# Kinetic Theory of Charged Particle Swarms in Neutral Gases

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#### Abstract

The kinetic theory of charged test particles in a neutral gas, in the presence of static and uniform electric and magnetic fields, is reviewed. The effects of inelastic processes and reactions are included. The general space-time development of the swarms is considered and the relation between the non-hydrodynamic and hydrodynamic developments is pointed out. The transport coefficients are identified as statistical averages over the configuration-space and phase-space distributions. The evaluation of these averages by computer simulations is briefly discussed.

The main emphasis, however, is on the Boltzmann equation treatment of the problem. Transport coefficients of any order are obtained as velocity moments of the solutions of the corresponding kinetic equations derived from the Boltzmann equation. These equations have similar structure and may be solved by similar methods. Methods of solution are classified and examined in detail for precise calculation of drift and diffusion. Illustrative examples are given.

Several representations of the Boltzmann collision integral suitable for use in these calculations are examined. A discussion of the calculation of matrix elements and the relationship between different matrix representations is given. Complete expressions to all orders in the Fokker–Planck expansion and in the expansions for the operator components of the spherical harmonic decomposition in the differential form are given. The advantages of using the adjoint of the collision operator and the cold gas collision operator in these derivations and in applications are shown and utilized.

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# Part I. General introduction

Dear reader, take a long look at the table of contents and bear with us in pity and sympathy, for we have the task of introducing this work and commending it to your attention.

Purpose and Scope Our purpose is: Firstly, to give a consolidated account of the theory and the scope of its applications. Secondly, and equally, to assess whether certain approximation schemes can produce results to the degree of accuracy required by present day experiments.

The topics dealt with here are connected, from the point of view of physics, in that they concern systems for whose description the kinetic theory of dilute gases should suffice. A majority of them are also connected from a mathematical point of view because they are governed by homogeneous or inhomogeneous linear equations involving basically a single operator, which varies from system to system through its dependence on a single function, namely the scattering cross section, and a small number of parameters.

In the past [1]\* these topics have been the subject of separate investigations, many of which have been designated as theories. The search for more reliable and accurate results has meant that such theories are increasingly seen as special methods of approximating the solutions of the Boltzmann equation, which embodies the relevant kinetic theory. Even the computer simulations [2] and the related correlation function methods, which have been regarded, with much justification, as independent ways of implementing kinetic theory ideas, can also be accommodated in this point of view. The consolidation mentioned above is made possible by, and can be best appreciated from, the same point of view.

Most of this development of theory has been stimulated by the high degree of accuracy of the data from experiments [3]. The theory is called upon not only to provide accurate and reliable values to compare with the data but also to account for, or predict, new phenomena that may be observed at these higher levels of refinement.

The paper is a review in the sense that we go over much of the ground covered in previous works and follow the suggestions made by others in various streams of literature, to consolidate and enlarge the conceptual and technical resources of the theory in this field. However, we do not give a presentation, discussion or comparison of earlier works in their original form. We have often found new ways of implementing earlier suggestions and carrying them further. Our assessments and discussions are then based on these findings. In the text, mostly the references that we have actually used or found useful are given. In the Notes, we give additional references and comments to communicate the perspective at which we have arrived. We make the apology, customary at this point, for omissions and inadequacies and we invite correspondence regarding them from those who may be interested.

\* Italic numbers in square brackets refer to notes of a historical and supplementary nature which are collected at the end of the paper (p. 429).

Organization

Part II

We now turn to the organization of this paper. We are mainly concerned here with the theory of swarms, that is, the motion of very small numbers of charged particles through neutral gases, in the presence of a static uniform electric field. This is a test-particle problem, some aspects of which have been studied under the names of 'foreign gas', 'weakly ionized gas' or 'thermalizer' problems. In experiments the space-time development of the charge number density is studied.

Part II, comprising Sections 1-7, deals with the space-time development of the (charge) number density n(r, t). Section 1 introduces the notion of swarms, points out the features of theory applicable to other systems, such as certain forms of plasma, and indicates the extent to which space-time dependent electric and magnetic fields may be included. The experiments can identify a state of steady or stationary transport, the so-called hydrodynamic regime, in which the number density n(r, t) satisfies a differential equation with constant coefficients. These coefficients are the transport coefficients. Section 2 gives a formal phenomenological description of this regime and identifies the transport coefficients as moments of the number density in the stationary state. Section 3 shows the relationship of the transport coefficients to the stationary time-correlation functions. The connection with the linear response theory and computer simulation is pointed out. The remaining sections, 4-7, give the Boltzmann equation treatment of the problem. In Section 4, kinetic equations for the hydrodynamic regime are derived. The transport coefficients are obtained as (velocity) averages of the solutions of these equations. These derivations are based upon the assumption that the solution of the Boltzmann equation has a certain form. We therefore collect, in Section 5, the information available about the solutions of the Boltzmann equation. We point out the sort of information still needed to secure the foundations of the theory and the need to bring the existence theory itself into closer contact with experiment. This naturally leads us to the consideration of the non-hydrodynamic regime. We take it to be the situation that precedes the establishment of the hydrodynamic regime. It has been studied by computer simulations and in terms of the initial-value problem of the Boltzmann equation. Section 6 briefly touches upon this problem.

In the vicinity of boundaries the velocity distribution is different from that in the bulk. Depending upon the interaction between the charged particles and the neutrals, the effect of boundaries can extend to large distances. This is also a non-hydrodynamic effect, but is usually not considered as such because sometimes it can be taken into account by using transport coefficients that depend upon the size of the apparatus or upon the density gradients. The theory can then be presented as a modification of the hydrodynamic\* theory, and this is briefly dealt with in Section 7. The theory of phenomena close to the electrodes

<sup>\*</sup> It should be noted that the term *hydrodynamic* is used here in a special sense: the conditions it refers to could not be further removed from those obtaining in liquids.

and boundaries (Lowke *et al.* 1977) and the theory of the Huxley– Townsend experiment (Huxley and Crompton 1974) are also related to this class of problems and require further attention, but these are not dealt with here.

In Part II, the collisions are described only formally. In particular, they may include reactions. The difference in the equations and interpretation of averages with or without reactions is pointed out at appropriate places.

Part III

To solve the equations developed in Part II one needs the collision operator in a concrete form. The demand for accurate solutions requires corresponding accuracy in the representation of this operator. This in turn requires a good understanding of the way the operator depends on parameters and functions.

Part III, comprising Sections 8-14, is devoted to the collision The presentation and some of the results are new. In operator. Section 9, the basic integral operator form is introduced. Its properties as a function of the gas distribution are pointed out and some properties with respect to translations are proved. These properties are of great importance for the development of subsequent sections. In Section 10, the collision operator is expressed as a power series in the mass ratio  $\mu_0 = m_0/(m+m_0)$  with coefficients that are differential operators. In Section 11, the spherical harmonic components of the collision operator are expressed in terms of a series of differential operators. We thus have two ways of expressing the collision operator in differential form. These expressions are complete in the sense that the general terms are given explicitly. The expressions for adjoints of these operators are also given. It is shown that the use of adjoint operators leads to essential simplifications in calculation. These sections are presented in some detail since this matter is not available elsewhere in the literature. The situation is different with respect to matrix forms. Several different representations have already been used in the literature and others are possible. Therefore, in Section 12, we consider the general properties of matrix representations. This is a part of the general theory of three-dimensional polynomial systems and the transformation theory of linear operators and is well known in the abstract. Here we have worked out the specific consequences in relation to our particular problem. Thus, the polynomials based on a gaussian weight function are emphasized and the problems of calculating with these are discussed. With the exception of those in Section 12d(ii), we have stopped short of giving explicit expressions for the matrix elements. References to the literature are given where such expressions may be found. In complex situations like the one under study here, models have an obvious Section 13 exhibits some model collision attraction and utility. operators.

The collision operators treated in Sections 9–12 involve only elastic scattering. The corresponding treatments of the operators that include inelastic scattering due to structure in the gas molecules are outlined in Section 14.

Part IV

After this preparation we turn, in Part IV, Sections 15-23, to the most important applications, namely the calculation of drift velocity (or mobility) and diffusion coefficients. In the examples considered, inelastic processes are excluded. In Section 16, the mobility and diffusion equations, taken from Section 4, are written in a more convenient form. Two linear operators are identified, one that occurs in the equations of mobility and longitudinal diffusion and another that occurs in the equation for transverse diffusion. These are simply related to the collision operator and can be constructed by the methods described in Part III. Now, with operators so given, in principle the whole arsenal of numerical methods for solving linear equations may be deployed. Indeed, several different methods have already been tried and these are surveyed. The method of most general applicability is that of moment equations (Section 17). In setting up procedures for solving these equations, information available from the solution of model problems (Section 18) is often useful [4]. Expansion of the distribution function in terms of orthogonal polynomials is a convenient way of arranging the moment equations. Among these polynomials, the ones orthogonal with respect to an isotropic gaussian weight function give rise to equations that are particularly rich in symmetry. There is only one parameter in the weight function and very good results may be obtained by proper choice of this parameter (Section 19). A general gaussian weight function can include drift as well as anisotropy. There are then more parameters to choose. The expansion in terms of polynomials orthogonal with respect to such weight functions is considered in Section 20. In both these sections (19 and 20), we investigate the best way of choosing the parameters that enter the solutions through the polynomial system. If a large enough set of polynomials is used the solution should not depend on the parameters at all; the problems implicit in this are discussed, along with the choice of basis sets in Sections 17, 19, 20 and 23. Brief accounts of non-polynomial methods (Section 21) and computer simulation studies (Section 22) are included. This part closes with a short discussion comparing different methods (Section 23).

Part V

In the presence of reactions or inelastic collisions, drift and diffusion can still be calculated by the methods described above by suitable modifications to the collision operator and the equations. However, in addition there are new measurable quantities, namely the reaction rates and equilibrium constants. The theory of reaction rates in the presence of unidirectional reactions and that of transport of charge in systems in chemical equilibrium is discussed in Part V, Sections 24–26. Section 26 implicitly contains the calculation of equilibrium constants.

Cold Gas

The cold gas [5] occurs quite often: in Section 18(c) as part of a solvable model; in Section 21 to illustrate the use of non-polynomial expansions; and, above all, throughout Part III as an important auxilliary in analysing the structure of the collision operator. Various forms of the collision operator for this case are derived in Appendix 2.

Notation

Different Parts of this paper have been provided with their own introductory sections and can be read independently. To a lesser extent this is also true of the longer sections. The notation is introduced as the need arises. Some symbols are necessarily used with different meanings in different sections but this should cause no confusion unless one insists on hurriedly mixing up disparate sections. A general guide to notation and frequently used formulae is provided in Appendix 1.

# Part II. The evolution of a swarm

# 1. Introduction (II)

For the purposes of this theory a swarm is defined as an ensemble of independent charged test particles moving in a neutral background gas. The motion of the particles is determined by the forces exerted by external electric and magnetic fields and collisions with the gas molecules, which may lead to reactions. The ensemble is to be interpreted as arising from a large number of identically prepared gas systems each with one test particle. The swarm is then described by the one-particle (six-dimensional) phase-space distribution function  $f(\mathbf{r}, \mathbf{c}, t)$ .

In experiments a swarm exists as a small collection of particles in a neutral background gas. The definition above is justified from a physical point of view if the charged particle number density and current are taken so small that both the mutual interactions between the charges and the influence of the swarm on the neutral gas distribution can be neglected. This can be tested experimentally. Mathematical justification is obtained by treating the whole system as a mixture and taking the limit of low charge densities (see also Section 5).

Swarm experiments are a well-recognized category [6] in atomic and molecular physics. Their results have been analysed to yield information about the underlying collision process, and, in principle, the differential cross section for all relevant processes can be inferred. Examples of such experiments are: the drift tube measurements of ion and electron drift velocities and diffusion coefficients, in the presence of homogeneous electric fields; afterglow and diffusion cell measurements of the decay of charge densities, usually in the absence of fields; and ion-cyclotron resonance experiments performed with an AC electric field and a constant magnetic field.

Our discussion will be mainly directed towards the analysis of drift tube experiments. However, the methods we discuss have wider applications. For example, application to some situations in discharge—and plasma—physics is possible. Specifically, these are the situations where the processes are dominated by collisions with the neutrals and the charge-charge interactions can be taken into account through space-charge fields acting as external fields, that is, when the fluctuating microfield is unimportant. A typical example is ambipolar diffusion in the positive column of a glow discharge (Rutscher 1977; Hirsh and Oskam 1978; Meek and Craggs 1978).

Throughout this Part the electric and magnetic fields are assumed uniform in space and constant in time. Specialization to uniform and constant electric field and zero magnetic field is made only in the applications considered in Part IV. Small modifications of the theory sometimes suffice to include space-time dependent fields. In particular, weak AC fields may be treated as perturbations. Existence theorems are known in the case of more general space-time dependence of fields (Section 5).

The phase-space distribution function f(r, c, t) contains all the information about the swarm behaviour but it is not directly measured. In the majority of experiments what is actually measured is a current incident upon some electrode. However, it is convenient to think that the charge density, that is, the distribution function in configuration space, defined by

$$n(\mathbf{r},t) = \int f(\mathbf{r},\mathbf{c},t) \,\mathrm{d}\mathbf{c}\,,\tag{1}$$

is the measured quantity.

The analysis of measurements of n(r, t) proceeds by first making some assumptions about the nature of the function n(r, t). On the basis of these assumptions, the experimental data are processed to yield values for other quantities such as transport coefficients, which are themselves usually thought of as the measured quantities. On the other hand, a theoretical analysis based on the same assumptions relates these quantities in the first instance to the distribution function f(r, c, t), typically as some averages over some parts of this distribution function. Then, a knowledge of the distribution function in terms of the cross section finally relates the cross section to measured quantities.

Sections 2–7 below provide the details of what has been sketched above. Another description of their content was given in the General Introduction (Part I).

### 2. Time Development of Number Density: Hydrodynamic Regime

The problem of a hydrodynamic description of a swarm is similar to that of a dilute neutral gas. The latter has been widely discussed (see e.g. Uhlenbeck and Ford 1963; Dorfman 1974; Wood 1974). The difference between the two problems arises for two reasons. Firstly, because of the presence of fields, certain transport coefficients (e.g. the anisotropy of the diffusion coefficient and  $\omega^{(3)}$ ) become important for the swarms, although they vanish identically for neutral gases. Secondly, whereas for neutral gases the effect of higher hydrodynamic coefficients is significant only at higher densities, where divergence difficulties arise in calculations (Dorfman 1974; Wood 1974), for the swarms the higher hydrodynamic coefficients, at Burnett and super-Burnett levels, are accessible even at very low densities (again because of fields) and the divergence difficulties are not encountered. Thus, the hydrodynamics in the present context has a different content than is normally associated with the term.

The hydrodynamic description is a phenomenological description of the time development of the number density n(r, t). One does not refer here to the distribution function f(r, c, t). The description is applicable in a stationary state, that is, when the memory of the initial state f(r, c, 0) has been lost and the distribution function has become a functional of n(r, t) as far as its space-time dependence is concerned.

The starting point of the hydrodynamic description is the continuity equation for the number density,

$$\partial_t n(\mathbf{r}, t) + \nabla \cdot (n u(\mathbf{r}, t)) = (\partial_t n(\mathbf{r}, t))_{\text{coll}}.$$
(2)

It describes the change in  $n(\mathbf{r}, t)$  due to a convective particle current  $n\mathbf{u}(\mathbf{r}, t)$  and a production term  $(\partial_t n(\mathbf{r}, t))_{coll}$ . One now assumes that both these quantities can be expressed as power series in the gradient operator  $\nabla$  with constant coefficients, and obtains the transport equation form of (2),

$$\left(\partial_t - \sum_{k=0}^{\infty} \boldsymbol{\omega}^{(k)} \odot (-\nabla)^k\right) n(\boldsymbol{r}, t) = 0.$$
(3)

The constants  $\omega^{(k)}$  are tensorial transport coefficients of order k, and  $\odot$  indicates a k-fold scalar product. The  $\omega^{(k)}$  can be taken to be symmetrical under permutation of space indices, since their antisymmetrical parts are lost in the scalar multiplication.

Fourier expansion of the quantities in equation (2) followed by a power series expansion in the wave number gives rise to the same results [7].

Equation (3), truncated at k = 2, is familiar as the diffusion equation

$$\partial_t n + W \cdot \nabla n - \mathbf{D} : \nabla \nabla n = -\alpha n \,. \tag{4}$$

We identify  $W = \omega^{(1)}$  as the drift velocity,  $\mathbf{D} = \omega^{(2)}$  as the diffusion tensor and  $\alpha = -\omega^{(0)}$  as the reaction rate. This equation itself is often called the continuity equation.

As the tensor **D** is real and symmetric, the coordinate axes can be chosen to lie along its principal axes. The fundamental solution P(r, t) of equation (4), i.e. the (unbounded) solution obtained with  $n(r, 0) = \delta(r)$ , is then given by

$$P(\mathbf{r},t) = P_1 P_2 P_3 \exp(-\alpha t), \qquad (5a)$$

with

$$P_i = (2\pi D_{ii}t)^{-\frac{1}{2}} \exp\{-(r_i - W_i t)^2 / 4D_{ii}t\}, \qquad i = 1, 2, 3;$$
 (5b)

or, in tensor notation,

$$P(\mathbf{r},t) = \{\det(2\pi \mathbf{D}\,t)\}^{-\frac{1}{2}}\exp\{-(\mathbf{r}-Wt)\cdot(4\mathbf{D}\,t)^{-1}\cdot(\mathbf{r}-Wt)\exp(-\alpha t)\,.$$
(6)

We now exhibit the transport coefficients  $\omega^{(k)}$  as time derivatives of the moments of the density. Let  $\psi(\mathbf{r})$  be any function of  $\mathbf{r}$  and

$$\langle \psi(\mathbf{r}) \rangle = N^{-1} \int \psi(\mathbf{r}) n(\mathbf{r}, t) \,\mathrm{d}\mathbf{r},$$
 (7a)

$$N \equiv N(t) = \int n(\mathbf{r}, t) \,\mathrm{d}\mathbf{r} \,. \tag{7b}$$

Assuming that  $n(\mathbf{r}, t)$  together with its derivatives vanish at the boundaries of the domain of integration, we obtain from equation (3) the following equations for the time development of the averages  $\langle \psi(\mathbf{r}) \rangle$ 

$$\mathrm{d}N/\mathrm{d}t - \omega^{(0)}N = 0, \qquad (8a)$$

$$d\langle \psi(\mathbf{r})\rangle/dt - \sum_{k=1}^{\infty} \omega^{(k)} \odot \langle (\nabla)^k \psi(\mathbf{r})\rangle = 0.$$
(8b)

If  $\psi(\mathbf{r})$  is a polynomial of order j in r, then in equation (8b) only the transport coefficients of order  $k \leq j$  occur. Taking successive moments we have, with  $\mathbf{r}^* \equiv \mathbf{r} - \langle \mathbf{r} \rangle$ ,

$$\omega^{(0)} \equiv -\alpha = d(\log N)/dt, \qquad (9a)$$

$$\boldsymbol{\omega}^{(1)} \equiv \boldsymbol{W} = \mathrm{d}\langle \boldsymbol{r} \rangle / \mathrm{d}t, \tag{9b}$$

$$\boldsymbol{\omega}^{(2)} \equiv \mathbf{D} = (1/2!) \, \mathrm{d} \langle \boldsymbol{r}^* \, \boldsymbol{r}^* \rangle / \mathrm{d}t \,, \tag{9c}$$

$$\boldsymbol{\omega}^{(3)} = (1/3!) \,\mathrm{d} \langle \boldsymbol{r}^* \boldsymbol{r}^* \boldsymbol{r}^* \rangle / \mathrm{d} t \,, \tag{9d}$$

$$\boldsymbol{\omega}^{(4)} = (1/4!) \operatorname{d}(\langle \boldsymbol{r}^* \, \boldsymbol{r}^* \, \boldsymbol{r}^* \, \boldsymbol{r}^* \rangle - 3 \langle \boldsymbol{r}^* \, \boldsymbol{r}^* \rangle \langle \boldsymbol{r}^* \, \boldsymbol{r}^* \rangle) / \operatorname{d} t.$$
(9e)

Since the transport coefficients are constant in time, the corresponding averages must be linear in time. If a transport coefficient vanishes then the corresponding average must be constant in time. Thus, there emerges a significant difference between the truncated equation (4) and the general transport equation (3). This can be illustrated by considering the deviations from the gaussian-shaped fundamental solution (6) of equation (4). The first two deviations, called respectively 'skewness' and 'excess' or 'kurtosis' are given by the quantities  $\langle r_i^{*3} \rangle / \langle r_i^{*2} \rangle^{3/2}$  and  $\{\langle r_i^{*4} \rangle / \langle r_i^{*2} \rangle^2 - 3\}$  (see e.g. Abramowitz and Stegun 1965, p. 928). Equation (3), via (9d) and (9e), predicts a time dependence  $\sim t^{-\frac{1}{2}}$  and  $\sim t^{-1}$  respectively for these quantities, while from equation (4) a much faster asymptotic decay,  $\sim t^{-3/2}$  and  $\sim t^{-2}$ , is predicted. Measurement of such deviations can therefore provide information on the magnitude of related coefficients.

It appears that  $\omega^{(3)}$ , which corresponds to the Burnett-level hydrodynamics, should be measurable in swarm experiments (Skullerud 1974; Whealton 1975). The coefficient  $\omega^{(4)}$ , corresponding to the super-Burnett level, would require further refinement of technique. In the hydrodynamics of neutral gases, because of the absence of fields,  $\omega^{(3)}$  vanishes identically as do all  $\omega^{(j)}$  for odd *j*, and the calculation of  $\omega^{(4)}$  is beset with difficulties.

The hydrodynamic description presupposes a stationary velocity distribution and small relative gradients  $\nabla n/n$  of density. It is therefore not expected to apply to situations involving fields that vary strongly in time or space or when density gradients are large. At material boundaries the gradients will always be large, and proper boundary conditions for the transport equations should always include a kinetic treatment of the boundary layer. However, in practice such layers can often be neglected and well-behaved solutions can be obtained for the transport equations. Such solutions are useful in many ways but cannot always be relied upon near the boundaries.

### 3. Transport Coefficients and Time-correlation Functions

The averages defined by equations (7) can be formed for any n(r, t). Thus, in general, the right-hand sides of equations (9a)–(9e) define time-dependent quantities  $\omega^{(k)}(t)$ . The hydrodynamic regime is expected to arise after sufficient time has elapsed. This expectation may be expressed in the form

$$\lim_{t \to \infty} \omega^{(k)}(t) = \omega^{(k)} = \text{const.}$$
(10)

Then, for large times the hydrodynamic equations (3), (8a) and (8b) are satisfied with constant coefficients  $\omega^{(k)}$ .

Note that by virtue of the relation (1) between  $n(\mathbf{r}, t)$  and  $f(\mathbf{r}, \mathbf{c}, t)$ , the averages (7a) and (7b) are also phase-space averages:

$$\langle \psi(\mathbf{r}) \rangle = N^{-1} \int \psi(\mathbf{r}) f(\mathbf{r}, \mathbf{c}, t) \,\mathrm{d}\mathbf{c} \,\mathrm{d}\mathbf{r},$$
 (11a)

$$N \equiv N(t) = \int f(\mathbf{r}, \mathbf{c}, t) \,\mathrm{d}\mathbf{c} \,\mathrm{d}\mathbf{r} \,. \tag{11b}$$

We now outline methods of constructing such averages and their use. Let a particle be released in the gas at a point  $r_0$  with velocity  $c_0$  at a time  $t_0$  and let its position r and velocity c be noted at a later time t. Then by repeating the process a large number of times with identically prepared gas systems one can form a conditional probability function  $\Pi(\mathbf{r}, \mathbf{c}, t | \mathbf{r}_0, \mathbf{c}_0, t_0)$ . The distribution function  $f(\mathbf{r}, \mathbf{c}, t)$  arising from an initial distribution  $f(\mathbf{r}_0, \mathbf{c}_0, t_0)$  is given by

$$f(\mathbf{r}, \mathbf{c}, t) = \int \Pi(\mathbf{r}, \mathbf{c}, t \,|\, \mathbf{r}_0, \mathbf{c}_0, t_0) f(\mathbf{r}_0, \mathbf{c}_0, t_0) \,\mathrm{d}\mathbf{c}_0 \,\mathrm{d}\mathbf{r}_0 \,. \tag{12}$$

The probability function has the property that for  $t_0 < t' < t$ 

$$\Pi(\mathbf{r}, \mathbf{c}, t \,|\, \mathbf{r}_0, \mathbf{c}_0, t_0) = \int \Pi(\mathbf{r}, \mathbf{c}, t \,|\, \mathbf{r}', \mathbf{c}', t') \,\Pi(\mathbf{r}', \mathbf{c}', t' \,|\, \mathbf{r}_0, \mathbf{c}_0, t_0) \,\mathrm{d}\mathbf{c}' \,\mathrm{d}\mathbf{r}' \,. \tag{13}$$

In developing this point of view further one is led to examine more carefully the meaning of ensemble averages that define  $\Pi$ . In particular, when models are used, attention has to be paid to the magnitude of the smallest subintervals into which a given time interval can be idivided. Formally, from here one can make contact with the path integral and intregal equation representations of the development of the distribution function (Notes [8], [9]).

We now have a procedure for constructing f(r, c, t), and therefore n(r, t) and the averages (7) or (11) for any given system, from which an ensemble may be generated. This procedure can be implemented in various ways. First of all, it can be implemented experimentally, since the probability function has been defined operationally. Secondly, it can be implemented numerically once the underlying particle dynamics are given in a suitable form. Note that no reference has been made to Hamiltonians or Liouville operators, although if the dynamics are governed by them and they are convenient for the purpose, they may be used to construct the  $\Pi$  function or the distribution function. Finally, kinetic equations, in particular the Boltzmann equation, may be used to obtain the distribution function and the averages formed from it.

If the gas system, including external fields, is time independent then the time dependence of the  $\Pi$  function is determined by the difference  $t-t_0$ . If in addition the system is also spatially uniform, the space dependence is similarly determined by the difference  $r-r_0$ . Then there is no loss of generality in assuming that all the test particles are released at the origin at time zero. In other words, one takes

$$f(\mathbf{r}_0, \mathbf{c}_0, t_0) = \delta(\mathbf{r}_0) f(\mathbf{c}_0)$$
 at  $t_0 = 0$ .

The procedure may then be phrased in terms of releasing particles at the origin at time  $t_0 = 0$ , with the velocities chosen stochastically to conform to an initial distribution  $f(c_0)$ , and obtaining the number n(r, t) of particles arriving at the point r at time t. Further, even the explicit reference to n(r, t) may be eliminated, if the averages are constructed from the formula

$$\langle \psi(\mathbf{r}) \rangle(t) = \lim_{s \to \infty} s^{-1} \sum_{i=1}^{s} \psi(\mathbf{r}_{i}(t)), \qquad (14)$$

where s is the number of trials. At the *i*th trial a particle is released at the origin with the velocity chosen as above and its position  $r_i(t)$  after a time t is noted.

This last procedure is the one actually followed in experiments and in computer simulations. When the gas distribution is also stochastically simulated,  $r_i(t)$  itself is the result of a similar averaging process and the left-hand side of equation (14) is

then a result of two averaging processes. By constructing  $\omega^{(k)}(t)$  from such averages one can study non-hydrodynamic behaviour and the approach to the hydrodynamic regime. In applications, reactions are frequently absent and only the drift and diffusion  $\omega^{(1)}$  and  $\omega^{(2)}$  are studied; references will be given in Section 22.

The coefficients  $\omega^{(k)}$  for  $k \ge 2$  can be expressed as integrals over time-correlation functions of the velocity by noting that r is the distance travelled in time t, so that it can be expressed as

$$\mathbf{r} \equiv \mathbf{r}(t) = \int_0^t \mathbf{c}(t) \, \mathrm{d}t \,. \tag{15}$$

For the case of diffusion one starts with the relation

$$\langle \boldsymbol{r}^* \, \boldsymbol{r}^* \rangle (t) = \int_0^t \int_0^t \mathrm{d}t' \, \mathrm{d}t'' \, \langle \boldsymbol{c}^*(t') \, \boldsymbol{c}^*(t'') \rangle \,, \tag{16a}$$

with

$$c^{*}(t) = c(t) - W(t).$$
 (16b)

For stationary distributions the time correlation in the integrand of equation (16a) can depend only on  $\tau = |t' - t''|$ . Accordingly,

$$\langle \boldsymbol{r}^* \boldsymbol{r}^* \rangle(t) = 2t \int_0^t \langle \boldsymbol{c}^*(0) \, \boldsymbol{c}^*(\tau) \rangle(1 - \tau/t) \, \mathrm{d}\tau \,, \tag{17}$$

and by equations (9c) and (10),  $\mathbf{D} = \lim \mathbf{D}(t)$ ,

$$\mathbf{D}(t) = \int_0^t \langle \boldsymbol{c}^*(0) \, \boldsymbol{c}^*(\tau) \rangle \, \mathrm{d}\tau \,. \tag{18}$$

For a general discussion of time-correlation functions, reference may be made, for example, to the texts by Egelstaff (1967) or McQuarrie (1976). Formulae similar to (18) involving higher correlation functions may be found in the articles by Dorfman (1974) and Wood (1974). Most commonly, the time-correlation formalism is used in the linear response theory of Green and Kubo, where systems only slightly perturbed from thermodynamic equilibrium are considered. The unperturbed distribution functions are then known, and given by the Hamiltonian of the system. Hamiltonian also defines the time-evolution operator, i.e. the Liouville operator. There is considerable literature based on this theory about the conductivity of solid systems (see e.g. Huberman and Chester 1975). An interesting application to mobility in gases has been made by Braglia and Dallacasa (1978). However, in the presence of strong fields, which is the usual situation in swarm experiments, the simplifications of the linear response theory cannot be used. The stationary distribution obtained in these situations cannot be directly related to the Hamiltonian or to the timeevolution operator.

