Maxwell interaction.

For diffusion in the case of a diagonal  $\mathbf{J}$ ,

$$[P(\mu)]_{01,v1}^{-1} = \delta_{v0} \delta_{11} / J_{00}^1 \quad (158)$$

and

$$\mathcal{D}_\mu = \{({}^0\mathcal{F}^{(01)})^2 \delta_{\mu 0} + {}^0\mathcal{F}^{(00)} - \sqrt{\frac{2}{3}} {}^0\mathcal{F}^{(10)} + \sqrt{\frac{10}{3}} (1\mu | 1\mu 20) {}^0\mathcal{F}^{(02)}\} / \alpha^2 n_0 J_{00}^1, \quad (159)$$

where we have inserted explicit forms of the matrix elements. In order to get a physical interpretation of the right-hand side of (159), we use equation (60) for the coefficients with the explicit forms of  $\phi^{(v)}$  given by equations (53)–(56). The results are

$$\mathcal{D}_L = \{\langle c_z^2 \rangle - \langle c_z \rangle^2\} / n_0 J_{00}^1, \quad (160)$$

$$\mathcal{D}_T = \{\langle c_x^2 + c_y^2 \rangle\} / 2n_0 J_{00}^1. \quad (161)$$

Hence the ratio  $\mathcal{D}_L/\mathcal{D}_T$  is equal to the ratio of the mean random energies parallel and perpendicular to the field. Wannier (1953) derived this result for the Maxwell interaction and conjectured that it should hold generally. From the derivation given above it is clear that it is a result of the rather special circumstance that  $\mathbf{J}$  is diagonal. We do not expect this to hold for cases other than the Maxwell model and heavy ions in a light gas. In fact, the electron case provides a counter example to Wannier's conjecture. Here the distribution function is nearly spherically symmetric so that

$$\langle c_x^2 \rangle = \langle c_y^2 \rangle \approx \langle c_z^2 \rangle \quad (162)$$

and

$$\langle c_z^2 \rangle \gg \langle c_z \rangle^2. \quad (163)$$

The conjecture would then suggest  $\mathcal{D}_L \approx \mathcal{D}_T$ , which is in general not correct, as shown by the recent calculations of Lowke and Parker (1969), Skullerud (1969), and Robson (1972*a*, 1972*b*).

### (c) Electrons

In the theory of electron swarms one retains only the first two terms in the spherical harmonic expansion of the distribution function. This is equivalent to retaining only the blocks corresponding to  $l = 0$  and  $l = 1$  in the  $\mathbf{M}$  matrix (see Section III(c)). One can obtain corrections to this approximation by including blocks of higher  $l$ 's, as was discussed by Robson and Kumar (1971). Equations (8a)–(8d) of that paper are another representation of the block structure of  $\mathbf{M}$ .

The formulae for  $\mathbf{J}$  quoted by Robson and Kumar (1971, equations (11)–(13)) are obtained from equations (79)–(83) by retaining terms of the lowest order in  $m/m_0$ . Thus

$$J_{v_1 v_2}^0 \approx (2m/m_0)(v_1 v_2)^{\frac{1}{2}} V_{v_1-1, v_2-1}^1, \quad (164)$$

$$J_{v_1 v_2}^l \approx V_{v_1 v_2}^l, \quad l \geq 1. \quad (165)$$

The success of the two-term approximation depends on the extraordinary smallness of the  $J^0$  block compared to the others. Considering other cases which may be treated by matrix equations this is rather an extreme approximation, although quite adequate for the electron case. It may be noted that the usual approximation using two coupled differential equations in  $c$  is more effective at high fields. On the other

hand, the present method being more systematic and detailed enables us to estimate higher anisotropies. When masses are comparable, as for ions, such effects become much more important.

(d) *Truncation of Matrices: Numerical Approximations for Realistic Potentials*

Potentials which describe ion-atom interactions usually have a strong short-range repulsion, a weaker medium-range attraction, and an  $r^{-4}$  polarization potential in the outermost regions. A potential of such a shape will have three parameters. No analytic approximation is adequate in this case, although some estimation can be made for the very high and very low temperatures and the qualitative form of the mobility as a function of  $\mathcal{E}$  can be inferred (Kihara 1953; Wannier 1953, 1970; Mason and Schamp 1958; Creaser 1969).