To make some further points about the nature of the time-correlation functions and to give an instance of the linear response argument, we derive now a correlationfunction expression for the differential mobility tensor

$$\mathbf{K}(t) = \partial W(t) / \partial E,$$

(19)

where E is the electric field. The acceleration a suffered by a particle of charge q and mass m in the electric field E is given by

$$\boldsymbol{a} = (q/m)\boldsymbol{E}. \tag{20}$$

We use the definition (14) and write

 $W(t) = \lim_{s \to \infty} s^{-1} \sum_{i=1}^{s} c_i(t).$  (21)

Now, for any t', with 0 < t' < t,

$$\boldsymbol{c}_{i}(t) = \boldsymbol{c}_{i}(\boldsymbol{c}_{i}(t'), t-t').$$
(22)

If a small change  $\delta a$  is made in the acceleration at time t' and it persists for a small duration dt', then the change in  $c_i(t)$  due to this perturbation is obtained from equation (22) by replacing  $c_i(t')$  by  $c_i(t') + \delta a dt'$ . To first order

$$\delta_{t'} W(t) = \delta \boldsymbol{a} \, \mathrm{d}t' \lim_{s \to \infty} s^{-1} \sum_{i=1}^{s} \left\{ \partial \boldsymbol{c}_i(t) / \partial \boldsymbol{c}_i(t') \right\}.$$
(23)

The meaning of the average (23) is as follows. The velocity of the particle, released at the origin at time zero with a velocity chosen to conform to some initial distribution, is measured at t' and an infinitesimal change  $\delta c_i(t')$  is made. The change  $\delta c_i(t)$ , caused by this in the velocity  $c_i(t)$  at a subsequent time t, is then measured and the ratios are formed. In terms of the phase-space average this means that

$$\langle \partial \boldsymbol{c}(t) / \partial \boldsymbol{c}(t') \rangle = \int \{ \partial \boldsymbol{c}(t) / \partial \boldsymbol{c}(t') \} f(\boldsymbol{r}', \boldsymbol{c}', t') \, \mathrm{d}\boldsymbol{r}' \, \mathrm{d}\boldsymbol{c}' \,.$$
(24)

A similar interpretation is needed for the averages in equations (16)–(18), connected with the diffusion tensor. Indeed, for any many-time correlation function, the earliest time has a special significance.

Using the stationarity property, the space-averaged distribution

$$f(\boldsymbol{c}) = N^{-1} \int f(\boldsymbol{r}, \boldsymbol{c}, t) \,\mathrm{d}\boldsymbol{r}$$
(25)

and  $\tau = t - t'$ , we can write the average (24) as

$$\mathbf{g}(\tau) = \langle \partial \boldsymbol{c}(\tau) / \partial \boldsymbol{c} \rangle = \int \{ \partial \boldsymbol{c}(\tau) / \partial \boldsymbol{c} \} f(\boldsymbol{c}) \, \mathrm{d} \boldsymbol{c} \,. \tag{26}$$

Using partial integration, and assuming that the boundary terms vanish, we have

$$\mathbf{g}(\tau) = -\langle \{ \mathrm{d}(\log f(\mathbf{c}))/\mathrm{d}\mathbf{c} \} \mathbf{c}(\tau) \rangle.$$
(27)

Returning now to equation (23), one argues that if the infinitesimal force  $m \,\delta a$  acts during the whole interval 0 to t, the resulting change in W(t) will be obtained by adding all the contributions arising from the infinitesimal intervals dt'. This is the linear response argument, but note that the change  $\delta a$  is imposed on an ensemble already subject to an acceleration field a. We thus have

$$\Delta W(t) = \delta \boldsymbol{a} \cdot \int_0^t \mathrm{d}\tau \ \mathbf{g}(\tau) \,. \tag{28}$$

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Hence from equations (28) and (19) and (20),

$$\mathbf{K}(t) = (q/m) \int_0^t \mathbf{g}(\tau) \, \mathrm{d}\tau \,, \tag{29}$$

where  $\mathbf{g}(\tau)$  is given by equations (26) and (27).

Note that when the distribution function f(c) of equation (25) has the form of a distorted Maxwellian,

$$f(\boldsymbol{c}) \sim \exp\{-(m/2k)\boldsymbol{c}^* \cdot \mathbf{T}^{-1} \cdot \boldsymbol{c}^*\},\$$

with T the temperature tensor and  $c^* = c - W$ , as defined above, equations (18) and (27) give the result

$$\mathbf{D}(t) = (k/q) \mathbf{T} \cdot \mathbf{K}(t).$$
(30)

In the limit  $t \to \infty$  this becomes a set of relations between the appropriate hydrodynamic coefficients. These are known as the generalized Einstein relations and have been widely discussed in the literature [10]. The Einstein relation itself is the limit  $E \to 0$  of equation (30) and it holds exactly since the distribution is then in fact Maxwellian. The generalized relations cannot be exact but they hold remarkably well [10]. Why they should be as good as they are, is to some extent understood but perhaps a better explanation should be given. However, in view of the above derivation, explanations starting from distribution functions of nearly Maxwellian form cannot be very illuminating. It should be noted that the differential mobility is not particularly easy to measure or calculate. Although the generalized Einstein relations are interesting and useful in making estimates, they are not important at the level of accuracy aimed for in this paper.

### 4. Boltzmann Equation: Kinetic Equations for Transport Coefficients

The Boltzmann equation for our problem has the form

$$\{\partial_t + \boldsymbol{c} \cdot \partial_r + \boldsymbol{a} \cdot \partial_c\} f(\boldsymbol{r}, \boldsymbol{c}, t) = -Jf(\boldsymbol{r}, \boldsymbol{c}, t), \qquad (31a)$$

$$\boldsymbol{a} = (q/m)(\boldsymbol{E} + \boldsymbol{c} \times \boldsymbol{B}), \qquad Jf = -(\partial \boldsymbol{f}/\partial t)_{\text{coll}}.$$
 (31b, c)

It is a continuity equation for the six-dimensional phase-space distribution function  $f(\mathbf{r}, \mathbf{c}, t)$ . The electric field **E** and the magnetic field **B** are both independent of **r** and t. The particles have charge q and mass m. The collision operator J is treated in detail in Part III. It is a linear operator which acts on f only through its c dependence; that is, it is a local operator in r and t corresponding to the assumption that both the range and the duration of collisions are negligible. The operator J depends functionally on the neutral distribution and the scattering and reaction cross sections. When the neutral distribution is isotropic and the colliding particles are unpolarized, J is rotationally invariant, i.e. its eigenfunctions are proportional to spherical harmonics. If reactions are present the operator J may be split into a particle-conserving part  $J^{PC}$  and a reactive part  $J^{R}$ . The latter is usually of a much simpler form than  $J^{PC}$ , but its presence may nevertheless introduce nontrivial complications in the solution of the Boltzmann equation. The reactions considered here are irreversible reactions of the type  $A + B \rightarrow C + D$ , and it is assumed that only the charged species A with the distribution function f(c) is measured. These will be called unidirectional reactions (Section 25). Further details of this operator are not needed in this section.

If available, a solution of equation (31a) would provide answers to any questions that may be asked about the behaviour of the system in the hydrodynamic or the non-hydrodynamic regime. In the hydrodynamic regime, complete knowledge of such a solution is not required. Rather one takes the distribution function in a form appropriate to this regime as a sum of certain components and derives simpler kinetic equations for these components from equation (31a). The 'observable quantities' of this regime, i.e. the transport coefficients, are then obtained from the solutions of these simpler equations (for further discussion see Section 5 and Note [11]).

The basic hydrodynamic assumption (Section 2) is that the number density satisfies equation (3) and the space-time dependence of the phase-space distribution has the form (see Note [7])

$$f(\mathbf{r},\mathbf{c},t) = \sum_{j=0}^{\infty} \mathbf{f}^{(j)}(\mathbf{c}) \odot (-\nabla)^{j} n(\mathbf{r},t).$$
(32)

The functions  $\mathbf{f}^{(j)}(\mathbf{c})$  are tensors of rank j and  $\odot$  indicates a j-fold scalar product. The space-time dependence of  $f(\mathbf{r}, \mathbf{c}, t)$  is thus functionally determined by  $n(\mathbf{r}, t)$ . In order that equation (32) be properly normalized and consistent with the definition (1), we have, using equation (7a)

$$f^{(0)}(c) = N^{-1} \int f(r, c, t) \,\mathrm{d}r, \qquad (33a)$$

$$\int f^{(0)}(c) \, \mathrm{d}c = 1 \,, \tag{33b}$$

$$\int \mathbf{f}^{(k)}(\boldsymbol{c}) \, \mathrm{d}\boldsymbol{c} = 0, \qquad k \neq 0.$$
(33c)

Substituting equations (3) and (32) into (31a) and for every k equating the coefficients of  $(-\nabla)^k n(\mathbf{r}, t)$  on both sides, we obtain the hierarchy of kinetic equations

$$(a \cdot \partial_c + J)f^{(0)} = -\omega^{(0)}f^{(0)}, \qquad (34a)$$

$$(a \cdot \partial_c + J)\mathbf{f}^{(k)} = c \, \mathbf{f}^{(k-1)}(c) - \sum_{j=0}^k \, \omega^{(j)} \mathbf{f}^{(k-j)}, \qquad k \neq 0.$$
 (34b)

These equations are to be solved successively by starting from (34a), the equation for the space average of the phase-space distribution function  $f^{(0)}(c)$ . Equation (34a) defines an eigenvalue problem and, corresponding to the assumption that the hydrodynamic regime is the long-time limit, one associates the lowest eigenvalue  $\omega^{(0)}$  with the reaction rate  $\alpha = -\omega^{(0)}$ . In the absence of reactions this eigenvalue is trivially zero. The eigenfunction belonging to the appropriate eigenvalue is the required solution  $f^{(0)}(c)$ , to be normalized according to equation (33b). The equations (34b) are inhomogeneous equations. A better appreciation of the structure of these equations and their relationship is obtained by introducing the linear operator

$$\mathscr{L} = \boldsymbol{a} \cdot \boldsymbol{\partial}_c + J + \boldsymbol{\omega}^{(0)} \tag{35}$$

and the tensors

$$\mathbf{b}^{(k)} = -\mathbf{\omega}^{(k)} f^{(0)} + c \mathbf{f}^{(k-1)} - \sum_{j=1}^{k-1} \mathbf{\omega}^{(j)} \mathbf{f}^{(k-j)}.$$
 (36)

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Equations (34a) and (34b) then become

$$\mathscr{L}f^{(0)} = 0, \tag{37a}$$

$$\mathscr{L} \mathbf{f}^{(k)} = \mathbf{b}^{(k)}, \qquad k \neq 0.$$
(37b)

Integrating with respect to c, recalling equations (33b) and (33c) and noting that only the reactive part  $J^{R}$  of the collision operator contributes to this integral, we have

$$\omega^{(0)} = -\int J^{\mathbf{R}} f^{(0)}(\mathbf{c}) \, \mathrm{d}\mathbf{c} \,, \tag{38a}$$

$$\omega^{(k)} = \int c \mathbf{f}^{(k-1)}(c) \, \mathrm{d}c - \int J^{\mathbf{R}} \mathbf{f}^{(k)}(c) \, \mathrm{d}c \,. \tag{38b}$$

These equations give the transport coefficients in terms of the solutions of the kinetic equation sets (34) or (37). Since a solution of the homogeneous equation (37a) can always be added to  $\mathbf{f}^{(k)}$  without altering (37b) a condition is needed to make  $\mathbf{f}^{(k)}$  unique. This is provided by equation (33c) and leads to the proper definition of the transport coefficients given by (38b). An eigenvalue problem needs to be solved only for determining the reaction rate  $-\omega^{(0)}$  and the space-averaged distribution  $f^{(0)}(c)$ . Once these are given, all  $\boldsymbol{\omega}^{(k)}$  for k > 0 are determined without solving any further eigenvalue problem.\*

Note that when reactions are present the calculation of a transport coefficient of rank k requires solutions of the equations up to order k. In the absence of reactions, solutions of equations to the order k-1 suffice for the same purpose. Thus, in the latter case, with  $\omega^{(0)} \equiv 0$ , the drift velocity  $\omega^{(1)}$  or the mobility is determined by equation (37a) and the diffusion tensor  $\omega^{(2)}$  by equation (37b) for k = 1. These will be called the mobility and diffusion equations respectively. Part IV below is devoted to their solution and applications.

Note further, that by virtue of equation (38b) with k = 1, the drift velocity  $\omega^{(1)}$  is a velocity moment of the space-averaged distribution function  $f^{(0)}$  only in the case where no reactions are present.

#### 5. Boltzmann Equation: Existence Theorems and Spectral Properties

In this section we formulate some questions which need to be answered in order to secure fully the foundations of the methods described in the rest of the paper. In this connection a number of mathematical works, which come from different streams of kinetic theory literature, become relevant. However, at the time of writing, these works are not yet in a form where they can be adopted or easily modified for direct use in the problems that concern us. We shall eschew technical details and describe the problems and results in an informal way.

\* The second term on the right-hand side of equation (38b) may be written as

 $\int J^{\mathbf{R}} h^{(k)} \, \mathrm{d} c + \omega^{(k)} \omega^{(0)}, \quad \text{with} \quad h^{(k)} = f^{(k)} + \omega^{(k)} f^{(0)},$ 

and equation (37b) may then be looked upon as an equation for  $h^{(k)}$  which does not involve an eigenvalue problem.

#### (a) Steady state and existence theorems

The basic assumption in transport calculations is that after some suitable time the distribution function can be written in the form (32), that is, as

$$f(\mathbf{r}, \mathbf{c}, t) = n(\mathbf{r}, t) f^{(0)}(\mathbf{c}) + \nabla n(\mathbf{r}, t) \cdot f^{(1)}(\mathbf{c}) + \dots$$

This is the assumption that makes it possible to derive transport coefficients which are independent of time. The state described by such a distribution function is sometimes called a steady or stationary state. This is to be taken informally—we are not making any allusions to any stationary random processes or stationary ensembles that may underlie the phenomena.

The problems underlying this assumption are quite similar to those underlying the justification of the Chapman-Enskog procedure and the existence of transport coefficients for ordinary gases (Grad 1949*a*, 1949*b*, 1960; Uhlenbeck and Ford 1963). The present problem is simpler in the sense that the reason for neglecting the non-linearity is very strong. It may be noted that there are two possible sources of non-linearity: the direct one due to ion-ion interaction and the indirect one due to the possible alteration of the neutral distribution by the ions and its reaction on the ion distribution; both are very small because the ion density is very small compared with the gas density. If the definition of the swarm given in Section 1 is adopted the non-linearity is excluded in principle.

On the other hand, the presence of the field term and the particular arrangement of equations are significantly different from the Chapman-Enskog development of neutral gas transport. A discussion of these equations along the lines of references quoted above is not available in the literature [11].

Thus, while there is no definite proof that the distribution function has the form (32), the agreement of the theories based on this form with experiments is already so good that it requires explanation. In other words, the form (32) has to be true in some sense and the task of mathematical theory is to make precise what this sense is.

Further work in this direction may well benefit from the existence and uniqueness theorems recently proved by Drange (1978). Specifically, Drange considers the Boltzmann equation (31a), and allows the electric and magnetic fields (E and B) to have space-time dependence, subject to some technical restrictions. The equation is solved by successive iterations. An essential part of the procedure is to split the collision integral into a multiplicative and an integral operator, for which some cutoff procedure is necessary. In an earlier paper Drange (1975) studied several cutoff procedures. His work concludes by showing the existence and uniqueness of the solution to equation (31a) for a class of potentials which include the power law  $V(r) = V_0 r^{-s}$  (s > 2) and the hard-sphere potential. These papers are heavily abbreviated and we have not been able to unravel the argument sufficiently to comment on its content. But it is evident that the structure postulated in equation (32) is out of the reach of such methods.

There are some indications that the solution of the Boltzmann equation (31a) may have a different structure from that postulated in equation (32). Recent experiments on  $H^+$  ions in helium have shown a novel situation, namely that a small group of ions travels as if it has suffered no collisions (these are called the runaways) and a larger group travels as if governed by ordinary time-independent transport coefficients (Howorka *et al.* 1979; Lin *et al.* 1979*a*). Loosely speaking, this suggests that the solution of equation (31a) should have a decaying part of the form (32) and a smaller part corresponding to free transport. This situation needs to be studied in relation to the velocity dependence of the cross sections.

#### (b) Position-independent Boltzmann equation and mobility equation

The position-independent Boltzmann equation is the name given to equation (31a) when the term involving the spatial gradient is omitted, that is, to the equation

$$\partial_t f + \boldsymbol{a} \cdot \partial_c f = J(f). \tag{39}$$

This equation has an interesting relation to the mobility equation (37a). Let B = 0 and E be independent of r and t, and let  $f_t$  be a solution of equation (31a) for some given initial distribution  $f_{to}$ ; then if there exists a limit

$$\lim_{t \to \infty} f_t = f(c), \tag{40}$$

the limit function satisfies the mobility equation

$$(q/m)E \cdot \partial_c f = J(f). \tag{41}$$

If one writes down the formal time-dependent solution of equation (39) (see e.g. Cavalleri and Paveri-Fontana 1972, or references quoted by them) and compares it with a related solution for equation (41), one sees that the existence of the limit (40) involves questions about the manner in which the memory of the initial state is lost.

Equation (39) has also been considered by Molinet (1977). He considers the initial value problem and proves the existence and uniqueness of the solution for power law potentials of the form  $Ar^{-s}$  ( $3 < s < +\infty$ ) and for hard-sphere potentials. Some technical restrictions are placed on the initial distribution  $f_{t_0}$ . The existence of the limit (40) is, however, not proved.

Molinet (1977) bases his proof on an iterative method applied to an integral equation derived from (39). The solution whose existence is proved satisfies equation (39) only in a generalized sense (i.e. almost everywhere). The integral equation used and the estimates of iterates depend upon an angular cutoff used to put the collision operator in a suitable form. The bounds on the iterates are time dependent, being proportional to  $\exp\{2\alpha(t-t_0)\}$ . The method thus breaks down as  $t \to \infty$ . The iterates also depend on the masses (Molinet 1977, equation 4.49) and become ineffective if the ion and gas masses are equal.

It is well to recall at this point that Wannier (1953, Section IID) has argued that, particularly for the equal mass case, the distribution function actually has a singularity.

It is clear that further work is needed on the solution of equation (39) if this is to be used to prove the existence of the solutions of the mobility equation (41). On the other hand, it is possible that equations (39) and (41) are not to be related in the way indicated. A solution of (41) necessarily satisfies (39) but such a solution may not be reachable from any solution of (39) in the limit.

Finally, we note that Cavalleri and Paveri-Fontana (1972) assume the existence of a steady state (i.e. of the limit 40) and from this derive a necessary condition for the

suppression of runaways. If, however, the runaways coexist with ordinary transport in some sense, then more refined analysis will be needed for the connection between equations (39) and (41).

# (c) Representation of operators and their spectrum

We expect that further work on questions outlined in previous sections will justify the use of mobility and diffusion equations in the form used in this paper. Even then some mathematical questions remain and we now turn to them. In calculating the mobility we solve the equation

$$\mathscr{L}f^{(0)} = 0. \tag{42a}$$

That is, we are seeking the eigenfunction of the operator  $\mathscr{L}$  belonging to the eigenvalue zero. In calculating diffusion we seek to solve the equation

$$\mathscr{L}\boldsymbol{f}^{(1)} = \boldsymbol{b}^{(1)}, \tag{42b}$$

and this calls for a knowledge of those eigenfunctions of the operator  $\mathscr{L}$  which are orthogonal to the eigenfunction belonging to the eigenvalue zero.

At the time of writing there is no information in the literature concerning the eigenvalues or eigenfunctions of the operator  $\mathscr{L}$  as such. Of the two operators whose sum it is (equation 35),  $a \cdot \partial_c$  has a continuous spectrum and its eigenfunctions are not square integrable. There is considerable literature on the operator J, the collision operator, but most of it is in connection with the linearized Boltzmann equation in the pure gas problem or in neutron transport theory. The operator that concerns us here is the one used in the so-called foreign gas problem.

Much of the work on the linearized collision operator is based upon splitting the operator into a multiplicative operator and an integral operator:

$$J(f) = vf - K(f).$$
(43)

This requires the introduction of some sort of cutoff in the collision cross section to make the two parts of the operator well defined (e.g. Grad 1963; Cercignani 1967; Drange 1975). This procedure is inconvenient for numerical work since it corresponds in some sense to representing a small quantity as a difference between two large quantities. From the literature it is easy to get the impression that for analytical work such a procedure is essential. This is, however, not the case: Pao (1974) has been able to establish the spectrum of linearized collision operators without using any cutoff procedure. He proves that for the class of power law potentials  $V(r) = V_0 r^{-s} (s > 2)$  the linearized collision operator for the pure gas has a purely discrete spectrum and that its eigenfunctions exist, are square-integrable and form a complete set for such functions. It is to be expected that Pao's technique will also be applicable to the foreign gas collision operator. The main difference will be in the dependence of the spectrum and eigenfunctions on masses.

For the hard-sphere case more detailed information is available in the works of Yan (1969), Jenssen (1972), Klaus (1976), and the references quoted by them. In particular Yan shows the close connection that exists between the pure gas linearized collision operator and the foreign gas collision operator. The relationship to the

operator occurring in neutron thermalization studies may also be seen from his work and the papers quoted by him. It appears (Jenssen 1972; Klaus 1976) that the spectrum for the hard-sphere case differs from that for the power law case in possessing a continuous as well as a discrete part. Furthermore, strong evidence is provided to show that the spherical components  $J_l$  for  $l \ge 3$  possess no discrete eigenvalues. There is no information on eigenfunctions. Again, these results are proved for a pure gas linearized operator, but may be expected to hold also for the foreign gas collision operator in view of the work of Yan cited above.

Although no precise information is available in the literature, the spectrum of the collision operators for more realistic short-range potentials may be expected to be purely discrete. However, in calculating transport coefficients of practical interest one often works not with potentials but cross sections, which are available from other sources, sometimes from *ab initio* quantum mechanical calculations. Such cross sections may not correspond to a simple classical potential scattering. What is needed therefore is a study of the operators in relation to typical behaviour of cross sections.

Returning to the operator  $\mathscr{L}$ , we may infer that it will have both a continuous and a discrete spectrum. It is not possible to say what the eigenfunctions will be. The question of interest is: to what extent do the moment equations, to be discussed in Section 17, capture the significant part of the operator equations? Or, in other words, to what extent are the operator equations well represented in terms of the matrix equations and other forms used elsewhere in this paper? No direct answer to these questions is available. But matrix representations are used in related problems such as that of sound propagation and are used also in the investigation of spectrum questions, as for instance in the work of Jenssen (1972). The relationship of the sound propagation problem to the problem of this paper was discussed earlier by Kumar and Robson (1973).

#### 6. General Space-Time Development: Non-hydrodynamic Behaviour

Non-hydrodynamic effects most often occur on short time scales and/or near the boundaries. They are difficult to measure because just in these regions the effects due to imperfections of geometries, contact potentials and reflection coefficients are the most difficult to control. In the search for significant and reproducible results most experiments are designed to minimize these effects (see e.g. Huxley and Crompton 1974, Section 10.3). Thus, in the first instance, the interest in the non-hydrodynamic effects is a negative one. The investigations, both theoretical and experimental, are carried out to delimit the phenomena so that they can be safely eliminated from the experiments to obtain the more reliable (hydrodynamic) information. This situation is often compared with the corresponding one in connection with the boundary layer problems in fluid dynamics. On the other hand, in discharge tubes and phenomena near electrodes as well as in some diffusion cell experiments (i.e. in those exhibiting diffusion cooling) the non-hydrodynamic behaviour is all important, although some of these problems can be treated with small modifications of the hydrodynamic scheme.

From the discussions in the previous sections it is evident that the non-hydrodynamic behaviour can be studied by constructing the time-dependent quantities  $\omega^{(k)}(t)$  defined in Section 3, from computer simulations or from the Boltzmann equation, by direct numerical solution of the space-time dependent Boltzmann equation, or by other

computer-based investigations designed to answer particular questions. As an example of the last kind, we mention the work of McIntosh (1974). He studied the space-time development of a highly localized pulse of electrons, and noticed a 'pear-shaped' component in the density distribution n(r, t). He obtained evidence in the time development of this component which indicated a non-hydrodynamic behaviour. This component is associated with the coefficient  $\omega^{(3)}$  in hydrodynamic theory. The example serves to emphasize that the hydrodynamic and non-hydrodynamic effects can have similar appearance and, in order to distinguish between them, particularly careful attention needs to be paid to the time development of such features.



Fig. 1. Ratio between the time-dependent values (see equation 18) and the hydrodynamic values of the transverse  $(D_{xx})$  and longitudinal  $(D_{zz})$  components of the diffusion tensor shown for two choices of the initial velocity distribution f(c, t = 0), namely  $\delta(c)$  and  $f(c, \infty)$ . Here  $\delta(c)$ is the distribution in which all particles are given the velocity zero and  $f(c, \infty)$  is the stationary distribution that is finally achieved. A cold gas model with hard-sphere interaction between the ions and the neutrals is assumed. The mass ratio  $m/m_0$  is unity. The mean free path  $\lambda = (n_0 \sigma)^{-1}$ , with  $n_0$  the gas density and  $\sigma$  the total cross section, is a scale parameter, and *a* is the magnitude of the acceleration of the particles in the *z* direction. The cold gas assumption means that the gas particles are stationary but subject to recoil (see Note [5]). (Diagram after Skullerud 1977.)

Numerical solution of the Boltzmann equation for the initial value problem with an initial distribution of the form

$$f(\mathbf{r}, \mathbf{c}, 0) = \delta(\mathbf{r}) f(\mathbf{c}) \tag{44}$$

is an instance where non-hydrodynamic behaviour can be studied without the complication of boundary effects. For this purpose a suitable form of time-dependent configuration-space functions has to be found in terms of which the space-time dependence may be expressed. It is then possible to solve for the space-time dependence by using polynomial expansion methods, rather similar to those used for finding the velocity dependence (cf. Section 17). In fact, the velocity dependence is also determined at the same time in a coupled calculation. These methods have been used both for the electron and the ion problem (Skullerud 1974, 1977). Among other things, a more precise understanding of the problem treated by McIntosh (1974) was obtained in this way. Fig. 1, taken from Skullerud (1977), shows the relaxation of time-dependent diffusion coefficients towards their hydrodynamic values. The precise shape of the curves before the hydrodynamic values are finally established is sensitive to the cross sections. In particular, for some models, oscillations around the final hydrodynamic values may occur. Apart from such information, these curves provide a vivid illustration of the difference between the physical mechanism underlying the transverse and longitudinal diffusion coefficients, at least to those who are able to follow the relevant details. Similar curves for  $\omega^{(3)}$  are available in the references quoted. Two further conclusions from these works may be noted to illustrate the motivation and use of such studies. These are: (1) that  $\omega^{(3)}$  effects should be measurable, and (2) that the transport coefficients relax rapidly towards their hydrodynamic values, and these can be found experimentally by difference measurements even when the non-hydrodynamic corrections to the pulse shape are quite large.

Similar questions for the case of electrons have been investigated by computer simulations in somewhat greater detail and good accounts are available in the works of Braglia (1977), Braglia and Baiocchi (1978) and Lin and Bardsley (1977). For the case of ions, the velocity and energy relaxation were studied by Lin *et al.* (1977) using both the simulation techniques and low-order Burnett expansions. The transition to the hydrodynamic regime has also been illustrated quite clearly by obtaining an explicit analytic solution of equation (31a) for a model collision operator (Robson 1975).

One of the earliest investigations of non-hydrodynamic effects to attract attention was the work of Thomas (1969) and of Thomas and Thomas (1969). They calculated the time-dependent reaction rate  $\alpha(t) = -\omega^{(0)}(t)$  for an electron avalanche using the two-term Boltzmann equation as well as Monte-Carlo simulations and showed that it oscillated about the hydrodynamic value that was finally achieved. More recent work by Sakai *et al.* (1977) and Tagashira *et al.* (1977) is noteworthy for putting this problem in a broader framework.

It has not been our intention to summarize the discussions or findings contained in the works mentioned, but only to pick out the common underlying themes in the investigations of the general space-time behaviour.

## 7. Effect of Boundaries

As observed in the General Introduction (Part I) and in the previous section the influence of boundaries may lead to large gradients and therefore non-hydrodynamic effects. These will occur when the relevant mean free path becomes comparable with the dimensions of the system, as in the Knudsen gas limit in rarefied gas dynamics. For a perfectly absorbing boundary surface S, the proper boundary condition is

$$f(\mathbf{r}, \mathbf{c}, t) = 0 \tag{45}$$

for r lying on S and  $\cos \theta = \hat{c} \cdot \hat{n} > 0$ , where  $\hat{n}$  denotes the unit vector normal to S and directed inwards towards the gas. However, the Boltzmann equation (31a) is generally difficult to solve with such boundary conditions, and to date little work has been done in this direction. Fortunately, there is a wealth of experience in neutron transport theory and rarefied gas dynamics on which to draw (e.g. Williams 1971) and it would seem logical that the next step would be to apply these methods to ion and electron transport problems, as far as possible.

Various approximations to the condition (45) exist in the literature:

(i) The integrated boundary condition (Robson 1976c)

$$\int_{0}^{\infty} c^{3} dc \int_{0}^{\frac{1}{2}\pi} \cos \theta f(\mathbf{r}, \mathbf{c}, t) \sin \theta d\theta = 0$$
(46)

is a statement that the *net* particle flux away from S vanishes. It is deficient from the physical point of view since it can lead to an f which has a negative as well as a positive part. Another suggestion in the same vein is to take

 $n(\mathbf{r},t) = 0 \tag{47}$ 

at a point obtained by extrapolating the density profile to a distance approximately equal to the mean free path  $\lambda$ , behind S. The relevant macroscopic length scale is determined by the length L of the vessel and, since we have  $L \ge \lambda$ , equation (47) is frequently assumed to apply on S itself, and becomes a boundary condition (McDaniel 1964).

(ii) Lowke *et al.* (1977) have argued that for the electron case where the two-term approximation  $f = f^{(0)} + f^{(1)} \cos \theta$  applies, the condition (45) can hold at only one particular angle. They take it to be  $\theta = \frac{1}{2}\pi$ . Assuming, as before  $L \ge \lambda$ , this leads to the condition

$$f^{(0)}(\mathbf{r}, \mathbf{c}, t) = 0$$
 on S. (48)

This is consistent with equation (47) but is a much stronger condition.

We believe that none of the forms (46), (47) or (48) will be satisfactory in general. On the other hand, the half-range expansions familiar in neutron transport theory (Williams 1971, Ch. 11) should allow direct implementation of the correct boundary condition (45), and may well be useful in future work.

It is interesting to discuss boundary effects for the simplest case where E = 0. For the electron problem, because of the smallness of  $m/m_0$  a distinct separation of time and space scales for energy and momentum transfer occurs. Thus, if  $\lambda$  is the mean free path for momentum transfer, then the mean free path for energy transfer is  $\lambda_{\varepsilon} \sim (m_0/2m)^{\frac{1}{2}}\lambda$  and it may happen that

$$\lambda \ll L$$
 but  $\lambda_{\varepsilon} \gtrsim L$ , (49a, b)

as, for example, is the case in the Cavalleri experiment (Huxley and Crompton 1974). The condition (49b) may be thought of as resulting in a good 'thermal contact' between electrons and the container walls: high energy electrons are lost preferentially by diffusion to the walls, leaving the bulk of the electrons at a temperature lower than that of the gas ('diffusion cooling'). On the other hand, from the condition (49a) it follows that the extrapolation length is small: it has therefore been assumed in previous work that equation (47) applies on the boundary walls (Parker 1965; Leemon and Kumar 1975; Robson 1976a).

The condition (49b) also indicates a non-hydrodynamic behaviour for the electrons, with density varying substantially across the container, which is itself of the order of  $\lambda_{\varepsilon}$  in size. Nevertheless it has been shown in the works cited that in the long-time limit where large gradients are still present the density *n* obeys a diffusion-like equation

$$\partial n/\partial t + D_{\rm eff} \nabla^2 n = 0, \tag{50}$$

where  $D_{\rm eff}$  is an effective diffusion coefficient which depends upon the geometry of the container, as well as on the cross sections and gas parameters. The deceptively simple appearance of equation (50) should not obscure the fact that it is generally applicable under both large-gradient and weak-gradient (hydrodynamic) conditions.

To look at the problem in the hydrodynamic regime

$$\lambda_{\varepsilon} |\nabla n| / n \approx \lambda_{\varepsilon} / L \ll 1, \qquad (51)$$

we employ equation (3), recognizing that all odd  $\omega^{(k)}$  vanish and the other coefficients are scalars for zero field, that is,

$$\partial_t n = \sum_{k=1} \omega^{(2k)} (\nabla^2)^k n.$$
(52)

Periodic boundary conditions then lead to the result

$$\nabla^2 n = \Lambda^{-2} n$$

where  $\Lambda \sim L$  is the so-called diffusion length (McDaniel 1964), and hence equation (52) can be written as

$$\partial_t n = \sum_{k=1} \left\{ \omega^{(2k)} / \Lambda^{2k-2} \right\} \nabla^2 n , \qquad (53)$$

which is of the same form as equation (50): the sum is effectively a series expansion of  $D_{eff}$ , which will converge under these conditions. The expansion is in terms of the parameter  $\lambda_{e}/L$ , since we have  $\omega^{(2k)} \sim (\lambda_{e})^{2k-2}$  (Robson 1976a). Clearly, in the limit of high gas pressures and large enclosures,  $\lambda_{e}/L \rightarrow 0$  and equation (53) becomes

$$\partial_t n = \omega^{(2)} \nabla^2 n, \tag{54}$$

which is the usual diffusion equation, with the (geometry-independent) diffusion coefficient  $D = \omega^{(2)}$ . Equation (50) therefore encompasses a whole range of behaviour of the electrons, from the large-gradient non-hydrodynamic regime to the opposite extreme indicated by the conditions (51).

The nonzero field situation has been discussed by Lowke *et al.* (1977). Apart from a possible inadequacy in their assumed boundary condition mentioned above, we note that they have *defined* the diffusion equation to be exact and therefore have to allow the diffusion coefficient to vary with position, which is contrary to normal practice.

An approximate treatment of boundary value problems, valid for both ions and electrons where gradients are not too large, is to solve equation (54), with the coefficients  $\omega^{(k)}$  found from boundary-free calculations (Skullerud 1974; Robson 1975) in, conjunction with the boundary condition (47). This sort of analysis was outlined above for the diffusion cooling, field-free situation. It should also be useful for nonzero fields and will provide a consistency check on any more sophisticated theories.

However, as mentioned before, we feel that the most satisfactory approach will be to do away with the full range (0 to  $\pi$ ) expansion in angular variables and adopt the half-range expansions (0 to  $\frac{1}{2}\pi$  and  $\frac{1}{2}\pi$  to  $\pi$ ) so often used elsewhere in transport calculations. This should account for the sharp changes in angular distributions which occur near material walls, as required by the condition (45).

# Part III. The form and substance of the collision operator 8. Introduction (III)

In this Part (Sections 8–14) we study several alternative forms of the Boltzmann collision operator J for ion-neutral interactions. Although our motivation is a practical one, namely to facilitate the computation of the moments of J for use in transport calculations, we have found that it is important to pay attention to the symmetries of the operator, in order to understand its structure and to bring out its dependence on parameters. The discussion is organized accordingly.

We treat in detail the collision operator for elastic scattering (Sections 9–13) and point out the modifications needed for including inelastic processes due to the internal structure in gas molecules (Section 14). For the latter we use the semiclassical form of the operator suggested by Wang-Chang and Uhlenbeck. The same operator in the case where both the ions and the gas molecules have internal structure is treated in the following paper (Kumar 1980*a*; present issue pp. 449–68).

In all cases J is a linear operator. Its action on a function f(c) of the ion velocity c, not necessarily the distribution function itself, is usually given in the form of an integral operator (Section 9). From this we derive its representation in terms of differential operators (Sections 10 and 11), and as an infinite matrix (Section 12). It is possible to go from any one of these forms to another. Thus one may use the differential forms to obtain matrix representations, or from any given matrix representation one may obtain the kernel of the integral operator. All these forms have been used earlier in approximations suitable to different circumstances. Our aim is to develop general expressions which may be used to carry the particular approximations to higher orders and also to show the relationships between different procedures so that one may effectively compare the efficiencies of the different methods to a given computational accuracy. Such use of the formulae developed here is implicit in the work reported in Part IV below.

In the integral and differential forms, the expressions for the collision operator are essentially unique with possible rearrangement of terms in the series representing the differential forms. However, in the matrix form there can be several representations depending on the system of basis vectors chosen. Usually, these come from the system of orthogonal polynomials in terms of which the ion distribution is expanded. The polynomial system introduces new parameters. The matrix elements of the collision operator then depend on these basis set parameters or b-parameters for short. The proper choice of these b-parameters is important in applications. Their special role in calculations is discussed later in Sections 19 and 20. In the discussion of matrix forms in Section 12 we concentrate mainly on the relationship between different matrix representations and some technical points in the calculation and arrangement of matrix elements. References are given to the literature where explicit formulae for the matrix elements in particular representations may be found.

It may be noted that matrix representations are not limited to orthogonal polynomial bases. It is possible to use non-orthogonal polynomials or even non-polynomial bases. Particularly, in the latter case, no general prescription for calculating the matrix elements of the collision operator can be given (see, however, Sections 17 and 21).

The differential operator form has been developed in two ways. The first, the Fokker-Planck form (Section 10, Note [13]) is an expansion in powers of the velocity

gradient operator  $\partial_c$ . It is appropriate for the case of heavy ions. The second form is obtained by first making a spherical harmonic decomposition of the collision operator and then developing differential operator forms for the spherical components of the operator. This expansion is suitable for light ions and has been most extensively used for the case of electrons (Section 11, Note [14]).

In the past, the Fokker-Planck expansion (also called Kramers-Moyal expansion in stochastic theory literature), usually carried only to the second order, has been expressed in terms of tensor coefficients. However, the tensors always occur in some scalar products. By using the axial symmetry of the operators with respect to the direction of the vector c, it is possible to obtain an expression in terms of scalar operators involving only the powers of the differential operators  $\nabla^2$  and d/dc.

The main reason for developing general expressions in differential form is the convenience in calculating the moments of the function J(f). The operators are expressed by a series such that to get the moment with respect to a polynomial of degree *n* only the first *n* terms of the series are needed. For the Fokker-Planck case the operator series is actually a power series in the mass ratio  $\mu_0 = m_0/(m+m_0)$  and the polynomials in question are polynomials in *c*. In the case of spherical harmonic decomposition each spherical component of the collision operator is a scalar differential operator arranged in a series. The *n*th member of the series has a leading term  $\sim (\mu\mu_0)^n$  with  $\mu = m/(m+m_0)$ , although the series is not a power series in  $(\mu\mu_0)$ . The calculation of moments is facilitated by using the adjoint J of the collision operator J. Hence expressions for the adjoints are also given. For further remarks on the use of the adjoint operator see Section 17*a*.

The derivation of differential operators is often motivated by noting that in collision with a neutral at rest the change  $\Delta c$  in the velocity and the change  $\Delta \varepsilon$  in the energy are

$$\Delta \boldsymbol{c} \sim \mu_0 \, \boldsymbol{c}, \qquad \Delta \boldsymbol{\varepsilon} \sim \mu \mu_0 \, \boldsymbol{\varepsilon}. \tag{55}$$

It is then said that the former is small when  $\mu_0$  is small and an expansion of the collision operator in powers of  $\Delta c$  does lead to a power series in  $\mu_0$  (the situation is plasma physics is somewhat different; see Note [13]). The second quantity  $\Delta \varepsilon$  is said to be small for small  $\mu$  and low-order expansions for spherical components of J have been obtained in the same way by expansion in powers of  $\Delta \varepsilon$ . It is evident, however, that these quantities are neither parameters nor small, except in some average sense. Furthermore, even accepting the vagueness, in the case of  $\Delta \varepsilon$  the smallness argument by itself is not sufficient to justify its mode of application:  $\Delta \varepsilon$  being small if either  $\mu$  or  $\mu_0$  is small. In our derivations we make no use of this argument. We are primarily guided by the symmetry of the problem and our motivation in obtaining suitable expansions for calculating the moments. Towards the end of Section 11, the difference between low  $\mu$  and low  $\mu_0$  situations for the spherical harmonic decomposition is pointed out.

In our treatment an essential role is played by the operators corresponding to a cold stationary neutral gas [5], for which

$$f_0(c_0) = n_0 \,\delta(c_0) \,. \tag{56}$$

This provides significant simplification, in that the  $c_0$  integration can be carried out immediately. Mathematically, the cold gas approximation corresponds to the zeroth

order term in a certain series expansion of the collision operator. Physically, the approximation corresponds to the situation where the ions are driven through the gas by an electric field so strong that the thermal motion of the gas molecules may be neglected. That is to say, the cold gas approximation should become exact in the high field limit. Hence one looks for an expansion in which the cold gas approximation occurs as the first term.

For all that, our interest here is not in the cold gas approximation itself but in the expressions suggested by it, in the information provided by the expansions about the structure of J and in their utilization in calculating transport coefficients to greater accuracy.

We consider here only the collisions described by a differential cross section  $\sigma(g, \chi)$  whose angular dependence is carried entirely by the polar angle  $\chi$  between the initial and final relative velocities g and g', with

$$\cos\chi = \hat{\boldsymbol{g}} \cdot \hat{\boldsymbol{g}}' \,. \tag{57}$$

Note that apart from central forces, this includes the case where scattering is from unoriented molecules and an averaged cross section may be used. The differential cross section always occurs with a Legendre polynomial and integrated over all angles, i.e. in the form of partial cross sections  $\sigma_l(g)$  defined by

$$\sigma_l(g) = 2\pi \int_{-1}^{+1} \sigma(g,\chi) \operatorname{P}_l(\cos\chi) \operatorname{d}(\cos\chi).$$
(58)

In classical scattering there is a singularity in  $\sigma(g, \chi)$  in the forward direction and the partial cross sections are not well defined. However, the combination

$$\sigma^{(l)}(g) = \sigma_0(g) - \sigma_l(g) = 2\pi \int_{-1}^{+1} \sigma(g,\chi) \{1 - P_l(\cos\chi)\} d(\cos\chi)$$
(59)

is usually well defined; the exceptions being in cases such as Coulomb scattering, where well-known 'cutoff' procedures have to be employed to ensure convergent integrals.

All formulae concerning elastic scattering have been arranged so that the cross section always occurs in the form  $\sigma^{(l)}(g)$ . For inelastic scattering a slightly modified function plays the same role. This avoids those cutoff procedures (cf. Section 5), which are introduced solely for the purpose of making the partial cross sections for clasical scattering well defined. The quantities  $\sigma^{(l)}(g)$  are the most naturally occurring forms in our context and it is desirable in general to work with quantities associated with an orthogonal function (see Note [12]).

# 9. Integral Form

The collision operator J acting on the ion distribution function f(c) has the basic definition

$$J(f) = \int \{ f(c) f_0(c_0) - f(c') f_0(c'_0) \} g \,\sigma(g, \chi) \,\mathrm{d}\hat{g}' \,\mathrm{d}c_0 \,, \tag{60}$$

where the explanation of the integral is the usual one. It is sometimes convenient (cf. Section 5, equation 43) to write

$$J(f) = v(c) f(c) - K(f),$$
 (61a)

with

$$v(\boldsymbol{c}) \equiv \int f_0(\boldsymbol{c}_0) g \,\sigma(g,\chi) \,\mathrm{d}\hat{\boldsymbol{g}}' \,\mathrm{d}\boldsymbol{c}_0 \,, \tag{61b}$$

$$K(f) \equiv \int f(\boldsymbol{c}') f_0(\boldsymbol{c}'_0) g \,\sigma(g,\chi) \,\mathrm{d}\hat{\boldsymbol{g}}' \,\mathrm{d}\boldsymbol{c}_0 \,, \tag{61c}$$

where v(c) is the so-called collision frequency. To make v and K well defined, in the case of classical scattering some cutoff has to be prescribed.

The operator J defined above takes a function f(c) into another function, say,  $\overline{f}(c)$ ,  $J: f \to \overline{f}(c) \equiv J(f)$  and depends on the gas distribution  $f_0(c_0)$ . It is therefore an operator functional of  $f_0(c_0)$ . We indicate this by

$$J(f) \equiv J([f_0]; f). \tag{62}$$

From the definition (60) it is seen that this can be written as a convolution

$$J([f_0]; f) = \int f_0(V) J([\delta(c_0 - V)]; f) \, \mathrm{d}V.$$
(63)

The operator on the right-hand side will be called the moving cold gas operator. From this we can calculate the collision operator for any neutral gas distribution by using equation (63).

Since c is a constant vector inside the integral (60) we can replace  $dc_0$  by dg and express the arguments of the distributions inside the integral in terms of c, g and g':

$$c_0 = c - g;$$
  $c' = c - \mu_0 (g - g');$   $c'_0 = c - \mu g - \mu_0 g',$  (64)

with  $\mu_0 = m_0/(m+m_0)$  and  $\mu = m/(m+m_0)$ , as before.

Let T be the translation operator, defined by

$$Tf(c) = f(c+V), Tf_0 = f(c_0+V);$$
 (65)

then from equations (60) and (62)

$$TJ([f_0]; f) = J([Tf_0]; Tf),$$
 (66a)

or

$$J([T^{-1}f_0]; f) = T^{-1}J([f_0]; Tf)$$
(66b)

This is a fundamental relation between the collision operators corresponding to different gas distribution functions related by translation. In particular, we have the relation between the operators for moving and stationary cold gas distribution functions:

$$J([\delta(c_0 - V)]; f) = T^{-1}J([\delta(c_0)]; Tf).$$
(67)

The adjoint  $\tilde{X}$  of any operator X is defined by

$$\int \varphi X(f) \, \mathrm{d}\boldsymbol{c} = \int f \, \widetilde{X}(\varphi) \, \mathrm{d}\boldsymbol{c} \,. \tag{68}$$

Hence from equation (60)

$$\tilde{J}(\varphi) = \int f_0(\boldsymbol{c}_0) \left\{ \varphi(\boldsymbol{c}) - \varphi(\boldsymbol{c}') \right\} g \,\sigma(g,\chi) \,\mathrm{d}\hat{\boldsymbol{g}}' \,\mathrm{d}\boldsymbol{c}_0 \,. \tag{69}$$

In addition, since  $\tilde{T} = T^{-1}$  equation (67) gives

$$\tilde{J}([\delta(\boldsymbol{c}_0 - \boldsymbol{V})]; \boldsymbol{\varphi}) = T^{-1} \tilde{J}([\delta(\boldsymbol{c}_0)]; T\boldsymbol{\varphi}).$$
<sup>(70)</sup>

This is a consequence of the following relation, easily derived from the definition (68),

$$[XYZ]^{\sim} = \tilde{Z}\tilde{Y}\tilde{X}, \qquad (71)$$

where, for longer expressions, we use the notation  $[A]^{\sim} \equiv \tilde{A}$ .

# 10. Differential Forms: Fokker-Planck Expansion

The usual form of the Fokker-Planck expansion is

$$J(f) = \sum_{n} \left( \partial/\partial c \right)^{n} \odot \left( \mathbf{A}^{n}(c) f(c) \right), \tag{72}$$

where  $\mathbf{A}^n(\mathbf{c})$  are tensors of *n*th order, the symbol  $\odot$  indicates an *n*th order scalar product and  $(\partial/\partial \mathbf{c})^n$  is a product of *n* operators  $\partial/\partial c_i$ , i = 1, 2, 3. To make it explicit one must supply *n* indices on the tensors and take account of the combinatorial problems that arise.

If the tensors are regrouped so as to transform like the spherical harmonics, the expansion (72) takes the form

$$J(f) = \sum_{nlm} \mu_0^{2n+l} \mathbb{Z}_m^{[nl]} (\Psi_m^{(nl)}(c) f(c)),$$
(73)

where the mass dependence coming from the velocity change has been made explicit;  $\mathbb{Z}$  is the tensor differential operator independent of interactions, defined in Appendix 2*a* (see also Appendix 3, p. 447); and the  $\Psi$  are tensor functions which contain all the information about the gas distribution and cross sections. The  $\Psi$ may also depend on other vectors (besides *c*) if they occur in the problem, for instance, through an anisotropic  $f_0$ . Thus

$$\Psi_m^{(nl)}(\boldsymbol{c}) \equiv \Psi_m^{(nl)}([f_0]; \boldsymbol{c}).$$
(74)

These tensors for arbitrary gas distribution may be expressed in terms of the corresponding quantities for the cold gas. We are then able to give compact expressions for these quantities to any order.

If  ${}^{\circ}\Psi_{m}^{(nl)}$  are the tensors for stationary cold gas then

$${}^{\circ}\Psi_{m}^{(nl)}(c) \equiv \Psi_{m}^{(nl)}([\delta(c_{0})]; c) = Y_{m}^{(l)}(\hat{c}) {}^{\circ}\Psi_{nl}(c).$$
<sup>(75)</sup>

This relation follows since c is the only vector in the problem. Explicit expressions for  ${}^{\circ}\Psi_{nl}(c)$  in terms of cross sections are derived in Appendix 2a.

Charged Particles in Neutral Gases

Applying the relations (67)–(73) and noting that  $\mathbb{Z}$  commutes with T, we have

$$\Psi_m^{(nl)}([\delta(\boldsymbol{c}_0 - \boldsymbol{V})]; \boldsymbol{c}) = T^{-1} \circ \Psi_m^{(nl)}(\boldsymbol{c}) = {}^{\circ} \Psi_m^{(nl)}(\boldsymbol{c} - \boldsymbol{V}).$$
(76)

With equation (63) this gives, for an arbitrary gas distribution,

$$\Psi_m^{(nl)}([f_0]; c) = \int f_0(V) T^{-1} \circ \Psi_m^{(nl)}(c) \, \mathrm{d}V.$$
(77)

It follows that when  $f_0$  is isotropic

$$\Psi_m^{(nl)}([f_0]; c) = Y_m^{(l)}(\hat{c}) \Psi_{nl}([f_0]; c).$$
(78)

In particular for a Maxwellian gas distribution (setting the number density  $n_0$  equal to unity for the present) we have

$$f_0(V) \equiv w_0(V) = (\alpha_0^2/2\pi)^{3/2} \exp(-\frac{1}{2}\alpha_0^2 V^2), \qquad \alpha_0^2 = m_0/kT_0,$$
 (79a)

$$\int f_0(V) \exp(-V. \partial_c) \,\mathrm{d}V = \exp(-\frac{1}{2}\alpha_0^{-2} \nabla_c^2), \qquad (79b)$$

$$\Psi_{nl}([w_0]; c) = \exp(-\frac{1}{2}\alpha_0^{-2} \nabla_l^2) \circ \Psi_{nl}(c).$$
(79c)

Here  $\nabla_c^2$  is the Laplacian and

$$\nabla_l^2 = \frac{1}{c^2} \frac{d}{dc} c^2 \frac{d}{dc} - \frac{l(l+1)}{c^2} .$$
(80)

If we substitute equation (78) into (73) then the sum over m indices can be carried out directly and we have for isotropic gas distributions

$$J(f) = \sum_{n,l=0}^{\infty} \mu_0^{2n+l} S^{nl} (\Psi_{nl}(c) f(c)),$$
(81)

where

$$S^{nl} = \frac{2l+1}{4\pi} \overline{N}_{nl}^2 \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} \nabla_c^{2(n+r)} \left(\frac{\mathrm{d}}{\mathrm{d}c} + \frac{2}{c}\right)^{l-2r},$$
(82a)

$$a_{rl} = 2^{-l} (-)^r {l \choose r} {2l-2r \choose l}, \qquad \overline{N}_{nl}^2 = 2\pi^{3/2} / n! \, \Gamma(n+l+\frac{3}{2}), \tag{82b}$$

and  $\left[\frac{1}{2}l\right]$  is the largest integer less than or equal to  $\frac{1}{2}l$ . The adjoint operator is given by

$$\tilde{J}(\phi) = \sum_{n,l=0}^{\infty} \mu_0^{2n+l} \Psi_{nl}(c) \, \tilde{S}^{nl}(\phi) \,, \tag{83}$$

where

$$\tilde{S}^{nl} = (-)^l \, \frac{2l+1}{4\pi} \, \overline{N}_{nl}^2 \sum_{r=0}^{\lfloor \frac{1}{2} l \rfloor} \, a_{rl} \left(\frac{\mathrm{d}}{\mathrm{d}c}\right)^{l-2r} \, \nabla_c^{2(n+r)} \,. \tag{84}$$

It is shown in Appendix 2a that the stationary cold gas functions  ${}^{\circ}\Psi_{nl}$  are given by

$${}^{\circ}\Psi_{nl}(c) = c^{2n+l+1} \sum_{\lambda=0}^{n+l} \sigma^{(\lambda)}(c) a_{nl}^{\lambda}, \qquad (85a)$$

where

$$a_{nl}^{\lambda} = \frac{1}{2}(2\lambda + 1) \int_{-1}^{+1} y^{2n+l} P_l(y) P_{\lambda}(x) dx; \qquad y = \{\frac{1}{2}(1-x)\}^{\frac{1}{2}}.$$
 (85b)

The coefficients  $a_{nl}^{\lambda}$  are pure numbers and the  $\sigma^{(\lambda)}(c)$  were defined in equation (59). Some properties and special values of the coefficients  $a_{nl}^{\lambda}$  are given in Appendix 2b. In particular it may be noted here that

$$a_{nl}^{\lambda} = 0$$
 for  $\lambda > n+l$ , (86)

so that the upper limit in the sum in equation (85a) need not be written down; it is automatically enforced by the properties of  $a_{nl}^{\lambda}$ . Further, from equations (85b) we have  $a_{00}^{\lambda} = \delta_{0\lambda}$  so that

$$\Psi_{00}(c) \equiv 0. \tag{87}$$

Equations (81) and (82) give complete Fokker-Planck expansions of the collision operator and its adjoint for isotropic gas distributions. The functions  $\Psi_{nl}$  for a Maxwellian gas are given by equations (79c) and (85a). For other isotropic distributions these are to be calculated from equations (77), (78) and (85a). In Table 1 we give explicit expressions for the adjoint collision operator for a stationary cold gas to fourth order (see also Appendices 2a and 2b).

In the above formulae the dependence of the operator on the parameters of the problem is explicitly seen. The mass-ratio dependence appears entirely through the factor  $\mu_0^{2n+1}$  and verifies the usual statement that the Fokker-Planck expansion is appropriate for the case of heavy ions  $m > m_0$  or  $\mu_0 < \frac{1}{2}$ .

An important feature of the formulae (83) and (84) for  $\tilde{J}$  is that  $\tilde{S}^{nl}$  is a homogeneous differential operator of degree (2n+l). It therefore annihilates all polynomials in c of degree less than (2n+l). To calculate the moment

$$\int \phi(\mathbf{c}) J(f(\mathbf{c})) d\mathbf{c} = \int f(\mathbf{c}) \tilde{J}(\phi(\mathbf{c})) d\mathbf{c}$$
(88)

with a polynomial of degree N in vector c, it is necessary to take only those terms in equations (81) or (83) for which  $(2n+l) \leq N$ . Higher terms in these expansions make no contribution to this moment. The highest  $\sigma^{(\lambda)}$  that can occur in this calculation corresponds to  $\lambda = N$ .

Finally, we note a property of the adjoint operator that is useful in the calculations of transverse diffusion coefficient. It may be verified from equations (83) and (84) that

$$\tilde{J}(\boldsymbol{c}\,\phi(\boldsymbol{c})) = \boldsymbol{c}\,\tilde{J}(\phi) + \tilde{K}(\phi)\,,\tag{89}$$

where  $K(\phi)$  is an isotropic operator given by

$$\tilde{K}(\phi) = \sum_{n,l=0}^{\infty} \mu_0^{2n+l} \Psi_{nl}(c) \tilde{S}_1^{nl}(\phi), \qquad (90a)$$

$$\widetilde{S}_{1}^{nl} = \frac{2l+1}{4\pi} \overline{N}_{nl}^{2}(-)^{l} \sum_{r=0}^{\lfloor \frac{1}{2}l \rfloor} a_{rl} \frac{l-2r}{c} \left(\frac{\mathrm{d}}{\mathrm{d}c}\right)^{l-2r-1} \nabla_{c}^{2(n+r)}.$$
(90b)

The similarities between  $\tilde{J}$  and  $\tilde{K}$  are evident. There is a similar relation for the operator J but the adjoint of K does not enter in it. In fact,

$$\tilde{J}(\boldsymbol{c}\,\phi) = \boldsymbol{c}\,\tilde{L}_1(\phi) \quad \text{implies} \quad L_1(\boldsymbol{c}\,f) = \boldsymbol{c}\,J(f)$$
(91a)

and

$$J(cf) = cL_2(f) \quad \text{implies} \quad \tilde{L}_2(c\phi) = c\tilde{J}(\phi). \tag{91b}$$

2n+l	n	l	λ	$a_{nl}^{\lambda}$	Function ${}^{\circ}\Psi_{ni}$	Operator <sup>A</sup> $\tilde{S}^{nl}$
0	0	0	0	1	0	
1	0	1	0 1	$-\frac{\frac{1}{2}}{\frac{1}{2}}$	$-\frac{1}{2}c^2\sigma^{(1)}$	$-2D_c$
2	1	0	0 1	$\frac{\frac{1}{2}}{-\frac{1}{2}}$	$-\frac{1}{2}c^{3}\sigma^{(1)}$	$\frac{2}{3}\nabla_c^2$
2	0	2	0 1 2	$\frac{\frac{1}{4}}{-\frac{1}{2}}$ $\frac{\frac{1}{4}}{\frac{1}{4}}$	$-\frac{1}{2}c^{3}\sigma^{(1)}+\frac{1}{4}c^{3}\sigma^{(2)}$	$2D_c^2 - \frac{2}{3}\nabla_c^2$
3	1	1	0 1 2	$-\frac{1}{3}$ $-\frac{1}{2}$ $\frac{1}{6}$	$c^4(-rac{1}{2}\sigma^{(1)}+rac{1}{6}\sigma^{(2)})$	$-\frac{4}{5}\mathrm{D}_{c}\nabla_{c}^{2}$
3	0	3	0 1 2 3	$-\frac{\frac{1}{8}}{\frac{3}{8}}$ $-\frac{1}{8}$	$c^4(-\frac{3}{8}\sigma^{(1)}+\frac{3}{8}\sigma^{(2)}-\frac{1}{8}\sigma^{(3)})$	$-\frac{4}{3}D_c^3+\frac{4}{5}D_c\nabla_c^2$
4	2	0	0 1 2	$\frac{\frac{1}{3}}{-\frac{1}{2}}$ $\frac{\frac{1}{6}}{\frac{1}{6}}$	$c^{5}(-\frac{1}{2}\sigma^{(1)}+\frac{1}{6}\sigma^{(2)})$	$\frac{2}{15}\nabla_c^4$
4	1	2	0 1 2 3	$-\frac{5}{24}$ $-\frac{17}{40}$ $\frac{7}{24}$ $-\frac{3}{40}$	$c^{5}(-\frac{17}{40}\sigma^{(1)}+\frac{7}{24}\sigma^{(2)}-\frac{3}{40}\sigma^{(3)})$	$\frac{4}{7}\mathrm{D}_c^2\nabla_c^2-\frac{4}{21}\nabla_c^4$
4	0	4	0 1 2 3 4	$ \frac{1}{16} -\frac{1}{4} -\frac{1}{4} -\frac{1}{4} -\frac{1}{16} $	$c^{5}(-\frac{1}{4}\sigma^{(1)}+\frac{3}{8}\sigma^{(2)}-\frac{1}{4}\sigma^{(3)}+\frac{1}{16}\sigma^{(4)})$	$\frac{2}{3}D_{c}^{4} - \frac{4}{7}D_{c}^{2}\nabla_{c}^{2} + \frac{2}{35}\nabla_{c}^{4}$

 Table 1. Adjoint collision operator to fourth order for stationary cold gas

 (See equation 84)

<sup>A</sup> In this table we have used the abbreviations  $D_c \equiv d/dc$ ,  $D_c^2 \equiv d^2/dc^2$  etc.