The formulae derived above may be evaluated numerically in these cases: for a given potential one determines the cross section  $\sigma(g, \chi)$  numerically and constructs the interaction integrals  $V_{vv}^l$  at a given temperature  $T_0$ . The collision matrix  $J_{vv}^l$  is then obtained from equations (79)–(83). The matrices  $\mathbf{M}$  and  $\mathbf{P}(\mu)$  can subsequently be formed for different values of the field parameter  $\mathcal{E}$  and inverted to obtain the transport coefficients (Section III (c), (d)).

To carry out this scheme we select a maximum value  $l_{\max}$  of  $l$  thus restricting the number of blocks. Then within each block we limit the values of  $v$  to a maximum value  $v_{\max}$ . This gives a square matrix of dimension  $\{(l_{\max} + 1)(v_{\max} + 1) - 1\}$ . The procedure is equivalent to approximating the distribution function by a finite number of terms, i.e.

$$f(c) \approx n \bar{w}(\alpha, c) \sum_{v=0}^{v_{\max}} \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l \mathfrak{F}_m^{(vl)} \phi_m^{[vl]}(\alpha c). \quad (166)$$

In the zeroth order

$${}^0f(c) \approx n \bar{w}(\alpha, c) \sum_{l=0}^{l_{\max}} {}^0f^l(c) P_l(\hat{c} \cdot \hat{E}), \quad (167)$$

with

$${}^0f^l(c) \approx \{(2l+1)/4\pi\} \sum_{v=0}^{v_{\max}} {}^0f^{vl} R_{vl}(\alpha c). \quad (168)$$

Except for the electron case where  $l_{\max} = 1$  is sufficient, the distortion from spherical symmetry is in general quite substantial at high fields, and hence many Legendre polynomials are needed to accurately represent the angular dependence by equation (167). At the same time, the distribution is also rather far from being in equilibrium at temperature  $T_0$ , so that a large number of terms are needed in equation (168) also. Thus in general we expect to have to invert a rather large matrix. This indeed has been the experience in the sound problem (Pekeris *et al.* 1962), whose similarity to the present problem was pointed out in Sections II and III.

Turning to the manner of truncation indicated above, we note that it is not the only possible one. It appears quite natural in view of equations (166)–(168), and one might say that the angular anisotropies represented by successively higher  $l$ 's are successively more difficult to establish, and hence less important. This is not a strong argument in either the physical or mathematical sense. It may be noted that this manner of truncation was used in the sound problem by Wang-Chang and Uhlenbeck (see de Boer and Uhlenbeck 1970). On the other hand, it is possible to



arrange the matrix according to  $p = 2v + l$ , which is the degree of polynomials in  $c$ , and for each  $p$  according to  $l$ . This arrangement suggests a different scheme for truncation. In their extensive calculations in the sound problem, Pekeris *et al.* (1962) have used a truncation based on  $v + l$ . Indeed, neither the formulae nor the physical intuition provides any strong reasons for preferring one manner of truncation over another.

In order to obtain a reliable determination the results must be shown to be independent of the manner of truncation in some sense. For any given value of  $\mathcal{E}$  one can successively enlarge the matrix to be inverted and see if the transport coefficients tend to a limit. That is to say, one goes on enlarging the matrices until there is no change in the values by further enlargement. This need not be strict mathematical convergence, but if it can be achieved within some given percentage it will be quite convincing. When such a situation is reached it is no longer very important how successive truncations were performed (barring pathological choices).

It is expected and has been confirmed by calculations, that as  $\mathcal{E}$  increases larger and larger matrices are needed to achieve a convergence of the transport coefficients. From this it also follows that for any given size of the truncated matrix the results are not expected to be good over the entire range of  $\mathcal{E}$ . A value of  $\mathcal{E}$  will be reached beyond which the error due to truncation will be large enough to mask even the qualitative character of transport coefficients as functions of  $\mathcal{E}$ . This is a serious drawback. It not only necessitates rather long calculations to establish convergence but beyond a certain point the matrices become very large and it is difficult to keep all quantities (e.g. cross sections and  $V_{vv}^l$ ) sufficiently accurate. Still, by using this procedure and without making the computing too formidable it has been possible to obtain results over a physically interesting range of  $\mathcal{E}$  (Robson and Kumar 1971; Part II).

The special cases and the numerical procedure described here do not exhaust the possibilities of the formulae we have derived. For instance, one might attempt to estimate the elements of the inverse matrix by some asymptotic method or by some manipulation of series expansions. We have not explored such possibilities.

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