The operators  $\tilde{L}_1$  and  $L_2$  are obtained by making small modifications in the operators  $\tilde{J}$  and J; namely, to get  $\tilde{L}_1$  from  $\tilde{J}$  replace (d/dc) by (d/dc+1) in the expression for  $\tilde{S}^{nl}$  and use equations (83) and (84); to obtain  $L_2$  from J replace (d/dc+2/c) by (d/dc+3/c) in the expression for  $S^{nl}$  and use (81) and (82a) (see also Section 16a).

# 11. Differential Forms: Spherical Harmonic Decomposition

The action of the collision operator on irreducible tensors of the form

$$f_m^{(l)}(c) = Y_m^{(l)}(\hat{c}) f(c)$$
(92)

can be expressed in terms of certain scalar operators  $J_l$  or  $J(n_1 l_1 l_2 l|.)$ , which act only on the scalar function f(c). These expressions are called the spherical harmonic

decomposition of the collision operator. In this section we give complete expressions for these decompositions for an arbitrary gas distribution function, as well as for special cases which are important in applications. It should be noted that the f(c) here are not the ion distribution functions but functions which may occur in the spherical harmonic expansion of them.

It is known that the spherical harmonic decomposition of the collision operator is diagonal when the gas distribution is isotropic, as for instance in the case of a stationary cold gas or a Maxwellian gas. In these cases we have

$$J(f_m^{(l)}(c)) = Y_m^{(l)}(\hat{c}) J_l(f).$$
(93)

This equation may be taken as a definition of the scalar operator  $J_l(f)$ , which is called a spherical component of J of rank l.

The spherical components in the case of a Maxwellian gas are related to those of the stationary cold gas, but the relationship is not very direct. In fact, to find this relationship one has to go through the case of a moving cold gas. It will be seen that it is then no more difficult to treat the most general case.

The collision operator for the moving cold gas is not diagonal in the above sense. The spherical symmetry is broken by the motion of gas, as explicitly shown by the presence of the translation operator T in equation (67). Since there is only one other vector, namely V, involved in the problem, the tensor decomposition is conveniently described in terms of the composite irreducible tensors

$$Y_{m}^{l_{1}l_{2}(l)} \equiv \sum_{m_{1}m_{2}} \left( l_{1} m_{1} l_{2} m_{2} | lm \right) Y_{m_{1}}^{(l_{1})}(\hat{V}) Y_{m_{2}}^{(l_{1})}(\hat{c}),$$
(94)

where the  $(l_1 m_1 l_2 m_2 | lm)$  are the Wigner coefficients.

We write

$$J\left(\left[\delta(\boldsymbol{c}_{0}-\boldsymbol{V})\right]; f_{m}^{(l)}(\boldsymbol{c})\right) = \sum_{n_{1}l_{1}l_{2}} \left(4\pi\right)^{\frac{1}{2}} \boldsymbol{V}^{2n_{1}+l_{1}} Y_{m}^{l_{1}l_{2}(l)} J\left(n_{1} l_{1} l_{2} l \mid f\right).$$
(95)

This equation defines the scalar operators  $J(n_1 l_1 l_2 l|.)$ . They are taken to be independent of the vector V and therefore depend only on the cross sections and the masses, there being no other parameter in the problem. The convenience of having these operators is seen in that the tensor decomposition of any gas distribution can be expressed in terms of these operators. Thus using the relation (63) and the definition

$$\langle V^{2n_1+l_1} Y^{(l_1)}_{m_1}(\hat{V}) \rangle = \int f_0(V) V^{2n_1+l_1} Y^{(l_1)}_{m_1}(\hat{V}) \,\mathrm{d}V,$$
 (96)

equations (94) and (95) give

$$J([f_0]; f_m^{(l)}(\mathbf{c})) = \sum_{n_1 l_1 l_2 m_1 m_2} (4\pi)^{\frac{1}{2}} (l_1 m_1 l_2 m_2 | lm) \\ \times \langle V^{2n_1 + l_1} Y_{m_1}^{(l_1)}(\mathbf{V}) \rangle Y_{m_2}^{(l_2)}(\hat{\mathbf{c}}) J(n_1 l_1 l_2 l | f).$$
(97)

The case of isotropic, i.e. spherically symmetric, gas distributions is particularly important in applications. Fortunately it is also particularly simple in as much as the averages (96) vanish for  $l_1 \neq 0$ . It is convenient to introduce new symbols for the operators in this case. We set

$$J_l^n(f) \equiv J(n0ll|f). \tag{98}$$

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For the Maxwellian gas (equations 79) we have

$$\langle V^{2n_1+l_1} \mathbf{Y}_{m_1}^{(l_1)}(\vec{V}) \rangle = \delta_{l_10} \,\delta_{m_10} (4\pi)^{-\frac{1}{2}} (2n_1+1)!! (kT_0/m_0)^{n_1}.$$
(99)

From equations (97) and (98) ( $f_0 \equiv w_0$ ; equation 79a),

$$J([w_0]; f_m^{(l)}) = Y_m^{(l)}(\hat{c}) J_l([w_0]; f), \qquad (100a)$$

$$J_l([w_0]; f) = \sum_{n=0}^{\infty} (2n+1)!! (kT_0/m_0)^n J_l^n(f).$$
 (100b)

The dependence of the collision operator on the parameter  $(kT_0/m_0)$  coming from the Maxwellian distribution is made explicit in this equation. The operators  $J_l^n$  do not depend on the gas distribution but only on the cross sections and masses.

The stationary cold gas corresponds to the limit  $T_0 \rightarrow 0$ , and hence to the first term in equation (100b)

$$J([\delta(c_0)]; f_m^{(l)}(c)) = Y_m^{(l)}(\hat{c}) J_l^0(f).$$
(101)

Now we come to a most important result: we show that all the scalar operators  $J(n_1 l_1 l_2 l|)$  needed for the general problem may be expressed in terms of the operators  $J_l^0$  which occur in the spherical harmonic decomposition (101) for the stationary cold gas case.

For this purpose we need the tensor decomposition of the translation operator, similar to equation (95) (see Appendix 3):

$$T(f_m^{(l)}) = \sum_{n_1 l_1 l_2} (4\pi)^{\frac{1}{2}} V^{2n_1 + l_1} Y_m^{l_1 l_2(l)} T(n_1 l_1 l_2 l | f),$$
(102)

where the scalar operators  $T(n_1 l_1 l_2 l|.)$  depend only on c. They are kinematic operators needing no reference to the dynamics of collisions or distribution functions. The tensor decomposition of  $T^{-1}$  may be obtained from equation (102) by replacing V by -V.

We define the adjoint  $\tilde{A}$  of a scalar operator A by means of the relation

$$\int \phi(c) \left( A f(c) \right) c^2 dc = \int \left( \widetilde{A} \phi(c) \right) f(c) c^2 dc, \qquad (103)$$

and note that

$$\hat{l}T(n_1 l_1 l_2 l|f) = (-)^{l_1} \hat{l}_2 \tilde{T}(n_1 l_1 ll_2 |f),$$
(104)

with  $\hat{l} = (2l+1)^{\frac{1}{2}}$ . Using these relations in equations (67) and (95) one can show that

$$J(n_{1} l_{1} l_{2} l | f) = \sum_{n_{1}' l_{1}' l_{2}' n_{1}'' l_{1}''} \delta(2n_{1} + l_{1} - (2n'_{1} + l'_{1} + 2n''_{1} + l''_{1})) \\ \times (-)^{\frac{1}{2}(l_{1}' + l_{1}'' - l_{1})} (l'_{1} 0 l''_{1} 0 | l_{1} 0) \hat{l}'_{1} \hat{l}''_{1} \hat{l}_{2} \overline{W} \begin{pmatrix} l_{1} l_{2} l \\ l'_{2} l'_{1} l''_{1} \end{pmatrix} \\ \times \overline{T} \Big( n''_{1} l''_{1} l'_{2} l_{2} | J^{0}_{l_{2}'} (T(n'_{1} l'_{1} l'_{2} l | f)) \Big).$$
(105)

The Wigner coefficient  $(l'_1 0 l''_1 0 | l_1 0)$  and the Racah coefficient  $\overline{W}$  in (105) arise from the recoupling of tensors. The sum on the right-hand side goes over all positive

integral values, and zero, of the indices as allowed by the  $\delta$  functions and the restrictions on the *l*'s implicit in the Racah and Wigner coefficients. It is a sum over a finite number of terms. Specifically, the  $\delta$  function implies that

$$(2n'_1, 2n''_1, l'_1, l''_1) \le (2n_1 + l_1) \tag{106}$$

and the Wigner and Racah coefficients imply that

$$l'_1 + l''_1 + l_1$$
 even, (107a)

$$|l_1'' - l_2| \le l_2' \le (l_1'' + l_2); \qquad |l - l_1'| \le l_2' \le (l + l_1'), \tag{107b}$$

where the more restrictive conditions take precedence. Further, from the properties of the T operators,  $l''_1 + l'_2 + l_2$  and  $l'_1 + l'_2 + l$  are even; together with the relations (107) this implies that  $l_1 + l_2 + l$  is even. That is to say, the operator defined by equation (105) vanishes identically if  $l_1 + l_2 + l$  is odd.

When  $l_1 = 0$ , the expression (105) simplifies and we have

$$J_{l}^{n}(f) \equiv J(n \, 0 \, l \, l \mid f)$$
  
=  $\sum_{n_{1}' l_{1}' n_{1}'' l_{2}'} \delta(n - (n_{1}' + n_{1}'' + l_{1}')) \tilde{T}(n_{1}' \, l_{1}' \, l_{2}' \, l \mid J_{l_{2}'}^{0}(T(n_{1}'' \, l_{1}' \, l_{2}' \, l \mid f))).$  (108)

We note that the sum is symmetric in  $n'_1$  and  $n''_1$  and the sum over  $l'_2$  is restricted to those values for which

$$l'_1 + l'_2 + l$$
 even and  $|l'_1 - l| \le l'_2 \le (l'_1 + l)$ . (109)

The meaning of operations on the right-hand side of equations (105) and (108) is that the function f is operated upon in succession by the three operators T,  $J_i^0$  and  $\tilde{T}$ . As an example of working with these formulae, note that in equation (108) if n = 0then  $n'_1 = n''_1 = l'_1 = 0$  and we have an identity since

$$T(00l_2l|f) = \delta_{l_2l}f.$$
 (110)

For n = 1 there are three possible sets of indices  $(n'_1 n''_1 l'_1)$ , namely (100), (010) and (001). Correspondingly equation (108) gives

$$J_{l}^{1}(f) = \tilde{T}\left(10ll|J_{l}^{0}(T(00ll|f))\right) + \tilde{T}\left(00ll|J_{l}^{0}(T(10ll|f))\right) + \tilde{T}\left(01l-1l|J_{l-1}^{0}(T(01l-1l|f))\right) + \tilde{T}\left(01l+1l|J_{l+1}^{0}(T(01l+1l|f))\right). \quad (111)$$

Using the expressions for the relevant T operators given in Appendix 3, we find

$$J_{l}^{1}(f) = \frac{1}{6} \left[ \nabla_{l}^{2} J_{l}^{0}(f) + J_{l}^{0}(\nabla_{l}^{2} f) - \frac{2l+2}{2l+1} \left\{ \left( \frac{d}{dc} + \frac{l+2}{c} \right) J_{l+1}^{0} \left( \frac{d}{dc} - \frac{l}{c} \right) f \right\} - \frac{2l}{2l+1} \left\{ \left( \frac{d}{dc} - \frac{l-1}{c} \right) J_{l-1}^{0} \left( \frac{d}{dc} + \frac{l+1}{c} \right) f \right\} \right].$$
(112)

This is the first-order temperature contribution for the Maxwellian gas as given by equation (100b), expressed in terms of the stationary cold gas operators  $J_l^0$ .
We now give the expressions for the stationary cold gas operators as derived in Appendix 2c:

$$J_l^0(f) = c^{-(l+1)} \sum_{n=0}^{\infty} \frac{(2\mu\mu_0)^n}{n!} \left(\frac{\mathrm{d}}{\mathrm{d}(c^2)}\right)^n \left(\Phi_{nl}(c) \, c^{l+1} f(c)\right), \tag{113a}$$

where

$$\Phi_{nl}(c) = c^{2n+1} \sum_{\lambda=0}^{n+l} \sigma^{(\lambda)}(c) b_{nl}^{\lambda}, \qquad (113b)$$

with

$$b_{nl}^{\lambda} = \frac{1}{2}(2\lambda+1)\int_{-1}^{+1} (1-x)^n \eta^l \mathbf{P}_l(\xi/\eta) \mathbf{P}_{\lambda}(x) \,\mathrm{d}x\,, \qquad (113c)$$

$$\xi = \mu + \mu_0 x, \qquad \eta^2 = \mu_0^2 + \mu^2 + 2\mu \mu_0 x.$$
 (113d)

The coefficients  $b_{nl}^{\lambda}$  depend on the masses. Their properties are discussed in Appendix 2d. It may be inferred from equations (113c) and (113d) that

$$b_{nl}^{\lambda} = 0, \qquad \lambda > n+l; \qquad (114a)$$

$$b_{0l}^{\lambda} = \delta_{\lambda l}, \qquad \mu \to 0,$$
 (114b)

$$=\delta_{\lambda 0}\,,\qquad \mu_0 \to 0\,. \tag{114c}$$

From equation (113a), for the two extreme limits we have

$$J_l^0(f) = c \,\sigma^{(l)}(c) f, \qquad \mu \to 0;$$
 (115a)

$$= 0, \qquad \mu_0 \to 0.$$
 (115b)

The spherically symmetric component  $J_0^0(f)$  is distinguished in the limit  $\mu \to 0$  since we have  $J_0^0 \equiv 0$  but  $J_l^0 \neq 0$  for  $l \neq 0$ . The components of the distribution function for  $l \neq 0$  thus decay in time and the distribution is dominated by its spherical component l = 0. The spherical harmonic expansion is suitable in this limit, that is, for electrons and light ions, since it leads to a separation of this distinguishing feature. Further distinction between  $l \neq 0$  components can only come from the cross sections and the structure of the equations in which these operators are to be used.

In the opposite limit  $\mu_0 \rightarrow 0$  no spherical component is distinguished and this is reflected in the fact that for heavy ions the spherical harmonic expansion has not been used with the same effectiveness.

However, smallness arguments of the above extreme form cannot be decisive in choosing a form of expansion. In precise calculations where many contributions have to be taken into account, the decisive requirement is that the formulae allow clear and efficient management of the terms. The present development is directed at this aspect of the problem.

We turn to the calculation of moments of these operators. The moments are defined by integrals like (103) where A is a  $J_l$  operator and  $\phi$  is a polynomial in c. The adjoint operators are of importance in this connection. If A and  $\tilde{A}$  are related by equation (103) and A is of the form

$$A(f) = (d/d(c^2))^n f,$$
 (116a)

then

$$\tilde{A}(\phi) = (-)^n c^{-1} \left( d/d(c^2) \right)^n c \phi \,. \tag{116b}$$

Consequently, from equation (113a)

$$\tilde{J}_{l}^{0}(\phi) = c^{l} \sum_{n=0}^{\infty} \frac{(-2\mu\mu_{0})^{n}}{n!} \Phi_{nl}(c) \left(\frac{d}{d(c^{2})}\right)^{n} \left(c^{-l} \phi(c)\right).$$
(117)

It is seen that for  $\phi(c)$  of the form

$$\phi(c) = c^l \phi_N(c^2), \qquad (118)$$

where  $\phi_N$  is a polynomial of degree N in  $c^2$ , one needs only terms up to n = N to calculate the moment exactly (see Appendix 3). The higher terms make no contribution to the moment of this polynomial.

The factor  $\mu\mu_0$  is a measure of relative change in the energy of an ion in collision with a stationary gas atom. The expansions (113a) and (117) thus bring out the importance of the energy change in the determination of spherical components. When the relative energy change is small a good representation of the collision operator is obtained from only a few terms in these expansions.

Since equation (108) is symmetric in  $n'_1$  and  $n''_1$  we have

$$\widetilde{J}_{l}^{n}(\phi) = \sum_{n_{1}'n_{1}''l_{1}'l_{2}'} \delta\left(n - (n_{1}' + n_{1}'' + l_{1}')\right) \widetilde{T}\left(n_{1}' l_{1}' l_{2}' l | J_{l_{2}'}^{0}\left(T(n_{1}'' l_{1}' l_{2}' l | \phi)\right)\right).$$
(119)

Now it is a property of the T operators that

$$T(n_1 l_1 l_2 l | c^l \phi_N(c^2)) = c^{l_2} \overline{\phi}_{N'}(c^2), \qquad N' \leq N,$$
(120)

where  $\overline{\phi}_{N'}$  is a polynomial in  $c^2$  of degree N'. From this it follows that in calculation of moments with  $\phi$  given by equation (118), the expansions (117) of all operators occurring in (119) need be carried only to n = N. This is an important property, which also holds for the operators  $\tilde{J}(n_1 l_1 l_2 l | .)$ , the proof being essentially the same.

To summarize this section: The simplest case is that of the stationary cold gas. The spherical harmonic decomposition of its collision operator is diagonal. The spherical components are the scalar operators  $J_l^0$  given by the equations (113) and derived in Appendix 2c. The tensor decomposition for the general gas distribution is given by equation (97) in terms of the scalar operators  $J(n_1 l_1 l_2 l_1)$ . These operators are constructed in terms of the cold gas operators  $J_l^0$  and the scalar kinematic operators  $T(n_1 l_1 l_2 l_1)$  by equation (105). Expressions for the T operators are given in Appendix 3. For a spherically symmetric gas distribution the decomposition is diagonal in l and expressed in terms of simpler operators  $J_l^n$  given by equation (108). A more detailed expression for  $J_l^1$  is given by equation (112). For the Maxwellian gas, the decomposition in terms of  $J_l^n$  is an expansion in powers of the parameter  $(kT_0/m_0)$  (equation 100b). The adjoints of scalar operators are defined by equation (103),  $\tilde{T}$  by (104),  $\tilde{J}_l^0$  by (117) and  $\tilde{J}_l^n$  by (119). The role of these expansions in the calculation of moments is noted following equation (118).

#### **12.** Matrix Forms: Properties and Principles

In matrix form an operator can have different *representations*, depending upon the choice of basic vectors. The matrix elements in different representations are different

and depend on parameters related to the particular representation chosen, in addition to the intrinsic parameters displayed in the integral and differential forms of the operator given in the previous sections. Here we discuss general properties of these representations, the connection between representations and some further points related to the actual calculations of the matrix elements. Several different representations have already been used in this problem. We give references to the original papers where the specific formulae for the matrix elements can be found.

#### (a) Representations and polynomial systems

The moments of the function W(c) are integrals of the form

$$\int \boldsymbol{c} \, \boldsymbol{c} \dots \, \boldsymbol{c} \, W(\boldsymbol{c}) \, \mathrm{d} \boldsymbol{c} \,. \tag{121}$$

If W(c) is such that all its moments exist, then it is possible to construct a set of polynomials  $p_n(c)$  such that

$$\int p_n^*(c) p_{n'}(c) W(c) dc = \delta_{nn'}, \qquad (122)$$

where the asterisk denotes complex conjugation and the right-hand side is a Kronecker delta. The polynomials  $p_n(c)$  are obtained from the moments (121). They depend on the function W(c) and thus on the parameters that may occur in it. The function W(c) is called the weight function, and the polynomials are said to be orthogonal with respect to this weight function in view of equation (122). This relation also fixes the normalization of the polynomials.

In one dimension a given weight function and normalization fixes the polynomial system uniquely but this is not the case in three dimensions. Thus, corresponding to a gaussian weight function we may take the polynomials as products of three Hermite polynomials in cartesian coordinates, or as Burnett functions in spherical polar coordinates or as other polynomials appropriate in cylindrical coordinates. Further, the index n on the polynomials is a composite index. Usually there are three independent indices and the numbering of polynomials requires a convention. If all three indices are shown, the delta function on the right of equation (122) is correspondingly modified.

A function f(c) of c may be expanded in a set of polynomials  $\{p_n\}$  in various ways. If we take the form

$$f(\mathbf{c}) = W(\mathbf{c}) \sum_{n} p_{n}(\mathbf{c}) f_{n}, \qquad (123)$$

the numbers  $f_n$  are obtained from equation (122) as

$$f_n = \int p_n^*(\boldsymbol{c}) f(\boldsymbol{c}) \, \mathrm{d}\boldsymbol{c} \,. \tag{124}$$

These numbers, called expansion coefficients of f(c), are linear combinations of the moments of the function f(c). The expansion (123) involves some assumptions about the function f(c), the most obvious of which is that its moments should exist. However, we do not go into this aspect of the problem but proceed formally as is usual in kinetic theory.

The function J(f), generated by the operator J acting on f(c), may be expanded similarly. The corresponding expansion coefficients are given by the integrals

$$\int p_n^*(c) J(f) \,\mathrm{d}c \,. \tag{125}$$

The moment equations of kinetic theory are obtained in terms of such integrals. These integrals may be expressed as linear combinations of the moments of f(c) or  $f_n$  if we use the expansion (123). We then have the matrix elements of the operator J given by

$$J_{nn'} = \int p_n^*(c) J(W(c) p_{n'}(c)) dc.$$
 (126)

The matrix elements so defined depend on the polynomial system  $\{p_n\}$ . One speaks then of a representation of the operator in the basis  $\{p_n\}$ , or just  $\{p_n\}$  representation. The matrix elements depend on the parameters and the weight function W(c). For a given weight function there can be different representations depending on the polynomial system chosen. The form of the matrix depends on the convention chosen to enumerate the basic polynomials. The matrix elements define the connection between the expansion coefficients of the two functions f and J(f), given by equations (124) and (126), and thus depend on the assumptions implicit in the expansion (123).

Using the expression (60) for the collision integral in equation (126) and the usual manipulations, we have

$$J_{nn'} = \int f_0(c_0) W(c) p_{n'}^*(c) \left( p_n(c) - p_n(c') \right) d\mathcal{V}, \qquad (127a)$$

where  $d\mathscr{V}$  is defined in equation (A22). The adjoint matrix element is given by

$$(J^{\dagger})_{nn'} = J^{*}_{n'n} = \int f_0(c_0) W(c) p^{*}_n(c) \left( p_{n'}(c) - p_{n'}(c') \right) d\mathscr{V}.$$
(127b)

This may be put in the form

$$J_{n'n}^{*} = \int p_{n'}(c) \left( f_0(c_0) W(c) p_n^{*}(c) - f_0(c'_0) W(c') p_n(c') \right) d\mathscr{V}.$$
(127c)

The right-hand sides of equations (127a) and (127c) are equal if

$$f_0(c_0) W(c) = f_0(c'_0) W(c').$$
(128)

This is the functional equation that occurs in the proof of the H-theorem and has the unique solution that both  $f_0(c_0)$  and W(c) are Maxwellian distributions at the same temperature.

Thus the matrix  $J_{nn'}$  is self-adjoint if W(c), the weight function used in expanding the ion distribution f(c) in equation (123) is a gaussian with the same temperature parameter that occurs in the gas distribution  $f_0(c_0)$ . This defines the so-called onetemperature representations. Note that the one-temperature representations may still differ depending on the choice of polynomial system chosen. It is found that the matrix elements are easiest to calculate and simplest in appearance if Burnett functions are used. If no further qualification is made here, the one-temperature representation will be taken to mean the one-temperature Burnett-function representation.

The self-adjoint property by itself is not essential. It has been found that there are advantages in using representations in which the matrix is not self-adjoint.

#### (b) Connection between different representations

Consider two weight functions  $W_1(c)$  and  $W_2(c)$  and associated polynomial systems  $\{p_{1n}(c)\}\$  and  $\{p_{2n}(c)\}\$ . The polynomials are linearly related,

$$p_{1n}^*(c) = \sum_{\nu} A^{n\nu} p_{2\nu}^*(c).$$
 (129)

Then from the orthogonality relation (122) we have

$$A^{n\nu} = \int p_{1n}^{*}(c) W_{2}(c) p_{2\nu}(c) dc. \qquad (130)$$

This defines the transformation matrix A. If  $d_1(n)$  and  $d_2(v)$  denote the degrees of polynomials  $p_{1n}$  and  $p_{2v}$  respectively, then it is clear that the sum in equation (129) is restricted to such values of v that  $d_2(v) \leq d_1(n)$ . It is therefore a finite sum. In other words, we have the general property of matrix A that

$$A^{nv} = 0$$
 if  $d_2(v) > d_1(n)$ . (131)

Hence the matrix may be arranged in blocks characterized by  $d_1(n)$  and  $d_2(v)$ . In such an arrangement it will be lower block triangular; that is, all elements of the blocks in the upper triangle will vanish.

We also have the relation

$$W_2(c) p_{2\nu}(c) = \sum_n W_1(c) p_{1n}(c) A^{n\nu}.$$
 (132)

In contrast to equation (129), the sum in (132) is, in general, an infinite sum.

The matrix A is invertible,

$$p_{2\nu}^{*}(c) = \sum_{n} (A^{-1})^{\nu n} p_{1n}^{*}(c), \qquad (133a)$$

$$W_1(c) p_{1n}(c) = \sum_{\nu} W_2(c) p_{2\nu}(c) (A^{-1})^{\nu n}, \qquad (133b)$$

and the matrix  $A^{-1}$  is also (block) lower triangular. Using these relations in equation (126) we see that matrices  $J_1$  and  $J_2$  representing the operator J in two representations are related by a similarity transformation

$$J_1 = A J_2 A^{-1}. (134)$$

It should be noted that in view of equation (133b) the matrix multiplication (134) involves an infinite sum.

The property of self-adjointness is not preserved in going from one representation to another unless A is unitary; that is, unless  $A^{-1} = A^{\dagger}$ . This is the case for which transformations between different polynomial systems belong to the same weight function.

#### (i) Mixed Representations

The representations considered above use the members of the same polynomial system in two places in equation (126). These may be called pure or unmixed representations. A mixed representation is defined as

$$J_{\nu n} = \int p_{2\nu}^{*}(c) J(W_{1}(c)p_{1n}(c)) dc. \qquad (135)$$

At least formally, the operator J may be recovered from its matrix representation as follows. Writing

$$J(f) = \int J(\boldsymbol{c}, \boldsymbol{c}') f(\boldsymbol{c}') \, \mathrm{d}\boldsymbol{c}', \qquad (136a)$$

we have

$$J(c,c') = \sum_{\nu,n} W_2(c) p_{2\nu}(c) J_{\nu n} p_{1n}^*(c').$$
(136b)

Pure representations are the ones most commonly used but in certain circumstances the mixed representations may prove more convenient.

#### (c) Choice of polynomial systems: gaussian weight functions

The first requirement on the polynomial system is that it should be possible to calculate readily the matrix elements of the collision operator in it. The collision operator is such a complex entity that this simple requirement limits us to those systems in which the polynomials are orthogonal with respect to a gaussian weight function of the general form

$$\overline{w}(x) = (\alpha^2 / 2\pi)^{3/2} (\det \tau) \exp(-\frac{1}{2} \alpha^2 x^2), \qquad (137a)$$

with

$$\mathbf{x} = \mathbf{\tau} \cdot (\mathbf{c} - \mathbf{W}), \qquad \alpha^2 = m/kT, \qquad (137b)$$

The factor  $\alpha^2$  has been introduced for the sake of convenience. The temperature T is an arbitrary constant not necessarily related to the gas temperature  $T_0$ ,  $\tau$  is a real nonsingular tensor and W is a real vector. The polynomial system thus depends on the parameters  $\alpha$ , W and  $\tau$ .

The reason for the pre-eminence of gaussian weight functions is that the integrations indicated in equations (127a) and (60) can then be carried out; mainly because with such functions it is possible to separate the relative and centre of mass variables.

As discussed in Sections 17, 19 and 20 different choices of polynomial systems are useful in different regions of the parameter values: apart from the masses of ions and gas atoms one also has to consider the gas temperature and cross sections, and above all the strength of the electric field. Although the field strength makes no appearance in the collision integral itself, it has a decisive influence on the ion distribution. Since the matrix elements  $J_{nn'}$  determine the relation between the expansion coefficients of J(f) and f, the choice of representation is influenced by the electric field strength, significantly although indirectly.

Burnett functions  $\phi^{(v')}(x)$  of the vector variable x (Appendix 1) are polynomials orthogonal with respect to the weight function (137a). The normalization is fixed by

$$\int \overline{w}(\mathbf{x}) \,\phi^{(\mathbf{v})}(\mathbf{x}) \,\phi^{(\mathbf{v}')}(\mathbf{x}) \,\mathrm{d}\mathbf{c} = \delta_{vv'} \,\delta_{\mu\mu'} \,\delta_{mm'} \,. \tag{138}$$

The index v stands for the triple (v, l, m).

We now give a summary of polynomial systems which have already been used in calculations:

(1) One-temperature representation. This is defined by

$$\alpha^2 = m/kT_0, \qquad \tau = \mathbf{1}, \qquad W = 0, \tag{139}$$

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where  $T_0$  is the gas temperature and the gas distribution is Maxwellian at this temperature. This is the representation most often used and is implicitly present in earlier works that do not use matrix language (e.g. Kihara 1953; Mason and Schamp 1958; Kumar and Robson 1973; Whealton and Mason 1974).

(2) Two-temperature representation. This is defined by

$$\alpha^2 = m/kT, \quad \tau = 1, \quad W = 0, \quad T \neq T_0.$$
 (140)

Such a representation was systematically applied to these problems by Viehland and Mason (1975), who also calculated the particular matrix elements. A different calculation of matrix elements and a critical study of some properties of approximate calculations in this representation is given by Forsth (1979). It is recognized by Forsth (1979) and Lin *et al.* (1979b) that if the gas distribution is expanded in a polynomial system orthogonal to a Maxwellian weight function appropriate to the temperature T then some formulae of Kumar (1967) can be used to calculate the matrix elements in this representation.

If the cold gas problem is treated by polynomial moment methods then one is necessarily dealing with a two-temperature representation.

(3) Drifted three-temperature representation. This is defined by

$$\alpha^2 = m/kT, \qquad \tau = \operatorname{diag}(\tau, \tau, \tau_0), \qquad W \neq 0, \qquad T \neq T_0. \tag{141}$$

Lin *et al.* (1979*c*) have calculated the matrix elements for a special choice of parameters in a Hermite polynomial basis; certain symmetries of the problem are obscured by the specialization they introduce. A calculation of matrix elements in a Burnettfunction basis is given by Kumar (1980*a*), along with the general case  $T \neq T_0$ ,  $W \neq 0$ , and  $\tau$  a real nonsingular (not necessarily diagonal) tensor.

#### (d) Calculation of matrix elements

#### (i) Use of Symmetries and Auxilliary Coefficients

In any representation the expression for matrix elements of a collision operator will be complicated and therefore can be arranged in various ways. Special coordinate systems and polynomial systems have often been used in the belief that they provide a straightforward or unique way of carrying out the calculations. There is enough truth in this belief but such derivations often obscure the symmetries and structure of the expressions. From the theoretical as well as from the computational point of view it is advantageous to carry the symmetries of the expressions as far as possible. The expressions should be assembled in terms of other matrices or coefficients whose properties can be studied separately and which can be calculated in separate subprograms. As an example, note that one expands a function in terms of spherical harmonics not because one expects it to be a spherical harmonic or even a sum of a small number of spherical harmonics but because one knows how to manipulate spherical harmonics in a convenient way. Considerations of this type have been advanced to show that Burnett functions are the most suitable for calculating matrix elements of collision operators. This remains true even for the most general case of equations (137).

It is of importance to keep the cross section in one integral, which should be made as convenient as possible since this is usually the most time-consuming part of the calculations. Having emphasized the complexity of these calculations, let us also say that it is possible to speak of a simplicity. The first point about simplicity is that it can be recognized—that requires familiarity. In the present context to recognize simplicity one has to familiarize oneself with the symmetries of the intermediate quantities that go into the sums which produce matrix elements and also with the problems of computation.

It may be noted that the principles outlined above have already been used in Sections 9, 10 and 11 in the treatment of other forms of the collision operator.

The matrix elements for various operators may be calculated using the integral or differential forms. However, it is found that the integral form is better suited to calculation of matrix elements and is the one most often employed. We now turn to a specific example.

# (ii) Calculations based upon Cold Gas Case

The matrix element of the stationary cold gas collision operator in a Burnett-function basis has the integral form

$$[J(0)]_{\mathbf{v}\mathbf{v}'} = \int \phi^{(\mathbf{v})}(\mathbf{x}) J([\delta(\mathbf{c}_0)]; \,\overline{\mathbf{w}}(\mathbf{x}) \,\phi^{[\mathbf{v}']}(\mathbf{x})) \,\mathrm{d}\mathbf{c} \,. \tag{142}$$

Let [T(V)] be the matrix representation of the translation operator in this basis,

$$[T(V)]_{vv'} = \int \phi^{(v)}(x) \left( \exp(V, \partial_c) \,\overline{w}(x) \,\phi^{[v']}(x) \right) \,\mathrm{d}c \,. \tag{143}$$

Then the matrix representation of the collision operator for the moving cold gas, from equation (67), is given by

$$[J(V)] = [T(V)]^{-1} [J(0)] [T(V)].$$
(144)

Comparison of this expression with equation (134) shows that this is also the matrix representing the stationary cold gas in the basis in which x is replaced by

$$x' = \tau \cdot (c - W + V). \tag{145}$$

The matrix representation for an arbitrary gas distribution is related to the cold gas representation by means of a super-operator matrix  $\mathscr{S}$  which is characterized by four indices:

$$[J]_{\mathbf{v}\mathbf{v}'} = \sum_{\mathbf{v}_1\mathbf{v}_2} \mathscr{S}^{\mathbf{v}\mathbf{v}';\mathbf{v}_1\mathbf{v}_2} [J(0)]_{\mathbf{v}_1\mathbf{v}_2}.$$
 (146)

From equations (63) and (144) we then have

$$\mathscr{S}^{\mathbf{v}\mathbf{v}';\mathbf{v}_{1}\mathbf{v}_{2}} = \int [T(V)]_{\mathbf{v}\mathbf{v}_{1}}^{-1} [T(V)]_{\mathbf{v}_{2}\mathbf{v}'} f_{0}(V) \,\mathrm{d}V.$$
(147)

For the Maxwellian gas (equation 79a), the integration may be carried out after expanding the matrix elements in powers of V, and the results may be expressed as a power series in the parameter  $(\alpha/\alpha_0)$ . We quote the result for the special case  $\tau = 1$  and W = 0 which corresponds to a two-temperature expansion. The matrix elements for the cold gas itself are derived in Appendix 2e.

Since we have

$$[J(0)]_{\mathbf{v}\mathbf{v}'} = \delta_{ll'} \delta_{mm'} [J^0_{l}]_{\mathbf{v}\mathbf{v}'}, \qquad (148)$$

we only need the elements of  $\mathscr{G}$  for which  $l_1 = l_2$  and  $m_1 = m_2$ :

$$\mathscr{S} = \sum_{n=0}^{\infty} (\alpha/\alpha_0)^{2n} \mathscr{S}_{(2n)}, \qquad (149a)$$

where

$$\mathscr{S}_{(2n)}^{\nu\nu';\nu_1\nu_2} = \delta_{ll'}\delta_{mm'}\,\mathscr{S}_{(2n)}^{\nu\nu'l;\nu_1\nu_2l_1}, \quad \text{for} \quad l_1 = l_2, \quad m_1 = m_2, \quad (149b)$$

with

$$\mathcal{S}_{(2n)}^{\nu\nu'l;\nu_{1}\nu_{2}l_{1}} = \frac{(2n+1)!!}{2^{n}} \frac{1}{4\pi} \sum_{l_{3}} (-)^{\nu+\nu'+\nu_{1}+\nu_{2}+l_{3}} \delta(n-(\nu_{3}+\nu_{4}+l_{3})) \\ \times \{\sigma(l_{1} \ l_{3} \ l)\}^{2} \frac{\overline{N}_{\nu'l}}{\overline{N}_{\nu l}} \frac{\overline{N}_{\nu_{1}l_{1}}}{\overline{N}_{\nu_{3}l_{3}}} \overline{N}_{\nu_{4}l_{3}}^{2}, \qquad (149c)$$

 $v_3$  and  $v_4$  being given by

$$2v_3 + l_3 = 2v_2 + l_1 - (2v'+l), \quad 2v_4 + l_3 = 2v + l - (2v_1 + l_1), \quad (149d, e)$$

and  $\sigma$   $(l_1 l_3 l)$  and  $\overline{N}_{\nu l}$  as given in Appendix 1.

The sum in equation (149c) is finite and in many ways similar to those encountered in previous sections. The values of  $l_3$  are restricted by the requirements that l and  $l_1$ couple to form  $l_3$  with  $l+l_1+l_3$  even and that the values for  $v_3$  and  $v_4$  given by (149d, e) are greater than or equal to zero. If either of the requirements is not met there is no contribution to the sum. The consequence is that for given (vv'l) and nthere are at most  $(n+1)^2$  sets of values of  $(v_1 v_2 l_1)$  for which the quantity defined by equation (149c) does not vanish. Thus in the *n*th order of the expansion defined by equations (146) and (149a), a given matrix element  $[J_{l}]_{vv'}$  requires, in general,  $(n+1)^2$  elements  $[J_{l_1}^0]_{v_1v_2}$  of the cold gas collision operator. For small values of (vv'l) this number would be smaller. These relationships may be summarized as follows.

Let 
$$l_1 = l - r$$
,  $l_3 = |r|, |r| + 2, ..., n$ , with  $r = n, n - 1, ..., -n$ .

For 
$$r \le 0$$
,  $v_1 = v, v-1, ..., v-(n+r)$ ,  $v_2 = v'+n, v'+(n-1), ..., v'-r$ .  
For  $r \ge 0$ ,  $v_1 = v-n, v-(n-1), ..., v-r$ ,  $v_2 = v', v'+1, ..., v'+(n-r)$ .

If any of the numbers  $(v_1, v_2, l_1)$  becomes negative there is no contribution.

It should be noted that if the restrictions  $l_1 = l_2$  and  $m_1 = m_2$  are not used the expression for  $\mathscr{S}_{(2n)}$  will involve the recoupling coefficients  $\overline{W}$  etc. It is instructive to compare this expansion of matrix elements with the operator expansion (100b). The parameter occurring there is  $(kT_0/m_0)$  which has the dimension  $[L^2T^{-2}]$ ; each term is dimensionless because the differential operators have the correct cancelling dimensionality. In the present expansion the parameter  $(\alpha/\alpha_0)^2 = (mT_0/m_0T)$  is dimensionless. But T is an arbitrary scale provided by the polynomial system. The smallness of this parameter is therefore not, by itself, very meaningful. As with the operator expansion (100b), reference has to be made to the functions operated upon and the magnitudes of their derivatives.

#### (iii) Matrix Elements and Collision Integrals

In this section we have given the general properties of the matrix elements and the relation between different representations and one example of a more specific nature. These are not available elsewhere in the literature. The actual evaluation of matrix elements remains a technical problem of some complexity even after a choice of representation has been made. Even to reproduce some of the formulae will require series of definitions and a lot of space. A recourse to the original papers is therefore necessary at this point.

As equation (127a) shows, a matrix element is a collision integral and thus all the enormous literature on evaluation of collision integrals could be relevant here. There are a variety of techniques and notations. The references given here on this topic are not exhaustive but should be adequate for the purpose at hand.

A comparative study of cartesian and spherical tensor notation may be found in the paper by Kumar (1966). The matrix form of the Boltzmann equation in a Burnett-function basis with isotropic weight functions was given by Kumar (1967). This latter work includes expressions for matrix elements and an explanation of technical points in the use of Burnett functions. A more limited study covering some of the same points has been made by Aisbett *et al.* (1974).

A technical point of some importance in calculations with gaussian weight functions is the proper treatment of the quadratic form in the exponential. This was first recognized in the work by Suchy (1964; see also Weinert and Suchy 1977). The transformation matrix connecting polynomials orthogonal with respect to gaussian weight functions is discussed in the second following paper by Kumar (1980*b*, present issue pp. 469–79).

Other references to particular matrix representations are given in Section 12c.

#### **13. Model Collision Operators**

Qualitative or semiquantitative information about transport processes can sometimes be found by solving the Boltzmann equation with a simplified model collision operator. The models to be described here fall into three categories: scattering models, truncated expansion models and relaxation models.

The scattering models are functionally simple angular cross sections  $\sigma(g, \chi)$  together with the exact collision operator. Three of these models will be mentioned.

The constant mean free time model assumes a cross section inversely proportional to the relative velocity, that is,

$$\sigma(g,\chi) = (g_0/g)\,\sigma(g_0,\chi),\tag{150}$$

where  $g_0$  is an arbitrarily chosen reference speed. Special cases of this model are the Maxwellian and the polarization potential models, corresponding to repulsive and attractive  $r^{-4}$  potential interactions respectively. The adjoint collision operator  $\tilde{J}$  is particularly simple with a cross section of the form (150) and, for any polynomial  $\psi(c)$ ,  $\tilde{J}\psi(c)$  can be expressed analytically as another polynomial of the same order in c (Maxwell 1866). It can be further shown that the one-temperature Burnett functions are eigenfunctions of the collision operator in this case (see e.g. Kihara 1953). Consequently, in any gaussian-based representation the collision matrix will be lower triangular. This suggests that for a general potential interaction the matrix elements in the upper triangle may be small, and decrease away from the diagonal.

This assumption has been used to set up approximate procedures for solving moment equations (see Section 18d below).

The hard-sphere model assumes a constant angular cross section

$$\sigma(g,\chi) = \sigma_0/4\pi \tag{151}$$

and consequently constant and equal transport cross sections

$$\sigma^{(l)} = \sigma_0 - \sigma_l = \sigma_0. \tag{152}$$

The kernel K(c, c') in the integral representation of the collision operator (equation 61c) can be found analytically in this case (Pidduck 1915):

$$K(\mathbf{c}, \mathbf{c}') \exp\left(\frac{mc^2}{2kT_0}\right) = \frac{\sigma_0}{\pi} \left(\frac{m_0}{2\pi kT_0}\right)^{\frac{1}{2}} \left(\frac{m_0 + m}{2m_0}\right)^2 \\ \times \frac{1}{|\mathbf{c} - \mathbf{c}'|} \exp\left(\frac{m_0}{2kT_0} \left(\frac{|\mathbf{c} \times \mathbf{c}'|}{|\mathbf{c} - \mathbf{c}'|}\right)^2 - \frac{m_0 - m}{2kT_0} (\mathbf{c} \cdot \mathbf{c}') - \frac{m_0}{2kT_0} \left(\frac{m_0 - m}{2m_0}\right)^2 |\mathbf{c}' - \mathbf{c}|^2\right).$$
(153)

In the solution of the Boltzmann equation, this does not lead, however, to essential simplifications, and the hard-sphere model exhibits all the principal difficulties encountered in calculations with more realistic potentials.

The idealized resonant charge transfer model has been used to describe approximately collisions between particles with identical nuclei, and it assumes that charge (electrons) can be transferred without any noticeable accompanied transfer of momentum. If the motion of the charged particle is followed, this corresponds to elastic scattering where the velocities of the collision partners are interchanged, i.e. where the scattering angle is close to  $\pi$ :

$$(\boldsymbol{c}_0, \boldsymbol{c}) = (\boldsymbol{c}', \boldsymbol{c}_0'), \qquad \sigma(\boldsymbol{g}, \boldsymbol{\chi}) = \frac{\sigma_{\mathrm{tr}}(\boldsymbol{g})}{2\pi} \lim_{\boldsymbol{\chi}_0 \to \pi} \delta(\cos \boldsymbol{\chi} - \cos \boldsymbol{\chi}_0). \tag{154}$$

The collision integral then reduces to

$$Jf(c) = f(c) \int f_0(c_0) g \,\sigma_{\rm tr}(g) \,\mathrm{d}c_0 \,-f_0(c) \int f(c_0) g \,\sigma_{\rm tr}(g) \,\mathrm{d}c_0 \,. \tag{155}$$

Two special cases of this can be noted. Firstly, for the case of a cold gas, the second term reduces to a  $\delta$ -function source term at c = 0, yielding

$$J^{0} f(c) = c \sigma_{tr}(c) f(c) \qquad (kT_{0} = 0, \ c \neq 0).$$
(156)

Secondly, for a charge transfer cross section  $\sigma_{tr}(g) \propto g^{-1}$  (constant mean free time), equation (155) reduces to a relaxation-type expression

$$Jf(c) = \{f(c) - f_0(c)\}\tau^{-1}, \qquad \tau = \{c\sigma_{tr}(c)\}^{-1} = \text{const.}$$
(157)

The forms (156) and (157) allow analytical solutions for f(c) to be obtained in certain cases.

The truncated expansion models may be obtained from the differential forms of the collision operator, given in Sections 10 and 11. They can be used with arbitrary cross sections  $\sigma(g, \chi)$ , and are most useful at extreme mass ratios.

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The Lorentz gas model assumes a vanishing mass ratio  $\mu = m/(m+m_0)$ , in which case the spherical harmonics decomposition of the collision operator reduces to (cf. equations 115)

$$J_{l}(f_{l}) = c \,\sigma^{(l)}(c) f_{l}, \qquad l \neq 0; \qquad (158a)$$

$$J_0(f_0) = 0,$$
  $l = 0.$  (158b)

The model describes satisfactorily the relaxation of anisotropies for an electron swarm, while the energy loss is not accounted for.

The quasi-Lorentz gas model keeps the Lorentz gas model expression (158a) for  $J_{l}$ , but expands  $J_{0}$  to first nonvanishing terms in mass ratio and gas temperature, to account for energy loss and to ensure relaxation towards a Maxwellian. This gives Davydov's expression for  $J_{0}$ :

$$-J_0(f_0) = \frac{\mu}{c^2} \frac{\mathrm{d}}{\mathrm{d}c} \left( c^4 \,\sigma^{(1)}(c) \,f_0 \right) + \frac{kT}{m_0 \,c^2} \frac{\mathrm{d}}{\mathrm{d}c} \left( c^3 \,\sigma^{(1)}(c) \frac{\mathrm{d}f_0}{\mathrm{d}c} \right). \tag{159}$$

The quasi-Lorentz gas model is fully satisfactory for describing elastic collisions between electrons and neutrals.

The Rayleigh gas model assumes a small mass ratio  $\mu_0 = m_0/(m+m_0) \ll 1$ , and neutral velocities much larger than ion velocities,  $c_0 \ge c$ . To second order in  $\mu_0$ , one then obtains, for example from equation (73), a Fokker-Planck expression with constant coefficients of the form

$$Jf = \zeta \{ \nabla_{\boldsymbol{c}} \cdot (\boldsymbol{c}f) + (kT/m) \nabla_{\boldsymbol{c}}^2 f \}.$$
(160)

A quasi-Rayleigh gas model has been used (e.g. Wannier 1953; Smirnov 1967) to describe collisions with  $\mu_0 \ll 1$ , but where the assumption  $c_0 \gg c$  cannot be made. The essential modification to equation (160) is obtained by expanding the coefficients  $\Psi_{nl}(c)$  (equation 74) to first order about a characteristic velocity  $c_*$ .

The relaxation models make explicit assumptions about the form of the velocity distribution 'after a collision', the physical meaning of the term 'collision' seldom being quite clear. The most well known of these models is the BGK model (Bhatnagar *et al.* 1954) where the distribution is taken to relax towards a Maxwellian one at the local gas temperature with a phenomenological time constant  $\tau$ . This gives rise to a collision term of the form (157), arrived at for the idealized charge transfer, constant mean free time model! The physical implications of using the BGK model for other cases seem unclear.

#### 14. Inelastic Collisions and Reactions

The foregoing results must be modified when inelastic collisions take place. Relative speeds g and g' before and after a collision are different in an inelastic collision and some symmetry is therefore lost in the analysis. These effects can largely be incorporated through a modification of the cross section formula (59) and the integrals in which they occur.

Reactions, including phenomena such as attachment in the case of electrons, can usually be treated more simply. For the unidirectional reaction

ion + neutral  $\rightarrow$  products,

one can express the collision operator in the form

$$J^*(f) = v^* f,$$
 (161a)

where

$$v^*(\boldsymbol{c}) \equiv \int f_0(\boldsymbol{c}_0) g \, \sigma^*(g) \, \mathrm{d}\boldsymbol{c}_0 \tag{161b}$$

and  $\sigma^*$  denotes the total cross section for all reaction channels. This effect is simply additive; that is, the right-hand side of the Boltzmann equation is

$$(df/dt)_{coll} = -J(f) - J^*(f), \qquad (162)$$

where J(f) denotes the nonreactive collision operator. It is the effect of inelastic collisions on this latter quantity which is of most interest here.

We may use the semiclassical model of Wang-Chang *et al.* (1964) to generalize equation (60) to the case where the ions and molecules have internal structure. The inadequacy of this model for dealing with degenerate internal states (e.g. angular momentum states) is well known (Waldmann 1965). However, we assume that any errors arising in this way are small (Ferziger and Kaper 1972). For simplicity, we consider the case where only the neutral molecules have internal degrees of freedom, the ions still being treated as point particles. This is appropriate for electrons or atomic ions, but not for molecular ions.

Let *i* denote the quantum number (or set of quantum numbers) characterizing the internal molecular states, the corresponding energy being  $E_i$ . The distribution of molecules in these states is Maxwell-Boltzmann, that is,

$$f_{0i}(\boldsymbol{c}_0) = n_{0i} w(\alpha_0, c_0), \qquad (163a)$$

where

$$n_{0i} = (n_0/Z) \exp(-\varepsilon_i/kT_0) \tag{163b}$$

is the number of molecules in state i and

$$Z = \sum_{i} \exp(-\varepsilon_i / kT_0)$$
(163c)

is the partition function. The Wang-Chang et al. (1964) generalization of equation (60) is then

$$J(f) = \sum_{i,j} \int \left( f(\boldsymbol{c}) f_{0i}(\boldsymbol{c}_0) - f(\boldsymbol{c}') f_{0j}(\boldsymbol{c}'_0) \right) g \,\sigma(ij; g\chi) \,\mathrm{d}\hat{\boldsymbol{g}}' \,\mathrm{d}\boldsymbol{c}_0 \,, \tag{164}$$

where  $\sigma(ij;g\chi)$  is the differential cross section for the scattering channel in which the internal state of the molecule changes from *i* to *j* and the relative speed from *g* to *g'*, where by conservation of energy

$$\frac{1}{2}m_{\rm r}g^2 + \varepsilon_i = \frac{1}{2}m_{\rm r}(g')^2 + \varepsilon_j, \qquad (165)$$

and  $m_r$  is the reduced mass. The microscopic reversibility relation

$$(g')^2 \sigma(ji;g'\chi) = g^2 \sigma(ij;g\chi) \tag{166}$$

is used in deriving the identity

$$\int \phi(\boldsymbol{c}) J(f) \, \mathrm{d}\boldsymbol{c} = \sum_{i,j} \int f(\boldsymbol{c}) f_{0i}(\boldsymbol{c}_0) \left( \phi(\boldsymbol{c}) - \phi(\boldsymbol{c}') \right) g \,\sigma(ij;g\chi) \, \mathrm{d}\boldsymbol{\hat{g}}' \, \mathrm{d}\boldsymbol{c} \, \mathrm{d}\boldsymbol{c}_0 \,, \tag{167}$$

for any function  $\phi(c)$ . We now consider how the results of previous sections are modified.

#### (a) Fokker–Planck expansion

We proceed from the identity (167). Equation (72) still applies in the same form, but the coefficients are defined differently; for example,

$$\boldsymbol{A}^{1} \equiv \langle \Delta \boldsymbol{c} \rangle = \sum_{i,j} \int f_{0i}(\boldsymbol{c}_{0}) \,\Delta \boldsymbol{c} \, g \, \sigma(ij; g\chi) \,\mathrm{d}\boldsymbol{\hat{g}}' \,\mathrm{d}\boldsymbol{c}_{0} \,. \tag{168}$$

Since momentum is still conserved in a collision (G' = G), equations (64) still apply.

It is shown in Section 10 and Appendix 2a how the general term in the Fokker-Planck expansion could be calculated for elastic collisions. The generalization of that analysis to include inelastic collisions is not difficult: instead of cross sections  $\sigma^{(\lambda)}$  defined by equation (59) we have the quantities

$$\sigma^{(\lambda;\nu)}(g) = Z^{-1} \sum_{i,j} \exp(-\varepsilon_i/kT_0) \left\{ \sigma_0(ij;g) - (g'/g)^{2\nu+\lambda} \sigma_\lambda(ij;g) \right\},$$
(169)

where the  $\sigma_{\lambda}(ij;g)$  are partial cross sections, defined for the differential cross section  $\sigma(ij;g\chi)$  in analogy with equation (58). Notice that the cross sections (169) appear to have a temperature dependence; we shall comment further on this observation below. For the cold gas limit, which now not only implies that the molecules are at rest but also that they are in their internal ground state, equation (169) gives

$$\sigma^{(\lambda;\nu)}(c) = \sum_{j=1} \left\{ \sigma_0(ij;c) - (c'/c)^{2\nu+\lambda} \sigma_\lambda(ij;c) \right\},$$
(170)

and instead of equations (85) we then have the generalization

$${}^{\circ}\Psi_{nl}(c) = c^{2n+l+1} \sum_{\lambda=0}^{n+l} \sum_{\nu=0}^{n} \sigma^{(\lambda;\nu)}(c) a_{nl}^{\nu\lambda} , \qquad (171a)$$

where the  $a_n^{\nu}$  are pure numbers defined by

$$a_{nl}^{\nu\lambda} = \sum_{\nu'\lambda'} \delta_{P,p+p'} \frac{(-)^{\lambda}(2\lambda+1)(2\lambda'+1)}{2^{2n+l}4\pi(2l+1)} \frac{\overline{N}_{\nu\lambda}^2 \overline{N}_{\nu'\lambda'}^2}{\overline{N}_{\nu l}^2} (\lambda 0 \lambda' 0 | l 0)^2,$$
(171b)

with P = 2n + l,  $p = 2\nu + \lambda$  and  $p' = 2\nu' + \lambda'$ . Because of the  $\delta$  function there is only one sum in equation (171b). It can also be verified that these coefficients vanish for  $\lambda > l + n$ . Evidently, a relationship exists between these coefficients and the coefficients  $a_{nl}^{\lambda}$  of Section 10 and Appendix 2b, but we will not go into that.

Equations (170) and (171) are the only changes to the cold gas formulae of Section 10, the form of the differential operator being otherwise maintained. Notice that the entries for  $\Psi_{nl}(c)$  in Table 1 would have to be modified according to equation (171a); in particular, the quantities  $\sigma^{(\lambda;\nu)}$  do not necessarily vanish for  $\lambda = 0$  (unlike their elastic collision counterparts  $\sigma^{(\lambda)}$ ) and must therefore appear. We can consider the elastic collisions separately by splitting off the j = i terms in equation (164):

$$J_{\rm el}(f) = \sum_{i} \int \left( f(c) f_{0i}(c_0) - f(c') f_{0i}(c'_0) \right) g \,\sigma(ii;g\chi) \,\mathrm{d}\hat{g}' \,\mathrm{d}c_0 \,. \tag{172}$$

This is formally equivalent to scattering of ions from a mixture of neutral gases; that is, the excited states i of the neutral molecules effectively behave as different species (see Note [15]).

Alternatively, we can write equation (172) in the condensed form

$$J_{\rm el}(f) = n_0 \int (f(c) w(\alpha_0, c_0) - f(c') w(\alpha_0, c'_0)) g \sigma(g\chi; T_0) \, \mathrm{d}\Omega \, \mathrm{d}c_0, \qquad (173a)$$

with a temperature-dependent cross section

$$\sigma(g\chi; T_0) \equiv Z^{-1} \sum_{i} \exp(-\varepsilon_i / kT_0) \,\sigma(ii; g\chi) \,. \tag{173b}$$

Only in the special cases where (i) the neutral molecules exist in one level only and (ii) the scattering cross sections are the same for all quantum numbers, that is, when

$$\sigma(ii;g\chi) = \sigma(g,\chi), \tag{174}$$

is this temperature dependence removed, and  $\sigma(g\chi; T_0) = \sigma(g, \chi)$ . It is worth noting that equation (60) and the subsequent analysis are based upon such assumptions.

### (b) Inelastic collision term for Lorentz gas

The spherical harmonic decomposition outlined in Section 11 is specially suited for electrons (or light ions) for which  $\mu = m/(m+m_0) \ll 1$ . We noted there and in Section 13 that the scalar part of the elastic collision operator vanishes in the Lorentz gas limit  $\mu \to 0$ , corresponding to a vanishingly small energy change for infinitely heavy molecules. On the other hand, energy exchange *can* occur with even infinitely heavy neutral molecules possessing internal degrees of freedom. It is possible to start from the Wang-Chang *et al.* (1964) collision operator (164) and show that the scalar part of the spherical harmonic decomposition of J(f) in the limit  $\mu \to 0$  is

$$J_{0}(f_{0}) = (2/m\epsilon)^{\frac{1}{2}} \sum_{i < j} \left\{ n_{0i} \left[ \varepsilon f_{0}(\varepsilon) \sigma_{0}(ij;\varepsilon) - (\varepsilon + \varepsilon_{ji}) f_{0}(\varepsilon + \varepsilon_{ji}) \sigma_{0}(ij;\varepsilon + \varepsilon_{ji}) \right] + n_{0j} \left[ \varepsilon f_{0}(\varepsilon) \sigma_{0}(ji;\varepsilon) - (\varepsilon - \varepsilon_{ji}) f_{0}(\varepsilon - \varepsilon_{ji}) \sigma_{0}(ji;\varepsilon - \varepsilon_{ji}) \right] \right\}, \quad (175)$$

where  $\varepsilon = \frac{1}{2}mc^2$  and  $\varepsilon_{ji} \equiv \varepsilon_j - \varepsilon_i > 0$  is the energy exchange in a collision. This is essentially of the same form as the expression of Frost and Phelps (1962) who modified Holstein's (1946) work to allow for 'superelastic collisions', that is, collisional de-excitation of the molecule represented by the second term in square brackets in equation (175).

The time-reversal symmetry relation (166) allows us to write equation (175) entirely in terms of excitation cross sections:

$$(\varepsilon - \varepsilon_{ii}) \sigma_0(ji; \varepsilon - \varepsilon_{ii}) = \varepsilon \sigma(ij; \varepsilon).$$

If the states are degenerate, statistical weights  $g_i$  of the appropriate states *i* have to be incorporated in the cross sections, that is,  $\sigma_0(ij;\varepsilon) \rightarrow g_i \sigma_0(ij;\varepsilon)$  and the  $\sigma_0$  are to be interpreted as averages over internal states.

Frost and Phelps (1962) also considered a differential form of equation (175) obtained by Taylor expansion of the terms on the right-hand side about  $\varepsilon$ . This is

essentially an expansion in  $\varepsilon_{ji}$ , a parameter that is small when the energy levels of the molecules are closely spaced, as sometimes happens for the case of rotational levels. In general, however, the usefulness of this expansion is not clear and it is probably better to use equation (175) or the more general form (164). The latter form is, of course, necessary when one wishes to go beyond the Lorentz approximation.

# (c) Matrix forms

For the electron case, matrix elements have been given by Lin *et al.* (1979b). General formulae for the case in which the charged particles as well as the gas molecules have internal structure are given in the following paper (Kumar 1980a). The effect of inelastic collisions appears only in the interaction integrals and the cross sections through which the matrix elements are defined.

# Part IV. Technique and precision in the calculation of drift and diffusion

# 15. Introduction (IV)

This Part of the paper (Sections 15–23) is devoted to the most important application of the theory, namely the calculation of the drift velocity (or the mobility) and the diffusion coefficients for ions and electrons in a uniform electrostatic field. Magnetic fields and reactions are excluded. The ions and the gas molecules are assumed structureless; that is to say, inelastic effects are also excluded. However, such effects due to the structure of gas molecules can be included by constructing the collision operator according to Section 14: no other modification of the methods is necessary. The modification needed in order to deal with the case of a mixture of neutral gases is pointed out in Note [15].

Transport coefficients of higher rank can also be calculated by the same methods. The only modifications required are in the details of inhomogeneous terms and in the operators that determine the anisotropic parts of these coefficients. These will be evident from the work in Section 16. There are no new questions of principle at these levels.

The collision operator is taken in one of the forms discussed in Part III and we have the problem of solving the kinetic equations derived in Section 4. These are homogeneous or inhomogeneous linear equations. We give a brief survey of the techniques available (Section 17) and discuss in detail those which have been actually used (Sections 19, 20 and 21). We are interested in those techniques which are capable of yielding accurate results. The standard for this is set by experiment [3] where at the present time the best results give mobilities to within 0.1% and diffusion coefficients to within 1%, apart from possible systematic errors.

The accuracy of a calculation based on a given method, scheme or theory—the words are interchangeable in current usage—depends on the mass ratio, the gas temperature and the field strength, for a given collision model. A method or theory is said to break down in a range of these parameters if the desired accuracy cannot be achieved. Properly speaking, such a breakdown is not of the theory but of the method of solving the equations in a calculation with limited time and effort.

The choice of a method of solution should be made in relation to the expected form of the solution, the information one wants from it and the ranges of parameters that need to be covered. Physical and mathematical considerations along with the information from known analytic solutions of model problems (Section 18) are useful in this connection.

Moment methods, in the form of a polynomial expansion of the unknown function, can be applied in fairly general circumstances and are the ones most often used. They are described and their effectiveness is discussed in Sections 19 and 20. In special circumstances, when more is known about the nature of the solutions or when the collision operator is simple, non-polynomial methods (Section 21) may be used. When applicable, they are capable of producing better results.

Computer simulation (or Monte Carlo) methods [2] are a means of obtaining the transport coefficients from the correlation functions and averages discussed in Section 3, without the use of kinetic equations. Comparison of results from these two independent approaches has been very useful in the development of methods for

precise calculation of transport coefficients. Section 22 gives a brief survey of the literature on computer simulations.

In the special problem dealt with in this Part, the only preferred direction is the one provided by the electric field E, that is, by the acceleration a = (q/m)E suffered by the particles. The kinetic equations and the transport coefficients therefore have cylindrical symmetry about this direction,  $\hat{a} = \hat{E}$ . In particular, the drift velocity W and the diffusion tensor **D** then have the form

$$W = W\hat{a}, \qquad \mathbf{D} = D_{\mathrm{L}}\,\hat{a}\,\hat{a} + D_{\mathrm{T}}(\mathbf{1} - \hat{a}\,\hat{a}). \tag{176}$$

Thus there are three transport coefficients to consider: the drift velocity W, the longitudinal diffusion  $D_{\rm L}$  and the transverse (or lateral) diffusion  $D_{\rm T}$ . The drift velocity is often expressed in terms of the mobility K, which is a scalar quantity in this problem defined by

$$W = KE. \tag{177}$$

It may be noted that it is the drift velocity W and not the mobility K that is the true transport coefficient according to the definition in Section 2.

The experimental results are expressed in terms of the reduced electric field  $E/n_0$ , where  $n_0$  is the number density of neutrals, specified in units of townsends  $(1 \text{ Td} = 10^{-21} \text{ Vm}^2)$ . The drift velocity W (m s<sup>-1</sup>), the reduced mobility  $n_0 K$ (m Td<sup>-1</sup> s<sup>-1</sup>) and the reduced diffusion coefficients  $n_0 D$  (m<sup>-1</sup> s<sup>-1</sup>) depend on the neutral number density and the acceleration only through the ratio  $a/n_0 = (q/m)(E/n_0)$ .

In the next section we simplify the relevant kinetic equations by using the cylindrical symmetry noted above and prepare the way for the subsequent sections.

# 16. Equations for Mobility and Diffusion

We shall take the equations for mobility and diffusion from Section 4, equations (37a) and (37b). Since reactions are not present,  $\omega^{(0)}$  is zero and the operator  $\mathscr{L}$  of equation (35) becomes

$$\mathscr{L} = \boldsymbol{a} \cdot \boldsymbol{\partial}_c + J. \tag{178}$$

For any function f(c) we have

$$\int \mathscr{L} f(\boldsymbol{c}) \, \mathrm{d}\boldsymbol{c} \equiv 0.$$
 (179)

The equation for mobility or drift velocity is the scalar equation

$$\mathscr{L}f^{(0)} = 0$$
, with  $\int f^{(0)}(c) dc = 1$ , (180a)

and

$$W = \langle \boldsymbol{c} \rangle = \int \boldsymbol{c} f^{(0)}(\boldsymbol{c}) \, \mathrm{d}\boldsymbol{c} \,. \tag{180b}$$

The equation for diffusion is a vector equation for the vector function  $f^{(1)}(c)$ :

$$\mathscr{L}f^{(1)} = (\mathbf{c} - \mathbf{W})f^{(0)}(\mathbf{c}), \quad \text{with} \quad \int f^{(1)}(\mathbf{c}) \,\mathrm{d}\mathbf{c} = 0, \quad (181a)$$

and

$$\mathbf{D} = \int c f^{(1)}(c) \, \mathrm{d}c \,. \tag{181b}$$

Equation (181a) is consistent with the property (179) of the operator  $\mathscr{L}$ . The origin of the coordinates in the velocity space is fixed by the requirement that the neutral gas is at rest in this frame, i.e. by  $\langle c_0 \rangle = 0$ .

If a matrix representation of these equations is chosen then the orientation of the coordinate axes is unimportant provided one uses the proper formalism. An orientation-independent form of the mobility equation has been given earlier by Kumar and Robson (1973) (it was called a coordinate-free form, which is not strictly correct). It may, however, be convenient to take the z axis along a.

To exploit the rotational invariance of the collision operator one uses spherical polar coordinates  $c \equiv (c, \theta, \varphi)$  and the operator  $J_l$  defined by the spherical harmonic decomposition of J,

$$J(f(c) Y_m^{(l)}(\theta, \varphi)) = Y_m^{(l)}(\theta, \varphi) J_l(f(c)).$$
(182)

Then from equation (180a)  $f^{(0)}(c)$  is independent of  $\varphi$ , so that it can be expanded in terms of Legendre polynomials as

$$f^{(0)}(c) = \sum_{l=0}^{\infty} f_l^{(0)}(c) \mathbf{P}_l(\cos\theta).$$
(183)

Using equations (182) and (183) and noting that  $J_i$  is independent of the normalization of the spherical harmonics, one finds that the equations leading to mobility become

$$d_{l,l-1}^{(0)}f_{l-1}^{(0)}(c) + J_l f_l^{(0)}(c) + d_{l,l+1}^{(0)} f_{l+1}^{(0)}(c) = 0, \qquad (184a)$$

with

$$d_{l,l-1}^{(0)} = a \frac{l}{2l-1} \left( \frac{\mathrm{d}}{\mathrm{d}c} - \frac{l-1}{c} \right), \qquad d_{l,l+1}^{(0)} = a \frac{l+1}{2l+3} \left( \frac{\mathrm{d}}{\mathrm{d}c} + \frac{l+2}{c} \right), \tag{184b}$$

and

$$\int_{0}^{\infty} f_{0}^{(0)}(c) c^{2} dc = 1, \qquad (184c)$$

$$W = \frac{1}{3} \int_0^\infty c^3 f_1^{(0)}(c) \, \mathrm{d}c \,. \tag{184d}$$

For the longitudinal or the z component of the vector  $f^{(1)}$  the right-hand side of equation (181a) is independent of  $\varphi$ . Consequently, we may use the expansion

$$f_z^{(1)} \equiv f^{(L)}(c) = \sum_{l=0}^{\infty} f_l^{(L)}(c) \mathbf{P}_l(\cos\theta).$$
(185)

The equations leading to the longitudinal diffusion coefficient  $D_{\rm L}$  then become

$$d_{l,l-1}^{(0)}f_{l-1}^{(L)}(c) + J_l f_l^{(L)}(c) + d_{l,l+1}^{(0)}f_{l+1}^{(L)}(c) = b_l^{(L)}(c), \qquad (186a)$$

with

$$b_{l}^{(L)}(c) = l(2l-1)^{-1} c f_{l-1}^{(0)} - W f_{l}^{(0)} + (l+1)(2l+3)^{-1} c f_{l+1}^{(0)}, \qquad (186b)$$

and

$$\int_{0}^{\infty} f_{0}^{(L)}(c) c^{2} dc = 0, \qquad (186c)$$

$$D_{\rm L} = \frac{1}{3} \int_0^\infty c^3 f_1^{\rm (L)}(c) \, \mathrm{d}c \,. \tag{186d}$$

The two transverse components of equation (181a) may be converted into two complex-conjugate equations for the functions  $f_x^{(1)} \pm i f_y^{(1)}$ . Since W is along the

z axis, the right-hand sides of these equations are therefore  $\sim \exp(\pm i\varphi)$ . The two equations then reduce to one equation for the transverse component  $f^{(T)}$  of  $f^{(1)}$  defined by

$$f_x^{(1)} \pm i f_y^{(1)} = f^{(T)} \exp(\pm i\varphi).$$
(187)

The appropriate expansion for  $f^{(T)}$  is

$$f^{(T)} = \sum_{l=1}^{\infty} f_l^{(T)}(c) P_l^1(\cos\theta), \qquad (188)$$

and the corresponding equations leading to the transverse diffusion coefficient  $D_{\rm T}$  are

$$d_{l,l-1}^{(\mathrm{T})}f_{l-1}^{(\mathrm{T})}(c) + J_l f_l^{(\mathrm{T})}(c) + d_{l,l+1}^{(\mathrm{T})}f_{l+1}^{(\mathrm{T})}(c) = b_l^{(\mathrm{T})}(c), \qquad (189a)$$

$$d_{l,l-1}^{(T)} = (l-1)l^{-1} d_{l,l-1}^{(0)}, \qquad d_{l,l+1}^{(T)} = (l+2)(l+1)^{-1} d_{l,l+1}^{(0)}, \tag{189b}$$

$$b_l^{(T)}(c) = (2l-1)^{-1} c f_{l-1}^{(0)}(c) - (2l+3)^{-1} c f_{l+1}^{(0)}, \qquad (189c)$$

and

with

$$D_{\rm T} = \frac{1}{3} \int_0^\infty c^3 f_1^{\rm (T)}(c) \, \mathrm{d}c \,. \tag{189d}$$

The condition corresponding to (181a) is automatically satisfied for  $f^{(T)}$  since equation (187) vanishes on integrating with respect to  $\varphi$ , and the term corresponding to l = 0 does not occur in the expansion (188).

The equations above are given in the normalization most frequently found in the literature. The normalization enters through the expansions (183), (185) and (188) and may be easily changed if required.

The preceding equations are particularly convenient when  $J_l$  is taken as a differential operator (Section 11) and the number of l values needed is not large. One then has a coupled system of differential equations for functions  $f_l$  of a single variable c. The difficulties in numerical integration of such a system arise from the need to adjust properly the boundary conditions (or the starting values) for the different functions  $f_l(c)$  and from the presence of higher derivatives in the operators  $J_l$ . The equations of this form have been most successful in the electron problem [16], where in most cases the distribution function is nearly isotropic and only the terms l = 0 and 1 are usually needed.

The left-hand side of equation (184a) shows that the operator  $\mathscr{L}$  is tridiagonal in the *l* indices. By a further expansion of the *c* dependence one can put the operators  $d^{(0)}$  and  $J_l$  in matrix form, to obtain block tridiagonal matrix equations.

If the distribution function deviates substantially from spherical symmetry and the decomposition (183) is not to be used, one can still preserve the advantages of cylindrical symmetry by taking the z axis along **a** and using cylindrical coordinates  $\mathbf{c} \equiv (c_{\mathrm{T}}, c_{z}, \varphi)$ . One now defines the operator  $\mathscr{L}_{|\mathbf{m}|}$  by the relation

$$\mathscr{L}(f(c_{\mathrm{T}}, c_{z}) \exp(\mathrm{i}m\varphi)) = \exp(\mathrm{i}m\varphi) \mathscr{L}_{|m|}(f(c_{\mathrm{T}}, c_{z}))$$
(190)

and obtains the equations

$$\mathscr{L}f^{(0)}(c_{\mathrm{T}},c_{z})=0,\qquad \qquad \mathscr{L}\equiv\mathscr{L}_{0},\qquad (191a)$$

$$W = \int c_z f^{(0)}(c_{\rm T}, c_z) \,\mathrm{d}\boldsymbol{c} \,; \tag{191b}$$

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$$\mathscr{L}f^{(L)}(c_{\mathrm{T}},c_{z}) = (c_{z} - W)f^{(0)}(c_{\mathrm{T}},c_{z}),$$
 (192a)

$$D_{\rm L} = \int c_z f^{\rm (L)}(c_{\rm T}, c_z) \,\mathrm{d}\boldsymbol{c}$$
; (192b)

$$\mathscr{L}_{\mathrm{T}}f^{(\mathrm{T})}(c_{\mathrm{T}},c_{z}) = c_{\mathrm{T}}f^{(0)}, \qquad \mathscr{L}_{\mathrm{T}} \equiv \mathscr{L}_{1}, \qquad (193a)$$

$$D_{\rm T} = \frac{1}{2} \int c_{\rm T} f^{\rm (T)}(c_{\rm T}, c_z) \,\mathrm{d}\boldsymbol{c} \,. \tag{193b}$$

These equations are the most appropriate to use with the Fokker-Planck type of differential form of the operator J, in the case where the distribution function is expected to deviate substantially from spherical symmetry.

# (a) Operator for transverse diffusion equation

To obtain an explicit form for  $\mathscr{L}_{T}$  note that from equation (190)

$$\mathscr{L}_{\mathrm{T}}f \equiv \mathscr{L}_{\mathrm{1}}f = 2(c_{-}/c_{\mathrm{T}})\mathscr{L}(c_{+}f/c_{\mathrm{T}}), \qquad (194a)$$

with

$$c_{\pm} = \pm (i/\sqrt{2})(c_x \pm ic_y) = \mp (i\sqrt{2})c_T \exp(\pm i\phi).$$
 (194b)

Using equations (81) and (82) for J in (194a) and (178) together with the following identities which hold for any function g of c:

$$\nabla_c^2(cg) = c \,\nabla_c^2 g \,, \qquad \left(\frac{\mathrm{d}}{\mathrm{d}c}\right)^n \left(cg\right) = c \left\{\frac{n}{c} \left(\frac{\mathrm{d}}{\mathrm{d}c}\right)^{n-1} + \left(\frac{\mathrm{d}}{\mathrm{d}c}\right)^n\right\} g \,, \tag{195}$$

with  $J_{\rm T}$  defined in analogy with equation (194a), one can write

$$\mathscr{L}_{\mathrm{T}} = a \,\partial/\partial c_z + J_{\mathrm{T}},\tag{196a}$$

$$J_{\rm T}(f) = \sum_{nl=0}^{\infty} S_{\rm T}^{nl}(\Psi_{nl}f),$$
(196b)

$$S_{\rm T}^{nl} = \frac{2l+1}{4\pi} \overline{N}_{nl}^{2} \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} c_{\rm T} \nabla_{c}^{2(n+r)} \left(\frac{\rm d}{\rm dc} + \frac{3}{c}\right)^{l-2r} c_{\rm T}^{-1}.$$
 (196c)

Other symbols in equations (196b) and (196c) are defined in equations (78) and (82).

The operators  $\mathscr{L}_m$  for m > 1 will occur in anisotropic parts of higher order transport coefficients and may be constructed in the same way (see remarks at the end of Section 10). It will be noted that the operator  $J_T$  above can be calculated by a simple modification of the program that calculates J.

#### 17. Methods of Solution: Moment Equations

In this section we make some general observations regarding the methods of solution for the equations derived above. Omitting the elaborations of symbols, we have equations of the form

$$\mathscr{L}f = b, \tag{197}$$

where, in particular, b may be zero. Such an equation may be converted to an integral equation [9] and solved by iteration (Section 5), or by Monte Carlo methods. Apart

from these two methods, all other methods of solving these equations may be seen as special cases of the weighting function or Galerkin method (see e.g. Hildebrand 1956; Prenter 1975). The latter have been the most successful in applications although there are indications that problems in numerical implementation of the first two methods may also be overcome (G. L. Braglia, personal communication).

The Galerkin method may be briefly characterized as follows: one takes two sets of linearly independent functions  $\Psi \equiv \{\psi_j(c)\}\$  and  $\Phi \equiv \{\phi_i(c)\}\$ , with  $i, j = 1, 2, ..., i_{max}$ , and assumes that

$$f(c) = \sum_{i=1}^{l_{\max}} \xi_i \phi_i(c).$$
 (198)

Then using the functions from the set  $\Psi$  one obtains a set of linear algebraic (i.e. matrix) equations for the unknowns  $\xi_i$ :

$$\sum_{i=1}^{i_{\max}} \xi_i(\psi_j, \mathscr{L}\phi_i) = (\psi_j, b), \qquad (199a)$$

where for any functions g(c) and h(c)

$$(g,h) = \int g(\boldsymbol{c}) h(\boldsymbol{c}) \,\mathrm{d}\boldsymbol{c} \,. \tag{199b}$$

These equations should be supplemented by the normalization or other conditions on f(c), and hence on  $\xi_i$ , which ensure that the system is uniquely solvable.

The choice of basis sets  $\Phi$  and  $\Psi$  is guided by one's expectations about the form of the solution. Typically one is interested in the moments (c, f) and (cc, f) and has some idea of their magnitudes. One also knows something about the asymptotic behaviour of f, and may expect to see properties similar to those exhibited by known analytic solutions of model problems. If a singularity is present in f, the sets should be primarily chosen to incorporate its effects.

Roughly speaking, the set  $\Phi$  is chosen to represent the function f as adequately as one can and the set  $\Psi$  is chosen with regard to the moments of f which one wants to know accurately. The optimal choice of basis sets is determined to a large degree by the practical requirement of being able to calculate the matrix elements of the collision operator occurring in  $\mathcal{L}$ . Only in the case of very light ions and electrons is the collision operator simple enough to admit a high degree of flexibility in this choice. In the general case, it is all a compromise. One is commonly limited to the sets

$$\Phi: w(x)\phi_i(x), \qquad \Psi: \phi_i(x), \qquad (200)$$

where the  $\phi_i(\mathbf{x})$  are polynomials orthogonal with respect to the weight function w(x) which is a gaussian in  $\mathbf{x}$ , with  $\mathbf{x}$  a linear function of  $\mathbf{c}$ . This choice has the drawback that it tends to place undue weight on the less important parts of the function f. The equations so obtained are linearly related to the *moment equations* (Note [17]) familiar in most kinetic theory work. The use of orthogonal polynomials somewhat simplifies the equations and is particularly useful in calculation of the matrix elements of J (see Part II and Kumar 1980a, 1980b).

It may be noted here that representation of f(c) by its values given in a finite number of points together with a prescription for interpolation between the points is quite a regular basis set expansion in the sense used here.

The equations above are written in terms of the vector variable c, but the same general remarks, with appropriate changes, apply as well to the equations of the previous section in terms of other variables, such as c,  $c_{\rm T}$  and  $c_z$ .

The results obtained from such a calculation, particularly the first few moments which are physically important, should be seen to be independent of the choice of the basis set. Their independence can be tested by calculating the quantities with successively larger sets, i.e. by increasing  $i_{max}$  in successive stages. If the calculated values do not change one speaks of *converged values*. This is, of course, not the true mathematical convergence, but for all practical purposes these numerically converged values can be taken as the true results of the theory. On the other hand, little reliance can be placed upon a calculation of this type if such a (numerical) convergence is not demonstrated. When converged values cannot be obtained it usually means that an inappropriate choice of basis sets was made.

It is convenient sometimes to take basis functions which depend upon some auxilliary parameters. We shall call such parameters the b-parameters. The basis sets are then altered by altering the b-parameters. It is found that the rate of convergence, or indeed whether the convergence is at all achieved, depends upon the choice of the b-parameters. How to make this choice is an important question in such calculations, and has to be discussed for each particular type of set separately. Evidently, the results from smaller sets depend upon the b-parameters. They may, therefore, be chosen from physical considerations, but since they cannot be allowed as adjustable parameters in the final results it is all important to show that convergence is achieved. The role of basis sets and the b-parameters is that of scaffoldings which must be removed (by ensuring convergence) before the structure can be recognized as being truly free standing.

Usually, the lower moments will converge before the higher ones. In view of the coupling of equations, the part  $f^{(0)}$  of the distribution function that determines the mobility must be sufficiently accurate before the equation for diffusion can be solved. In particular, at least the second moment of  $f^{(0)}$ , that is, the mean square random velocities, needs to have converged before a meaningful calculation of the diffusion coefficients can be attempted.

#### (a) Use of adjoint operator

When the set  $\Psi$  consists of polynomials of maximum degree k, it is convenient to calculate the matrix elements in equation (199a) in the form

$$(\phi_i, \tilde{\mathscr{L}}\psi_i) = (\psi_i, \mathscr{L}\phi_i).$$
<sup>(201)</sup>

The adjoint of the operator  $a \cdot \partial_c$  is  $-a \cdot \partial_c$  and that of the collision operator J, which was developed in Section 10, has the form

$$\tilde{J} = \sum_{r=1}^{\infty} \mu_0^r \sum_{s=0}^{[\frac{1}{2}r]} A_{rs}(c) (\hat{c} \cdot \partial_c)^{r-2s} (\nabla_c^2)^s,$$
(202)

where the  $A_{rs}(c)$  are linear combinations of  $\Psi_{nl}(c)$  (cf. equations 83 and 84). These functions depend on the cross sections but are independent of the basis sets and may be tabulated once for all in a calculation involving any basis sets and any values of the electric field.

When the  $\psi_j$  are polynomials of maximum degree k then, no matter what the other functions  $\phi_j$ , the left-hand side of equation (201) can be calculated without any approximation by retaining only the first k terms in equation (202); that is to say, one effectively has a finite k-term expansion of the matrix element. It will be noted that this simplicity is not available if the right-hand side of equation (201) is evaluated. This economy in calculational effort enables us, in Section 20 below, to go to much higher orders than have been previously considered.

Similar techniques can be used in the calculation of transverse diffusion where the adjoint of the operator  $\mathscr{L}_T$  should be used. In working with the spherical harmonic decomposition, the adjoint operators  $\tilde{J}_l$  can be used to effect similar economies.

# 18. Solutions of Model Problems

Model collision operators were discussed in Section 13. Here we show how some of them can be used to obtain analytical expressions for the velocity distributions and the transport coefficients. One hopes that the solutions of real problems would have some of the features shown by these expressions. Four model problems are considered: in the first two cases (a and b), the results although analytic are approximate; in the last two (c and d), the results are exact solutions of the model problem.

#### (a) Quasi-Lorentz gas model

This model has been treated in detail in the literature and only a summary of the basic equations and results is given below. One assumes that the mass ratio is very small,  $m/m_0 \ll 1$ , that only elastic collisions occur and that the stationary distribution function is nearly isotropic. In the spherical harmonic decomposition (equations 183–6) the terms with l > 1 are omitted, and simplified forms of the spherical components of the collision operator,  $J_0$  and  $J_1$  (equations 100) are used. The kinetic equations (184a) then reduce to the two coupled equations

$$\frac{1}{3}a(d/dc + 2/c)f_1^{(0)} + J_0 f_0^{(0)} = 0, \qquad (203a)$$

$$a(d/dc)f_0^{(0)} + v^{(1)}f_1^{(0)} = 0, \qquad (203b)$$

where  $v^{(1)}(c) = n_0 c \sigma^{(1)}(c)$  is the collision frequency for momentum transfer. From this one finds Davydov's expressions for  $f_0^{(0)}$  and  $f_1^{(0)}$ :

$$f_0^{(0)} = A \exp\left(-\frac{3m}{m_0} \int_0^c \left\{ (a/\nu^{(1)})^2 + 3kT_0/m_0 \right\}^{-1} c' \, \mathrm{d}c' \right), \tag{204a}$$

$$f_1^{(0)} = -(a/v^{(1)}) df_0^{(0)}/dc.$$
(204b)

Expressions for the velocity distributions  $f^{(L)}(c)$  and  $f^{(T)}(c)$  associated with diffusion are found in a similar way, and one finally obtains from equations (183)–(189)

$$W = \langle v(c) \rangle \equiv \langle c^{-2} \operatorname{d}(c^{3} a/v^{(1)})/\operatorname{d} c \rangle, \qquad (205a)$$

$$D_{\rm T} = \langle c^2 / 3v^{(1)} \rangle, \qquad (205b)$$

$$D_{\rm L} = D_{\rm T} + a^{-1} \int_0^\infty \frac{1}{(a/v^{(1)})^2 + 3kT_0/m_0} \left( -2c(a/v^{(1)})^2 + \frac{3(a/v^{(1)})I(c)}{c^2 f_0^{(0)}(c)} \right) I(c) \, \mathrm{d}c \,, \quad (205c)$$

where

$$I(c) = \int_0^c \left\{ v(c') - W \right\} f_0^{(0)}(c') \, c'^2 \, \mathrm{d}c' \,.$$
 (205d)

#### (b) Quasi-Rayleigh gas model

This model describes the motion of heavy ions in a light gas, and it is obtained by expanding the elastic collision operator J to second order in the mass ratio  $\mu_0 = m_0/(m+m_0)$ . The mass ratio expansion of J is given by equations (81) and (82). Insertion of this expansion into equation (180a) gives a Fokker-Planck type of equation, which can be written in the form

$$\nabla_{c} \cdot ([\mathscr{E} + \hat{c} \,\Psi_{01}] f^{(0)}) + \mu_0 \{ \nabla_{c} \nabla_{c} : (\hat{c} \,\hat{c} \,\Psi_{02} \,f^{(0)}) + \frac{1}{3} \nabla_{c}^2 ([\Psi_{10} + \Psi_{02}] f^{(0)}) \} = 0, \quad (206)$$

where  $\mathscr{E}$  is the electric field parameter:

$$\mathscr{E} = \{q(m+m_0)/mm_0\} E/n_0 = (q/m_r) E/n_0.$$
(207)

The coefficients  $\Psi_{nl}(c)$  were defined in Section 10. Their behaviour for large c may be seen from Table 1, while at small values of c they vary as  $c^{l}$ . Those occurring in equation (206) are always negative.

To bring out clearly the behaviour as  $c \to 0$ , we write the  $\Psi_{nl}$  in the form

$$\Psi_{nl}(c) = -c^l Q_{nl}(c) \sim -c^l Q_{nl}(0), \qquad c \to 0, \qquad (208a)$$
$$\sim -c^{2n+l+1} \sigma_{nl}(c), \qquad c \to \infty, \qquad (208b)$$

which defines the quantities  $Q_{nl}(c)$  and  $\sigma_{nl}(c)$ . Specifically, one finds for  $c \to 0$ 

$$Q_{01}(0) = \frac{16}{3}\Omega^{(1,1)}(kT_0/m_0), \qquad Q_{10}(0) = (3kT_0/m_0)Q_{01}(0), \qquad (209)$$

where  $\Omega^{(1,1)}(kT_0/m_0)$  is one of the usual ' $\Omega$  integrals' of kinetic theory. Inserting the forms (208) into equation (206) we get

$$\nabla_{c} \cdot ([c Q_{01} - \mathscr{E}] f^{(0)}) + \mu_{0} \{ \nabla_{c} \nabla_{c} : (c c Q_{02} f^{(0)}) + \frac{1}{3} \nabla_{c}^{2} ([Q_{10} + c^{2} Q_{02}] f^{(0)}) \} = 0.$$
 (210)

We modify this equation to make it separable, and to ensure the correct Maxwellian solution for  $\mathscr{E} \to 0$ .

For small fields, one can assume  $c^2 \ll 3kT_0/m_0$ , use for  $Q_{01}$  and  $Q_{10}$  their values at c = 0, and neglect the  $c^2Q_{02}$  terms. With these approximations, however, one must also replace  $\mu_0 = m_0/(m+m_0)$  by  $m_0/m$ , to get the correct zero-field solution. The resulting equation and its solution are

$$\nabla_{c} \cdot \left( \left[ c \, Q_{01}(0) - \mathscr{E} \right] f^{(0)} \right) + \left( k T_0 / m_0 \right) Q_{01}(0) \, \nabla^2 f^{(0)} = 0 \,, \tag{211a}$$

$$W = \langle c \rangle = \mathscr{E}/Q_{01}(0), \qquad (211b)$$

$$f^{(0)}(\mathbf{c}) = A \exp\{-(m_0/2kT_0)(\mathbf{c} - \mathbf{W})^2\}.$$
 (211c)

Equation (211c) gives the true Rayleigh gas solution. The distribution of random velocities is unchanged by the field, while the drift velocity can become much larger than the random velocities.

When the drift velocity is large  $(W^2 \ge (c - W)^2)$  another approximation can be made to equation (210). Firstly, we determine W from (210) to the lowest order  $\mu_0$ :

$$W \approx c_* = \mathscr{E}/Q_{01}(c_*). \tag{212}$$

We then expand the coefficients in equation (210) to the lowest nonvanishing order in  $(c-c_*)$ , to obtain the separable equation (still with  $m_0/m$  substituted for  $\mu_0$ )

$$Q_{01}\left(f^{(0)} + c_x \frac{\partial f^{(0)}}{\partial c_x}\right) + \frac{m_0/m}{3} \left(Q_{10} - c_*^2 Q_{02}\right) \frac{\partial^2 f^{(0)}}{\partial c_x^2} + Q_{01}\left(f^{(0)} + c_y \frac{\partial f^{(0)}}{\partial c_y}\right) + \frac{m_0/m}{3} \left(Q_{10} - c_*^2 Q_{02}\right) \frac{\partial^2 f^{(0)}}{\partial c_y^2} + \left(Q_{01} + c_* Q_{01}'\right) \left(f^{(0)} + (c_z - c_*) \frac{\partial f^{(0)}}{\partial c_z}\right) + \frac{m_0/m}{3} \left(Q_{10} + 2c_*^2 Q_{02}\right) \frac{\partial^2 f^{(0)}}{\partial c_z^2} = 0, \quad (213)$$

where  $Q'_{01} = dQ_{01}(c)/dc$  and the coefficients are to be evaluated at  $c = c_*$ . We then have the following results:

$$f^{(0)}(c) = A \exp\left(-\frac{c_x^2 + c_y^2}{2\langle c_x^2 \rangle} - \frac{(c_z - c_*)^2}{2\langle (c_z - c_*)^2 \rangle}\right),$$
(214a)

with

$$\langle c_x^2 \rangle = \frac{m_0/m}{3} \frac{Q_{10} - c_*^2 Q_{02}}{Q_{01}} \xrightarrow[c_* \to \infty]{} \frac{m_0/m}{6} \frac{c_*^2 \sigma^{(2)}}{\sigma^{(1)}},$$
 (214b)

$$\langle (c_z - c_*)^2 \rangle = \frac{m_0/m}{3} \frac{Q_{10} + 2c_*^2 Q_{02}}{Q_{01} + c_* Q_{01}'} \xrightarrow{m_0/m} \frac{m_0/m}{2} \frac{c_*^2 (1 - \frac{1}{3}\sigma^{(2)}/\sigma^{(1)})}{1 + \frac{1}{2}d(\ln\sigma^{(1)})/d(\ln c)}.$$
 (214c)

Equations (213) and (214b) are seen to subsume the weak-field equations (211a) and (211b).

As the distribution (214a) is gaussian, the diffusion coefficients are related to the differential mobility **K** through the generalized Einstein relations (equation 30; see Note [10]),  $K_{xx}$  is equal to the total mobility  $K = \langle c_z \rangle / E$ , since without approximation as  $E_x \to 0$  we have  $\partial W_x / \partial E_x = K$ , while

$$K_{zz} = \partial \langle c_z \rangle / \partial E = K \{ 1 + d(\ln K) / d(\ln E) \}.$$

This gives

$$D_{\rm T} = D_{xx} = (m/q) \langle c_x^2 \rangle K.$$
(215a)

$$D_{\rm L} = D_{zz} = (m/q) \langle (c_z - c_0)^2 \rangle K \{ 1 + d(\ln K)/d(\ln E) \}.$$
(215b)

# (c) Cold neutral gas, idealized charge transfer model

This model is represented by the collision operator  $Jf(c) = n_0 c \sigma_{tr}(c) f(c)$ , where  $\sigma_{tr}(c)$  is the cross section for charge transfer. With this form of the collision operator, the drift equation (180a) or (191a) becomes essentially one dimensional, yielding the solution

$$f^{(0)}(c) = A \,\delta(c_x) \,\delta(c_y) \exp\left(-(n_0/a) \int_0^{c_x} c \,\sigma_{\rm tr}(c) \,{\rm d}c\right).$$
(216)

Insertion of this into the diffusion equation (192a) gives

$$f^{(\mathrm{L})}(\mathbf{c}) = a^{-1} \{ \frac{1}{2} (c_z^2 - \langle c_z^2 \rangle) - \langle c_z \rangle (c_z - \langle c_z \rangle) \} f^{(0)}(\mathbf{c}), \qquad (217a)$$

$$D_{\rm L} = a^{-1} \{ \langle c_z \rangle^3 - \frac{3}{2} \langle c_z \rangle \langle c_z^2 \rangle + \frac{1}{2} \langle c_z^3 \rangle \}, \qquad (217b)$$

where the averages  $\langle c_z^n \rangle$  are to be evaluated with the distribution (216). The lateral diffusion coefficient is zero.

The form of the distribution (216) has more general interest than indicated by the model used. The very high energy tail of a velocity distribution will always (except at extreme mass ratios or very small fields) be expected to be strongly peaked in the forward direction, and populated nearly exclusively by direct acceleration of particles from lower velocities. The collisions will then represent a pure loss term, as in the present model case. The shape of the high energy tail will therefore be expected to be similar to that in the distribution (216), with  $\sigma_{tr}(c)$  replaced by some effective total cross section. The singularities represented by the delta functions will, of course, be ameliorated in a real problem.

Further discussion of the charge transfer problem may be found in the studies by Sena (1946), Wannier (1954, 1966), Smirnov (1967), Fahr and Müller (1967), Skullerud (1969) and Lin and Mason (1979).

#### (d) Constant mean free time model

This model was defined in Section 13, where its relation to the Maxwell and polarization force model was pointed out. For cross sections appropriate to the model (cf. equation 150) the constant mean free time  $\tau$  and a function  $\Pi(\chi)$  may be defined by the relation

$$n_0 g \sigma(g, \chi) = \Pi(\chi) / \tau.$$
(218)

On introduction of the collision frequencies  $v_l$  for l = 1, 2, 3, ..., by

$$v_{l} = n_{0} g 2\pi \int \{1 - P_{l}(\cos \chi)\} \sigma(g, \chi) \sin \chi \, d\chi$$
$$= \tau^{-1} 2\pi \int \{1 - P_{l}(\cos \chi)\} \Pi(\chi) \sin \chi \, d\chi, \qquad (219)$$

it can be shown, for example by the moment method of Wannier (1953), that the following relations hold exactly:

$$W = a/\mu_0 v_1 = qE/m_r v_1, \qquad m\langle c^2 \rangle = 3kT_0 + (m+m_0)W^2, \quad (220a, b)$$

$$m\langle c_x^2 \rangle = kT_0 + \frac{1}{3}(m+m_0)W^2 / \{1 + (2m/m_0)v_1/v_2\},$$
(220c)

$$D_{\rm L}/K = (m/q)\langle (c_z - W)^2 \rangle, \qquad D_{\rm T}/K = (m/q)\langle c_x^2 \rangle.$$
 (220d, e)

The mobility given by

$$K = W/E = q/m_{\rm r} v_1 \tag{221}$$

is a constant, independent of the field. Equations (220d) and (220e) are the generalized Einstein relations [10]. Note also that all moments  $\langle c \dots c \rangle$  can be calculated exactly

for this model (e.g. Ferrari 1978). Another exact result for the model is the theorem of Wannier (1953), which connects the time-averaged distribution function  $f^{(0)}(c)$  with its high-field (or cold gas) limit h(c):

$$f^{(0)}(\boldsymbol{c}) = \int w(\alpha, |\boldsymbol{c} - \boldsymbol{v}|) h(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v}, \qquad (222)$$

where  $\alpha^2 = m/kT_0$  and  $w(\alpha, c)$  is the Maxwellian at  $T_0$ . In other words, it is necessary only to obtain the high-field solution and the general solution follows from the convolution above.

The usefulness of the model derives from the fact that most real ion-molecule potentials are dominated by the polarization force  $(\sim r^{-5})$  at large distances, so that for low relative speeds we have  $\sigma(g, \chi) \sim g^{-1}$ . Hence, for low  $T_0$  and low  $E/n_0$ —the so-called 'polarization limit'—an ion swarm may be expected to conform to this model. For this reason the model has received a great deal of attention in this problem (McDaniel 1964; McDaniel and Mason 1973); elsewhere in kinetic theory it is popular for its mathematical simplicity alone.

The model has been widely used in developing various approximations. It is assumed that, in the general case when  $g \sigma(g, \chi)$  is not a constant, certain equations valid for the model may be taken over with the replacement of (speed-independent) averages by average values determined at the mean speed. The moment equations simplified in this way yield the so-called momentum-transfer theories [18]. A number of authors (e.g. Kihara 1953; Mason and Schamp 1958; Viehland and Mason 1975, 1978; Lin *et al.* 1979*c*) have developed successive approximation schemes for the solution of moment equations, with the first approximation based on equations truncated so as to have the same structure as those for the constant mean free time model.

#### 19. Polynomial Expansions: Isotropic Gaussian Weight Function

This section contains a discussion of what, in the terminology of Lin *et al.* (1979*c*) is called a two-temperature expansion. One temperature is an intrinsic parameter of the problem: it is the temperature  $T_0$  of the neutral gas. The other temperature  $T_b$  is introduced through the basis set. It is a b-parameter (Section 17), to be adjusted to improve convergence. When  $T_b = T_0$  we have the one-temperature expansion.

In the terminology of Section 17, the chosen basis sets are

$$\Phi: w(\alpha, c) \phi^{[\nu]}(\alpha c), \qquad \Psi: \phi^{(\nu)}(\alpha c), \qquad (223a)$$

where

$$w(\alpha, c) = (\alpha^2/2\pi)^{3/2} \exp(-\frac{1}{2}\alpha^2 c^2), \qquad \alpha^2 = m/kT_{\rm b}.$$
 (223b)

The functions  $\phi^{[v]}(\alpha c)$  are polynomials orthogonal with respect to the isotropic gaussian weight function  $w(\alpha, c)$ ; they are effectively normalized Burnett functions:

$$\phi^{[\mathbf{v}]}(\alpha c) = R_{\mathbf{v}l}(\alpha c) Y_m^{[l]}(\hat{c}), \qquad \mathbf{v} \equiv (\mathbf{v}, l, m), \tag{224a}$$

$$R_{vl}(\alpha c) = N_{vl}(\alpha c/\sqrt{2})^{l} S_{l+\frac{1}{2}}^{(v)}(\frac{1}{2}\alpha^{2}c^{2}), \qquad (224b)$$

$$N_{\nu l}^{2} = 2\pi^{3/2} \Gamma(\nu+1) / \Gamma(\nu+l+\frac{3}{2}), \qquad (224c)$$

where the  $Y_m^{[l]}$  are spherical harmonics and the  $S_{l+\frac{1}{2}}^{(v)}$  are Sonine polynomials. The set  $\Psi$  consists only of polynomials

$$\phi^{(\mathbf{v})}(\alpha c) = (\phi^{[\mathbf{v}]}(\alpha c))^*.$$
(225)

The use of the constant  $T_b$  here is similar to that of Viehland and Mason (1975) and Lin *et al.* (1979*b*). If differs from that of Viehland and Mason (1978) and Lin *et al.* (1979*c*) in that the temperature  $T_b$  here does not depend on the density gradients, all gradient dependence having been eliminated in the decomposition (32) leading to the equations (34). Further discussion of this point will be given in Section 23.

Table 2. Interpretation of coefficients in Burnett-function expansion of  $f^{(k)}$ (See equations 268a, b)

k	vlm	<sup>k</sup> f <sup>(v)</sup>	Comment Normalization Gives drift velocity Vanishes if $3kT_b = m^0 \langle c^2 \rangle$						
0	000 01 <i>m</i> 100	$\frac{1}{\sqrt[6]{c_m^{(1)} \alpha}}$							
1	000 01 <i>m</i> 100	$0 \\ \frac{1 \langle c_m^{(1)} \rangle \alpha}{1 \langle 3 - \alpha^2 c^2 \rangle / \sqrt{6}}$	Consistency requirement (cf. eqn 181 <i>a</i> ) Gives diffusion tensor <sup>A,B</sup> Vector quantity $\sim E^A$						

<sup>A</sup> This quantity is an average with respect to the vector function  $f^{(1)}(f_{m'}^{(1)})$ . <sup>B</sup> In the coordinate system chosen this quantity takes the form  $\delta_{mm'} D_m$ , where  $D_0 = D_L$  and  $D_{\pm 1} = D_T$  (see Kumar and Robson 1973).

The functions  $f^{(k)}(c)$ , later generically denoted by f(c), are expanded about  $w(\alpha, c)$  in terms of the set  $\Phi$  as

$$f^{(k)}(c) = \sum_{\mathbf{v}} w(\alpha, c) \phi^{[\mathbf{v}]}(\alpha c)^k f^{(\mathbf{v})}, \qquad (226a)$$

where, by virtue of the orthonormality of the basis functions, the expansion coefficients are given by

$${}^{k} f^{(\mathbf{v})} = \int f^{(k)}(\mathbf{c}) \, \phi^{(\mathbf{v})}(\alpha \mathbf{c}) \, \mathrm{d}\mathbf{c} = {}^{k} \langle \phi^{(\mathbf{v})}(\alpha \mathbf{c}) \rangle \,. \tag{226b}$$

We note the conditions on the expansion coefficients and identify the transport coefficients in Table 2.

#### (a) Structure of matrix equations

In view of the isotropy of the weight function the matrix elements of the collision operator are diagonal in the l and m indices,

$$J_{\mathbf{v}\mathbf{v}'} = J^l_{\mathbf{v}\mathbf{v}'} \delta_{ll'} \delta_{mm'}, \qquad (227)$$

and the equations (199a) are tridiagonal in the l indices (cf. equations 184a, 186a and 189a). To emphasize that we are dealing with the specific representation introduced above, we use symbols slightly different from the ones used in Section 17.

Because of cylindrical symmetry (z axis along  $\hat{a}$ ) the equations are diagonal in the *m* indices: in those for mobility and longitudinal diffusion one takes m = 0, and in those for transverse diffusion m = 1. In each case one has a system of the form

<b>∫</b> J⁰	$d_{+}^{0}$	0	0	••		••	0 ]	$\lceil f^0 \rceil$		<b>b</b> <sup>0</sup> <sup>-</sup>		
$d^1$	$oldsymbol{J}^1$	$d_{+}^{1}$	0	••			:	$f^1$		<b>b</b> <sup>1</sup>		
0	$d_{-}^{2}$	$J^2$	$d_{+}^{2}$				:	:		•		
:				••			:	:	_	:	,	(228)
:				•••			0	:		:		
:			••	••	$d_{-}^{L-1}$	$J^{L-1}$	$d_{+}^{L-1}$	:		:		
0	0	0	0		0	$d^{L}_{-}$	$J^L$	$\lfloor f^L  floor$		<b>_ b</b> <sup>L</sup> _		

where the  $f^{l}$  and  $b^{l}$  are column vectors, the  $J^{l}$  are matrices and L is the maximum allowed value of l. If  $v_{*}$  is the maximum allowed value of v then  $d^{l}_{\pm}$  and  $J^{l}$  are  $v_{*} \times v_{*}$  matrices and  $f^{l}$  and  $b^{l}$  are column vectors with  $v_{*}$  entries. The matrices  $d^{l}_{-}$ are diagonal and the  $d^{l}_{+}$  have nonvanishing elements only along a subdiagonal.

One exploits the tridiagonal nature, and the structure of the  $d_{\pm}^{l}$  matrices by a suitable adaptation of the well-known backward substitution method for tridiagonal matrices. (A general method for solving block tridiagonal systems by backward substitution has been given recently by Calimon and Ligon (1979).) Briefly, from the last equation one obtains  $f^{L-1}$  in terms of  $f^{L}$  and  $b^{L}$ , then, from the last but one equation,  $f^{L-2}$  in terms of  $f^{L}$ ,  $b^{L}$  and  $b^{L-1}$ , and so on. In the end, from the zeroth equation one has a  $v_* \times v_*$  matrix equation for  $f^{L}$  and this is solved by standard procedures. The method may also be used with other truncation schemes to be discussed below. There is considerable saving in computation time compared with a direct inversion of the whole matrix.

It is evident that in place of  $f^L$  any other  $f^l$  with  $0 \le l \le L$  could have been chosen and the system (228) converted to a set of  $v_* \times v_*$  equations for that  $f^l$ . In practice, it is convenient to choose l = 0 or L. The fact that the system of equations in the spherical harmonic decomposition of the Boltzmann equation (not just the Burnettfunction representation given above) can be reduced to a size effectively independent of the number of l values included in the calculation seems to have been first indicated by Wannier (1953). The application of iterative methods (e.g. Kihara 1953; Mason and Schamp 1958; Viehland and Mason 1975, 1978; Lin *et al.* 1979*c*) to equations like (228) appears to offer no real advantage.

#### (i) Truncation Schemes

The way in which the matrices or the sets are enlarged, that is, the way one chooses successively a larger number of allowed indices, is called a truncation scheme. The choice of an efficient scheme is of some importance from the point of view of limiting the computational effort.

For small mass ratios  $m/m_0$  and low field strengths an independent truncation in the *l* and *v* indices seems the most efficient, as the maximum *l* value is in any case low.

For mass ratios  $m/m_0 \sim 1$ , both the above truncation and a coupled truncation  $l+v \leq n$  (Viehland and Mason 1978) have been used, the latter being probably somewhat more efficient.

For mass ratios  $m/m_0 \gtrsim 2$ , except at weak fields, with small basis sets both of the above-mentioned truncation schemes tend to yield pathological values of the mean square random velocities and diffusion coefficients. This can be overcome by using a method due to Baraff (1964), where the relation between  $f^{L-1}$  and  $f^L$  is modified to what it would be if the distribution function had a form  $\sim \delta(\cos \theta - 1)$ . This takes some account of the high anisotropy of the distribution function. It is a method of truncating the equations but not in the same sense as defined above. When large basis sets are used, which is necessary to obtain reliable and accurate results, the precise form of the truncation scheme is not of importance, nor should it be.

For mass ratios  $m/m_0 \ge 3$ , the isotropic weight function expansion of this section, in any case, converges too slowly to be useful. It may be said that the method then breaks down. The expansion becomes inappropriate because in these cases the anisotropy increases very rapidly with the field strength and the basis set is inadequate to take account of it.

## (ii) Explicit Forms

At first sight the matrix equation for mobility is homogeneous. It can be converted to the inhomogeneous form (228) by removing a row and a column (see e.g. Kumar and Robson (1973) for the one-temperature case; the method carries over to the general case unaltered). With the z axis taken along a we have m = 0 and

$$\boldsymbol{b}^{l} \to \boldsymbol{b}_{v}^{l} = (\alpha a/n_{0})\delta_{v0}\,\delta_{l1}\,,\tag{229a}$$

$$d_{+}^{l} \to d_{+\nu\nu'}^{l} = (\alpha a/n_{0})(2\nu)^{\frac{1}{2}} \{(l+1)/(2l+1)\} \delta_{\nu',\nu-1}, \qquad (229b)$$

$$d_{-}^{l} \to d_{-\nu\nu'}^{l} = -(\alpha a/n_{0})(2\nu+2l+1)^{\frac{1}{2}}\{l/(2l+1)\}\delta_{\nu'\nu}.$$
(229c)

For longitudinal diffusion (m = 0), the  $d_{\pm}$  operators remain the same as above but

$$b^{l} \to b^{l}_{v} = {}^{0}f^{(vl)}{}^{0}f^{(01)} + \sum_{v_{1}l_{1}} (l0|10l_{1}0)(vl||\alpha c^{[1]}||v_{1}l_{1}){}^{0}f^{(v_{1}l_{1})}, \qquad (230)$$

where the  ${}^{0}f^{(\nu l)}$  are the solution of the mobility equation obtained by using equations (229) in (228). Note that the equation corresponding to ( $\nu = 0$ , l = 0) does not occur in (228) because it is lost in the process of converting the homogeneous equation to an inhomogeneous one.

For transverse diffusion, the m = 1 and m = -1 equations are equivalent. Taking m = 1, then with the same  ${}^{0}f^{(vl)}$  we have

$$\boldsymbol{b}^{l} \to \boldsymbol{b}^{l}_{\boldsymbol{v}} = \sum_{\boldsymbol{v}_{1} l_{1}} (l \, | \, 11 \, l_{1} \, 0) (\boldsymbol{v} l \, || \, \alpha c^{[1]} \, || \, \boldsymbol{v}_{1} \, l_{1})^{0} f^{(\boldsymbol{v}_{1} l_{1})}, \tag{231a}$$

$$d_{+}^{l} \to d_{+\nu\nu'}^{l} = (\alpha a/n_{0})(2\nu)^{\frac{1}{2}} \{ l^{\frac{1}{2}}(l+1)^{\frac{1}{2}}/(2l+1) \} \delta_{\nu',\nu-1}, \qquad (231b)$$

$$d_{-}^{l} \to d_{-\nu\nu'}^{l} = -(\alpha a/n_{0})(2\nu+2l+1)^{\frac{1}{2}}\{(l^{2}-1)^{\frac{1}{2}}/(2l+1)\}\delta_{\nu'\nu}.$$
 (231c)

In equations (230) and (231a) we have the usual Wigner coefficients and

$$(vl \|\alpha c^{[1]} \| v'l') = (-)^{v'+v} \bar{\sigma}(l'1l) \sqrt{2} \left( \delta_{p'+1,p} \frac{\overline{N}_{v'l'}}{\overline{N}_{vl}} + \delta_{p'-1,p} \frac{\overline{N}_{vl}}{\overline{N}_{v'l'}} \right), \qquad (232a)$$

with

$$p = 2\nu + l, \qquad \overline{N}_{\nu l}^2 = 2\pi^{3/2} / \Gamma(\nu + 1) \, \Gamma(\nu + l + \frac{3}{2}), \qquad \overline{\sigma}(l'1l) = (l'0\,10\,|\,l0)\,i^{l'-l+3}.$$
(232b)

The formulae (231) and (232) may be obtained following the work of Kumar and Robson (1973). The explicit forms for the matrix elements  $J^{l}$  have been derived by Viehland and Mason (1975, 1978), Lin *et al.* (1979*b*), Forsth (1979) and in the following paper by Kumar (1980*a*). All the formulae are too detailed to be given here (see, however, Part III, Section 12).

#### (b) Matrix elements $J_{yy'}^{l}$ : approximations

For small basis sets, typically  $(2l + v + v') \le 8$ , the matrix elements may be calculated exactly from the general formulae given in the references quoted above. However, the required computational effort increases rapidly with the size of the basis sets and it is not possible to go much higher in this way, except when  $T_b = T_0$ . But in the case of electrons we have  $m/m_0 \le 1$  and it is justifiable to retain terms only to first order in  $m/m_0$  in the formulae for  $J_{vv'}^l$ . It is then possible to go to very much higher values of v and l. In the work of Lin *et al.* (1979b) values up to v = 29 and l = 6 occur.



Fig. 2. Mobilities (a) and longitudinal diffusion coefficients (b) calculated with a cold gas expansion, for a unit mass ratio, and a hard-sphere interaction;  $\lambda$  is the mean free path:

wf, weak-field expansion, with  $kT_b = kT_0$ ; cg, cold gas approximation;

pcg, perturbed cold gas expansion to second order in  $kT_0/kT_b$  (Burnett-function expansion with  $I_{\text{max}} = v_{\text{max}} = 8$ ).

To go further, approximate expressions for  $J_{\nu\nu'}^{l}$  may be used, provided one later justifies the approximations. It has been noted (Section 8) that the cold gas approximation should be very good at high fields. There is a natural expansion of the general matrix element  $J_{\nu\nu'}^{l}$  based on the cold gas matrix elements in powers of the parameter  $(kT_0/m_0)/(kT_b/m)$ . When  $T_b = T_0$  this is, of course, an expansion in the mass ratio  $m/m_0$ . Since this parameter involves  $T_b$ , which is an (auxilliary) b-parameter (see Section 17), the nature of the approximation involved may not be clear. However, if, for some given value of the b-parameter, convergence is achieved with approximate  $J_{\nu\nu'}^{l}$  and the results improve in successive approximations, one has an acceptable situation. Usually  $T_b$  will be close to the ion temperature, so that it is still meaningful to speak of  $(kT_0/m_0)/(kT_b/m)$  as an expansion parameter.

In Fig. 2, for  $m/m_0 = 1$ , we show the results for the drift velocity and the diffusion obtained for the cold gas approximation (cg), the perturbed cold gas (pcg) approxi-

mation to second order in  $T_0/T_b$  and the one-temperature or the weak-field (wf) expansion with  $T_0 = T_b$ . The results show that whereas the cg approximation does not produce good results at low fields, the pcg approximation for mobilities seems good over the entire range. Should the pcg results prove reliable then, for longitudinal diffusion, the entire range can be covered by using wf and pcg approximations in different ranges. Other work not presented here shows that for  $m/m_0 \leq 0.2$  the pcg expansion alone suffices, that is, pcg corrections are small also over the range covered by wf, while for  $m/m_0 \gtrsim 1$  there remains a gap in the range which is covered neither by wf nor by pcg (see also Skullerud and Forsth 1979).



Fig. 3. Successive approximations in a Burnett-function basis with isotropic weight function shown as a function of the basis temperature  $T_b$ , for (a) mobilities and (b) longitudinal diffusion. A hardsphere cold gas model with a mass ratio  $m_0/m = 1$  is used. The curves are labelled by the order n $(= I_{max} = v_{max})$  of the approximation. Normalization is provided by  $kT_1 = \frac{1}{2}m\langle (c-W)^2 \rangle$ ,  $W = 1.1467(a\lambda)^{\frac{1}{2}}$  and  $D_L = 0.2202(a\lambda^3)^{\frac{1}{2}}$ , with  $\lambda$  the mean free path. Oscillations in a curve show that the convergence is not uniform (nor is it expected to be).

#### (c) Choice of basis temperature

A convenient scale for comparing  $T_{\rm b}$  is provided by the ion temperature  $T_{\rm i}$ , defined by

$$\frac{3}{2}kT_{i} \equiv \frac{1}{2}m\langle c^{2}\rangle.$$
(233)

An initial estimate for  $T_b$  is provided by adapting the formulae for the constant mean free time model (Section 18*d*):

$$kT_{\rm h} \approx kT_0 + \frac{1}{3}(m+m_0)W^2$$
, (234a)

where

$$W \approx a/\mu_0 v_1(g), \qquad \{mm_0/(m+m_0)\}g^2 = 3kT_0 + m_0 W^2.$$
 (234b)

Fig. 3 shows how a range of  $T_i$  can be covered using one value of  $T_b$ , the example being that of a rigid sphere interaction and a cold gas, for which  $m/m_0 = 1$ . We have plotted the ratio of calculated to converged values of transport coefficients as a function of  $T_b/T_i$ . It is clear that as long as we have  $T_b \approx T_i$  we can expect convergence of the successive approximations. On the other hand, if we have  $T_b/T_i \ll 1$ , as for example in one-temperature theories at high fields  $(T_b = T_0 \ll T_i)$ , there is no convergence.

Thus while there is some relationship between a properly chosen  $T_b$  and the ion temperature  $T_i$  they need not be equal, and  $T_b$  may be chosen to improve other aspects of the distribution function. Thus, for example, in the work of Lin *et al.* (1979*b*)  $T_b$  has been chosen to optimize the fit over certain energy regions, namely the 'tail' of the distribution function when inelastic processes occur with high energy thresholds. In the earlier work of Viehland and Mason (1975) the choice  $T_b = T_i$  was made. With this choice the expansion coefficient  ${}^0f^{(10)}$  must vanish (see Table 2). This so-called self-consistency condition provides one equation for determining  $T_b$  for a given value of  $E/n_0$ . In actual practice it is more convenient to take  $T_b$  as the independent parameter and to find the corresponding  $E/n_0$  from equation (233) with  $T_b = T_i$ . It is clear that such a choice of  $T_b$  is unnecessarily restrictive; for further discussion see Section 23.

In the following section, we consider expansions involving more than one basis parameter.

# 20. Polynomial Expansions: Gaussian Weight Function with Anisotropy and Drift

This type of expansion was introduced in the theory of swarms by Lin *et al.* (1979*c*) and was designated by them as a 'three-temperature expansion' (for earlier applications in other areas of kinetic theory see Note [17]). They used Hermite polynomials and carried out the calculations with small basis sets. The analysis given here differs from that of Lin *et al.* (1979*c*) insofar as the expansion parameters are constants, independent of the density gradient (see Section 23).

The expansion is most appropriate to high mass ratios, where the expansion of the previous section is no longer useful, and may be motivated with reference to the results for the quasi-Rayleigh gas obtained in Section 18b. It is interesting to note that Langevin (1905) also employed a gaussian with drift, although not in the context of a polynomial expansion.

The three b-parameters in this problem are the transverse and longitudinal 'temperatures'  $T_b^{(T)}$  and  $T_b^{(L)}$  respectively and the drift velocity parameter  $W_b$ , which is directed along the field direction (z axis). By defining

$$\boldsymbol{c}' = \left(\tau_{\rm T}^{\pm} c_x, \, \tau_{\rm T}^{\pm} c_y, \, \tau_{\rm L}^{\pm} (c_z - W_{\rm b})\right),\tag{235a}$$

where

$$\alpha^{2} \tau_{\rm T} = m/kT_{\rm b}^{({\rm T})}, \qquad \alpha^{2} \tau_{\rm L} = m/kT_{\rm b}^{({\rm L})}, \qquad (235b)$$

$$\alpha^2 = m/kT_{\rm h}, \qquad T_{\rm h} = \frac{1}{3}(2T_{\rm h}^{\rm (T)} + T_{\rm h}^{\rm (L)}), \qquad (235c)$$

$$2/\tau_{\rm T} + 1/\tau_{\rm L} = 3$$
, (235d)

we have the weight function

$$w(c) = (\tau_{\mathrm{T}}^2 \tau_{\mathrm{L}})^{\frac{1}{2}} \overline{w}(\alpha, c')$$
(236a)

and, in the terminology of Section 17, the basis sets

$$\Phi: w(c)\phi^{[\nu]}(\alpha c'), \qquad \Psi: \phi^{(\nu)}(\alpha c'). \qquad (236b)$$

Instead of  $T_b^{(T)}$  and  $T_b^{(L)}$ , one may take  $\alpha$  and one of the  $\tau$ 's as parameters.

The form of kinetic equations appropriate for this case are given by the formulae (191a)–(193b), with  $\mathcal{L}_{T}$  given by the formulae (196). With these equations, maximum

use of symmetry can be made and the basis polynomials need be functions of only two velocity variables  $c_{\rm T} = (c_x^2 + c_y^2)^{\frac{1}{2}}$  and  $c_z$ . Nevertheless, the calculations in this case are much more complicated than in the previous section. In general, no matrix element of  $\mathscr{L}_0$  or  $\mathscr{L}_{\rm T}$  vanishes so that the block tridiagonal structure of the equations of the previous section is lost, along with the advantages of backward substitution, and the calculation of the matrix elements of the collision operator are now more difficult. Thus we not only have three parameters instead of one, but they also occur in more complicated equations.

In the applications below we again use the cold gas model, as was indeed done by Lin *et al.* (1979c). Our main interest is to see how the choice of parameter influences the calculations so that inessential complications may be avoided in the future.

#### (a) Matrix elements

The calculation of the matrix element of the field term  $a \cdot \partial_c$  offers little difficulty in any representation.

Matrix elements of the collision operator J have been given in a Hermite polynomial representation by Lin *et al.* (1979*c*) and in a Burnett-function representation by Kumar (1980*a*). In either case, the general formulae contain many nested summations and the cross sections occur in two-dimensional integrals involving b-parameters, so that most of the calculation has to be done anew for each new set of parameters. Lin *et al.* (1979*c*) were able to go up to the fourth order, but it may be difficult to go much higher with these representations.

It is here that the use of the Fokker-Planck expansion for the adjoint collision operator J (Section 10) according to Section 17*a* introduces essential simplifications in the problem. The reason is not that the Fokker-Planck expansion is good at these mass ratios but that, without approximation, the matrix elements can be calculated by a shorter series. Further simplification comes from the appropriate form of kinetic equations used (see above) so that polynomials in only two variables  $c_{\rm T}$  and  $c_z$  may be used. The two-dimensional integrals obtained for the matrix elements have been calculated with a Gauss-Hermite-Laguerre quadrature. We found that a  $10 \times 5$  point formula yielded sufficient accuracy.

#### (b) Choice of basis parameters

The use of a drifted gaussian weight function is appropriate when the ion velocity distribution is mainly confined to a relatively small region away from the origin in the velocity space. The distance from the origin is related to the field strength. Similarly, the temperature parameters which determine the shape of the distribution localized in this region will also depend on the field strength. We thus have three b-parameters, which have to be chosen in relation to the field strength.

The most important parameters are  $W_b$  and  $\alpha^2 = m/kT_b$ . They can be estimated from the constant mean free time model in a way similar to that used for the isotropic weight function (cf. equations 234).

The anisotropy of w(c) around  $c = W_b$  may be estimated by appeal to quasi-Rayleigh gas expressions (Section 18b). Estimates are somewhat improved by replacing  $m_0/m$  by  $m_0/(m+m_0)$  and evaluating the coefficients at  $c_* = (\overline{w}_b^2 + 3kT_b/m)^{\frac{1}{2}}$ ; this is to compensate for approximations made in that model. However, these estimates cannot be critical, that is, it is not necessary that the weight function have exactly the same drift and anisotropy as the true distribution function. Both the one-temperature and two-temperature approximations are known to produce drift and anisotropy in calculated distributions. Their failure at high mass ratios and large fields shows only that it is difficult to produce large drifts and anisotropies, when none is initially present. Thus, to correct the situation at high mass ratios it would be sufficient if approximately right amounts of drift and anisotropy were introduced into the weight function. In other words, a given choice of b-parameters will be effective over a range of  $E/n_0$  values. Further, it seems very likely that anisotropy itself may not be so important. If a  $T_b$  is chosen properly then it will probably not matter what  $T_b^{(T)}$  and  $T_b^{(L)}$  are, particularly if  $T_b$  is greater than  $(T_1^{(T)}, T_1^{(L)})$ .

#### Table 3. Effect on convergence of choice of temperature and drift parameters in weight function

Here a hard-sphere cold gas model with a mass ratio  $m/m_0 = 2.5$  is used. The 'order' *n* of the calculation in the Burnett-function basis is defined by  $n = l_{max} = v_{max}$ . Converged values are  $W = 1.7069(a\lambda)^{\frac{1}{2}}$  and  $D_L = 0.2981(a\lambda)^{\frac{1}{2}}$ , with  $\lambda$  the mean free path. The parameter sets  $(W_b/W, T_b/T_i, T_b^{(T)}/T_b^{(L)})$  are  $\alpha = (1, 1, 0.586)$ ,  $\beta = (1, 1, 1)$ ,  $\gamma = (1, 1.5, 1)$  and  $\delta = (0.75, 1.5, 1)$ , with  $kT_i = \frac{1}{2}m\langle (c - W)^2 \rangle$ ,  $kT_1^{(T)} = \frac{1}{2}m\langle (c_z - W)^2 \rangle$  and  $kT_1^{(L)} = \frac{1}{2}m\langle c_x^2 \rangle$ ;  $T_1^{(T)}/T_1^{(L)} = 0.586$  is the converged value used in the set  $\alpha$ 

Order		$D_{\rm I}^{(n)}/D_{\rm I}$ for set						
n	α	β	γ	δ	α	$\tilde{\beta}$	γ	δ
2	0.9920	0.9919	0.9897	0.9883	1.187	1.168	1.238	1.193
3	0.9994	0.9998	0.9933	0.9951	0.992	0.989	1.015	0.902
4	0.9998	0.9996	0.9978	1.0008	1.018	1.026	1.023	1.028
5	0.9996	0.9995	0.9990	0.9988	0.998	0.995	1.004	0.986
6	1.0002	1.0002	0.9996	1.0000	1.000	1.006	1.001	0.989
7	1.0001	0.9998	0.9998	1.0002	1.000	0.999	$1 \cdot 001$	1.006
8	1.0001	1.0000	1.0000	0.9999	0.986	1.005	$1 \cdot 000$	0.997
9	$1 \cdot 0001$	1.0004	1.0000	1.0002	0.999	1.001	1.000	1.001

The above expectations were confirmed by calculations on a hard-sphere cold gas model with polynomial expansions to order n = 9 with  $n = l_{max} = v_{max}$ . Several mass ratios were used. The results for a mass ratio of 2.5 are presented in Table 3. It was found that the convergence becomes better as the mass ratio increases, provided suitable parameters are used. For  $m/m_0 \ge 4$  answers obtained with quite low values of *n* are already equal to the converged values to the required accuracy. For smaller mass ratios increasingly larger *n* values are required.

#### 21. Non-polynomial Expansions

As pointed out before (e.g. Section 17), the expected asymptotic behaviour of f(c) should be taken into account in the choice of basis sets. In particular, if a singularity is present or expected, the functions of the set should have the correct asymptotic behaviour near it. In most cases precise information of this kind is not available. One should then use functions which are flexible enough to represent arbitrary shapes in different regions. Examples of such functions are cubic splines and finite difference sets. The discussion in Sections 19 and 20 may be taken to mean that the sets based on gaussian weight functions are not very flexible in this sense.

The difficulty with the more general type of sets mentioned above is that matrix elements of the collision operator cannot be easily calculated for them. For this
reason only special cases, where the collision operator is reasonably simple, have been treated using such sets. Note that the sets mentioned above are non-polynomial; the splines are represented by polynomials in a given range, but they are not true polynomials.

The examples below show that, when applicable, such sets are capable of producing very high accuracy.

### (a) Modified Bessel functions and non-integral moments

This method was devised by Wannier (1953) for the case of a cold gas and an interaction potential  $\sim r^{-n}$ . In this case

$$\sigma(g,\chi) = \sigma(g_0,\chi)(g/g_0)^{\gamma}, \qquad \gamma = -4/n, \qquad (237a)$$

$$\int c^s J_l^0(f) \,\mathrm{d}\boldsymbol{c} = \kappa_l^{(s)} \langle c^{s+1+\gamma} \rangle, \qquad (237b)$$

$$\langle c^r \rangle = \int c^r f \, \mathrm{d}c \,,$$
 (237c)

where  $g_0$  is an arbitrary (scaling) constant and  $J_l^0$  is the *l*th spherical component of the cold gas collision operator (equations 113). The constant  $\kappa_l^{(s)}$  is defined by equation (237b) and is obtained as an integral over the angular distribution in the scattering.

In this case the moment equations obtained from the spherical harmonic decomposition (184a-c) may be analytically reduced to equations connecting moments  $\langle c' \rangle_0$ with respect to the function  $f_0$  only. The process of reduction determines new quantities  $\alpha$  and  $\beta$  in terms of the collision quantities  $\kappa_l^{(s)}$ . The equations for the unknown moments  $\langle c' \rangle_0$  have the form (Wannier 1953; Skullerud 1976)

$$\sum_{j=1}^{l+1} \alpha_j^{(l)} \langle c^{l-1+j(2+\gamma)} \rangle_0 = \beta^{(l)} .$$
(238)

The exponent in the moment is, in general, non-integral because  $\gamma$  is.

One can now expand  $f_0$  in any basis set

$$f_0(c) = \sum_i \xi_i \,\varphi_i(c) \,, \tag{239}$$

substitute in equation (238) and solve the equations for  $\xi_i$ . The use of modified Bessel functions for  $\varphi_i$  in the cold gas case, with  $m/m_0 = 1$  and a hard-sphere interaction, was suggested by Wannier (1953). These functions give the right asymptotic behaviour for both large and small c, and the expected logarithmic singularity at  $c \to 0$  is correctly represented. This in turn results in a drift velocity correct to five significant figures,  $W = 1.1467(a\lambda)^{\frac{1}{2}}$ , from the fifth approximation onwards. A Burnett-function expansion gives only four figures correctly even in the tenth approximation ( $l_{\max} = v_{\max} = 10$ )  $W^{(10)} = 1.1461(a\lambda)^{\frac{1}{2}}$ . One of us (H.R.S.) has tried several other basis sets for this problem, such as gaussians with different widths, sometimes combined with modified Bessel functions and polynomial expansions, and cubic B-splines. When the asymptotic behaviour is correctly represented the convergence is always good. The results obtained by this method have been used as 'bench marks' against which the results from other approximation schemes may be tested. The assumption or hope is that an approximation scheme which is good for this model, and is also applicable to a real interaction situation will give good results for the latter also. The method described here, however, cannot be applied to real systems for the reasons pointed out earlier in this section.

Table 4 compares the results obtained in this way with those from a Burnettfunction expansion. The Burnett functions were obtained from an isotropic weight function with an 'optimal' choice of temperature  $kT_b = kT_i = 3m\langle c^2 \rangle$ . In the Wannier-type expansion the functions  $\varphi_i$  were of the form

$$\varphi_i = c^i \mathcal{K}_0(mc^2/2a\lambda), \qquad (240)$$

with  $K_0$  the modified Bessel function of order zero. The calculations are for a hardsphere cold gas model with  $m/m_0 = 1$ , and  $\lambda = (n_0 \sigma)^{-1}$  is the mean free path.

# Table 4. Comparison of successive approximations in two different expansion schemes

Here the results obtained from ( $\alpha$ ) an optimum Burnett-function basis are compared with those from ( $\beta$ ) a Wannier-type basis (equation 240). A hard-sphere cold gas model with a mass ratio  $m/m_0 = 1$  is used. The parameter *n* determines the size of the basis set in the two expansions. For the Burnett-function basis  $n = I_{\text{max}} = v_{\text{max}}$  and the corresponding set is used for the Wannier-type expansion. The normalization is provided by  $W = 1.1467(a\lambda)^{\ddagger}$ ,  $D_L = 0.2202(a\lambda^3)^{\ddagger}$  and  $D_T = 0.3202(a\lambda^3)^{\ddagger}$ , with  $\lambda$  the mean free path. The values for  $D_L^{(2)}$  and  $D_T^{(2)}$  are too crude to be meaningful; between n = 6 and 10 the change in numbers is very small

Order n	$W^{(n)}/W$		$D_{\mathrm{L}}^{(n)}/D_{\mathrm{L}}$		$D_{\mathrm{T}}^{(n)}/D_{\mathrm{T}}$	
	α	β	α	β	α	β
2	0.9692	0.9923				
3	0.9985	0.9989	0.876	0.998	1.016	0.992
4	0.9963	0.9998	1.023	0.998	1.004	0.996
5	0.9986	1.0000	0.991	1.003	1.001	0.997
6	0.9989	1.0000	1.000	1.000	1.000	0.998
10	0.9997	1.0000	1.000	1.000	0.999	1.000

#### (b) Special methods for electron transport

The quasi-Lorentz gas model (Section 18*a*) is fully satisfactory for electron transport calculations, when only elastic collisions are of importance. When inelastic collisions occur, the form of the collision operator is still quite simple, but analytical solutions to the transport problem cannot be obtained.

If the collisional energy transfer rate is small compared with the momentum transfer rate, a two-term expansion of the velocity distribution in spherical harmonics will still be sufficient and, as in the quasi-Lorentz gas case, the kinetic equation can be reduced to one equation for the isotropic part  $f_0(c)$  of the velocity distribution. This difference-differential equation can be solved by standard finite difference methods (see e.g. Huxley and Crompton 1974; Kitamori *et al.* 1978; Tagashira *et al.* 1978).

If the collisional energy transfer rate is large, as is the case over certain energy ranges in some molecular gases, the velocity distribution may become quite anisotropic, and more terms must be retained in the spherical harmonic decomposition of the equations. A reduction of the system of equations to one equation for  $f_0(c)$  can then no longer be easily performed, and one will have to revert to expansions involving the full distribution function f(c).

A general treatment of the electron problem in a Burnett-function representation has been given by Lin *et al.* (1979b).

A different approach, using a cubic B-spline expansion of the spherical harmonic components  $f_i(c)$  of the velocity distribution, has been used by L. C. Pitchford (personal communication). The cubic B-splines are constructed by joining together cubic polynomials defined in adjoining intervals. They are continuous functions with continuous first and second derivatives, and are nonzero only in four adjoining intervals (see e.g. Prenter 1975). The B-spline expansion will still lead to a block tridiagonal system of linear equations (cf. equation 184a), but the subdiagonal blocks will be band-diagonal, and not strictly diagonal as in the Burnett-function expansions. This does not lead to substantial computational problems, however, as band-diagonal matrices are quite easily inverted.

The B-spline expansions offer advantages especially when an accurate representation of the high energy tail of the distribution function is wanted. The convergence properties of B-spline expansions are, in general, remarkably good and they do not depend critically on any assumed form of asymptotic behaviour. The basis set sizes needed in B-spline representations are large compared with 'normal' Burnett-function basis set sizes, but the disadvantage of this is compensated by a considerably easier matrix element evaluation.

A finite element approach to electron transport calculations, without any spherical harmonic expansion, has also been reported by Kleban and Davis (1977, 1978), but this approach seems not to offer any advantages compared with B-spline and Burnett-function methods (Lin *et al.* 1979b).

### 22. Computer Simulations

In computer simulations, the dynamic behaviour of one or several ions is followed through a succession of collisions and free paths. Velocity distributions, velocity moments and spatial moments are, in general, time-dependent quantities formed by averaging the behaviour of a large number of independent ions. If stationary transport can be assumed, as in drift and diffusion calculations, the same results are found if time averages over the behaviour of one ion are formed, which is usually more convenient.

The dynamic behaviour is modelled by choosing stochastically the lengths of the free paths, the velocities of the neutral collision partners and the outcome (scattering angles, energy loss) of the collisions, in agreement with probability distributions obtained from the prescribed scattering cross sections and neutral velocity distributions. The modelling can be made numerically exact, avoiding approximations involved in numerical integrations, by the use of a 'null-collision technique', described by Lin and Bardsley (1977).

The simulation approach—quite often classified as experiment by theoreticians and as theory by experimentalists—is closely related to so-called free path methods in transport theory. These methods are, in dilute gases, fully equivalent to a Boltzmann equation approach, as shown in our context, for example, by Fahr and Müller (1967). The main advantages of the simulation approach are the conceptual simplicity, the ease with which correlation functions and other 'difficult' averages can be calculated, and the appearance of safe error estimates in the form of standard deviations. Drawbacks are the need for quite detailed differential cross sections  $\sigma(c, \chi)$ , and the slow improvement of the accuracy (proportional to  $[\text{time}]^{\frac{1}{2}}$ ) with increased computational effort.

A good exposition of the simulation method as applied to ion transport problems is given by Lin (1976), while applications to electron transport problems have been discussed very satisfactorily by Braglia (1977), and Braglia and Baiocchi (1978).

### 23. Discussion

Let us begin by recapitulating the main points:

(1) Section 4 gives the derivation of kinetic equations and identifies the transport coefficients as moments of the respective functions  $f^{(k)}$  which are solutions of these equations. Limitations of the theory are pointed out in Section 5 and Note [11].

(2) The kinetic equations were obtained by eliminating the density gradients. Their solutions are functions of c and E only. (In Sections 15–20, we have used f(c) as a generic symbol for the functions  $f^{(k)}(c)$  and it is not necessarily the distribution function itself.)

(3) The business of solving the equations is separated entirely from the method of deriving them.

(4) The choice of basis sets in expansions is an auxilliary to the process of solution. The weight function chosen may in some sense represent the true distribution function but that may be likened to a scaffolding which resembles the structure it helps to build. Some of the parameters in the weight function will therefore be related to some physical quantities, but they are not, in general, precisely those quantities.

(5) The examples given in previous sections are for a cold gas hard-sphere model for different mass ratios. They are intended to be only illustrative. We point out the features that are likely to survive in the calculations for realistic cross sections.

We believe that we have outlined an economical path through the complexities of the problem from the conceptual as well as the computational point of view. It is, of course, possible to obtain results without following this path, but whenever that has been done, it has led to some complications. We illustrate this remark by an example:

Suppose we make a polynomial expansion of the complete space-time dependent distribution function, that is,

$$f(\mathbf{r}, \mathbf{c}, t) = n(\mathbf{r}, t) w(\alpha, c) \sum_{\mathbf{v}} \phi^{[\mathbf{v}]}(\alpha c) f^{(\mathbf{v})}(\mathbf{r}, t), \qquad (241a)$$

where

$$f^{(\mathbf{v})} = \langle \phi^{(\mathbf{v})}(\alpha \mathbf{c}) \rangle.$$
 (241b)

The quantities of physical interest, the average velocity  $\langle c \rangle$  and mean ion energy  $\frac{3}{2}kT_i = \frac{1}{2}m\langle c^2 \rangle$ , now depend upon space and time. They may be calculated from equation (241b) by setting  $\mathbf{v} = (0, 1, m)$  and (1, 0, 0) respectively (cf. Table 2). Now if one argues that the basis parameter  $T_b$  is equal to  $T_i$ , then  $\alpha^2 = m/kT_i$  and we have

$$3 = \alpha^2 \langle c^2 \rangle. \tag{242}$$

In the hydrodynamic regime, all space-time dependence is carried by n(r, t) and its derivatives, and we write

$$f^{(\mathbf{v})}(\mathbf{r},t) = \sum_{k=0}^{\infty} {}^{k} f^{(\mathbf{v})} \odot (-\nabla)^{k} n, \qquad (243a)$$

$$T_{\mathbf{i}}(\mathbf{r},t) = n^{-1} \sum_{k=0}^{\infty} T_{\mathbf{i}}^{(k)} \odot (-\nabla)^k n.$$
 (243b)

Equation (242) is equivalent to  $f_0^{(10)} = 0$ , and by equation (243a) we have the constraints

$${}^{k}f_{0}^{(10)} = 0, \qquad k = 0, 1, 2, ...,$$
(244)

which provide the means for determining the coefficients  $T_{i}^{(k)}$  in equation (243b).

The transport equations are obtained by substituting the expansion (241a) into Boltzmann's equation, expanding all quantities, including  $\alpha$ , in gradients of n(r, t)and equating coefficients of  $(\nabla^k)n$ . This is a possible scheme and has actually been implemented for k = 0, 1 by Viehland and Mason (1978)\* for the single b-parameter situation outlined above and by Lin et al. (1979c) for several b-parameters. Their notation is, of course, different. There are three points to be made: (1) no matter what notation is used the fact that  $\alpha$  of the weight function has to be expanded in terms of  $\nabla n$ , generates lengthier expressions at all levels; (2) the constraints (244) have to be imposed at all levels of approximation; (3) most importantly, one loses the flexibility of being able to adjust the parameter  $\alpha$ , which has been found so important in computations (see e.g. Lin et al. 1979b; Forsth 1979). Some criterion for relating  $T_{\rm b}$  to  $E/n_0$  has, of course, to be provided, but this may be different for different problems; for example, when inelastic collisions occur, it was found by Lin et al. (1979b) that a  $T_{\rm b}$  which gave a good fit to the distribution function in regions of dominant energy exchange provided optimal convergence of successive truncation approximations.

These remarks concern accurate calculations with large basis sets. The original motivation for introducing a  $\nabla n$  dependence in  $\alpha$  seems to have been to obtain a justification for qualitative formulae, such as the generalized Einstein relations [10]. For these purposes and low order calculations, the approach has some advantages.

With regard to future applications we can sum up our findings as follows.

(1) Formulae for drift and diffusion are given by equations (176), (180), (181), (184), (186), (189), (191), (192) and (193) and in Table 2; they are to be used as indicated in conjunction with methods suited to particular representations.

(2) Accuracies comparable with or better than those from the currently available experimental data (0.1%) for K and 1% for D) may be achieved from the best methods. Actual calculations will need larger basis sets than have been previously used. The difficulties with the computation time, reported in earlier work, can be largely overcome with proper management as outlined above.

<sup>\*</sup> In this case equation (243b) takes the form  $T_i = T_i^{(0)} - T_i^{(1)} \cdot \nabla n$ . Since the only constant vector in the problem is E we have  $T_i^{(1)} \sim E$ , so that we may write  $T_i = T_i^{(0)}(1 - \lambda E \cdot \nabla n)$ . That is to say, the scalar temperature  $T_i$  can depend on the density gradient only through its component  $\partial n/\partial z$ in the field direction. Hence, the quantities  $\lambda_{\pm}$  in equations (33), (34) and (35) of Viehland and Mason (1978) should vanish identically.

(3) Gaussian weight functions provide basis sets adequate for most purposes if the cross sections are well behaved. We have indicated how the parameters in the basis sets are to be chosen, and the conditions under which these methods are applicable.

(4) With polynomial moments, that is, when the set  $\Psi$  of Section 17 consists of functions c, cc, ..., the use of the adjoint operator (Section 17*a*) will make it possible to compute the collision operator matrix elements for many different types of functions in the set  $\Phi$ . Thus one is no longer constrained to use gaussian-based sets  $\Phi$ . The same computational method will also be suitable in the case of more unruly cross sections such as those for the cases of charge transfer and electron-mercury interactions.

# Part V. The treatment of reactions

# 24. Introduction (V)

In the discussion of drift and diffusion calculations in Part IV it was assumed that the number and properties of the charged particles were not changed in collisions with neutrals. In this part, we remove this restriction and allow reactive processes to take place. The term 'reactive processes' is here to be interpreted in a wide sense; it includes not only processes where a change in the chemical composition of the constituents takes place, but also processes such as electron impact ionization and attachment, and positron annihilation in gases (Massey 1976; Campeanu and Humberston 1977). As in Part IV, we consider only homogeneous electrostatic field conditions, with no magnetic field present.

Our discussion will be restricted to *unidirectional reactions* and *systems in chemical equilibrium*, as these two cases can be treated within a hydrodynamic framework. The unidirectional reactions are irreversible ones of the type  $A+B \rightarrow C+D$ , and it is supposed that only the transport properties of the charged species A with the distribution function f(c) are measured. Examples of such reactions are the loss and attachment type of reactions involving electrons lost by capture to form negative ions, or positrons lost by annihilation. For this type of reaction, we will be primarily interested in determining the asymptotic reaction rate  $\alpha$ , defined by equations (4) and (8a). On the other hand, systems in chemical equilibrium are governed by reversible reactions of the type  $A+B \rightleftharpoons C+D$ . The overall reaction rates are zero, and the interest is primarily in finding the drift velocities and diffusion coefficients describing the transport not of the particles but of the *electric charge*, and the relative numbers of the different charge-carrying species.

A general reacting system with different charged species i, j = 1, 2, ... all present in trace amounts only, can be described by a system of kinetic equations of the form

$$(\partial_t + \boldsymbol{c} \cdot \partial_r + \boldsymbol{a}_i \cdot \partial_c + J_i^{(\text{PC})} + J_i^{(\text{RL})}) f_i(\boldsymbol{n}, \boldsymbol{c}, t) - \sum_{j \neq i} J_{ij}^{(\text{RG})} f_j(\boldsymbol{n}, \boldsymbol{c}, t) = 0, \quad (245)$$

where  $J_i^{(PC)}$  is the particle-conserving or nonreactive part of the collision operator,  $J_i^{(RL)}$  represents reactive losses, summed over all reactive channels depleting the *i* species, and  $J_{ij}^{(RG)} f_j(c)$  represents 'reactive gain', i.e. the influx of particles *i* with velocity *c* from reactive *i*-neutral collisions, integrated over all initial *j* velocities *c'*. Expressions for the collision operator with reactive terms included are given in the following paper by Kumar (1980*a*).

In the case of unidirectional reactions, the reactive gain term in the equations (245) is zero, and the determination of the asymptotic behaviour of  $f_i(\mathbf{r}, \mathbf{c}, t)$  can be formulated as an eigenvalue problem. This will be considered in the next section (25).

For systems in chemical equilibrium, all the reacting species will asymptotically have the same distribution in configuration space, and the kinetic equations in the hydrodynamic limit can be found by using this as an ansatz in the equations (245), together with the usual expansion in powers of the spatial gradients. This will be considered in Section 26.

The solution of the equations (245), in the hydrodynamic limit, is considerably more demanding in terms of computer time than the solution of the similar equations without reactive terms, but not prohibitively so. More serious for practical calculation on real ion-molecule systems is the nearly complete lack of reasonable inelastic and reaction cross section data, needed as input for the transport calculations. However, a lot of effort is presently being invested in improving this situation (Miller 1976), and it is to be hoped that this will increase the usefulness of a transport theory for reacting ion systems.

## 25. Unidirectional Reactions

In the case of unidirectional reactions, one charged species only is involved in the transport problem, and the formal description presented in Sections 2 and 4 applies. There we have noted that the presence of reactions not only leads to the introduction of the reaction rate as an additional transport coefficient, but also makes invalid the usual association of the drift velocity with the average velocity and of the diffusion tensor with the velocity autocorrelation function. However, the modification to these transport coefficients due to the reactions can be found, after the reaction rate has been determined, by using essentially the same methods as for nonreacting systems. This was discussed in some detail in the last part of Section 4, and we will therefore here only consider the problem of calculating the reaction rate.

We assume the reactive gain term  $J^{(RG)}$  in the equations (245) to be zero, and integrate over dr to obtain an equation of the form

$$\partial_t f(\boldsymbol{c}, t) + \mathscr{L} f(\boldsymbol{c}, t) = 0, \qquad (246a)$$

$$\mathscr{L} \equiv \boldsymbol{a} \cdot \partial_c + J^{(\text{PC})} + J^{(\text{RL})}.$$
(246b)

The linear operator  $\mathscr{L}$  will be assumed to generate a complete set of orthonormal eigenfunctions  $f_i(c)$  with associated eigenvalues  $\lambda_i$ :

$$\mathscr{L}f_i(\boldsymbol{c}) = \lambda_i f_i(\boldsymbol{c}), \qquad \int w(\boldsymbol{c}) f_i(\boldsymbol{c}) d\boldsymbol{c} = \delta_{ij}. \qquad (247a, b)$$

We make no attempt to justify this assumption. It can be shown to be correct with certain model collision operators, but is certainly incorrect when runaways can occur. For the sake of consistency the weight function w(c) must be given by the eigenfunction belonging to the lowest eigenvalue  $\lambda_0$ ,

$$w(\mathbf{c}) = \{f_0(\mathbf{c})\}^{-1}.$$
(248)

In terms of the eigenfunctions  $f_i(c)$  the general solution of equation (246a) can be written in the form

$$f(\boldsymbol{c},t) = \sum_{i} \beta_{i} f_{i}(\boldsymbol{c}) \exp(-\lambda_{i} t) \xrightarrow[(t \to \infty)]{} \beta_{0} f_{0}(\boldsymbol{c}) \exp(-\lambda_{0} t).$$
(249)

The hydrodynamic (i.e. long-time) behaviour is determined by the lowest eigenvalue  $\lambda_0$  (assumed distinct from all others), which is equal to the reaction rate,  $\alpha = \lambda_0$ .

The determination of  $\lambda_0$  from equation (247a) is in principle a standard eigenvalue problem, which can be solved by well-known methods. We will first sketch a general—and usually also quite laborious—way of proceeding, related to, but not equivalent to, the matrix methods for determining energy eigenvalues in quantum mechanics. However, when the reactions are 'weak', often a simpler perturbational approach can be used, and a scheme for this will be outlined subsequently.

## (a) Matrix eigenvalue method

To transform equation (247a) to a matrix eigenvalue problem, we first expand f(c) in some basis set  $\varphi^{(\nu)}(c)$  and then form moment equations by multiplying with moment functions  $\psi^{(\nu')}(c)$  and integrating over dc, in the same way as explained in Section 17. We thus arrive at a set of *homogeneous* equations for the expansion coefficients  $\xi_{\nu}$ , analogous to equations (199a),

$$\sum_{\nu'=1}^{\nu_{\max}} \xi_{\nu'} \{ (\psi^{(\nu)}, \mathscr{L} \varphi^{(\nu')}) - \lambda(\psi^{(\nu)}, \varphi^{(\nu')}) \} = 0.$$
 (250)

This is an overdetermined system of equations, and has a solution only if the determinant is zero:

$$\det\{(\mathbf{\psi}, \mathscr{L}\mathbf{\varphi}) - \lambda(\mathbf{\psi}, \mathbf{\varphi})\} = 0.$$
(251)

The 'secular equation' (251) is a  $v_{max}$ -order algebraic equation for the eigenvalue  $\lambda$ . Its solution thus gives  $v_{max}$ , in general different, eigenvalues. We are only interested in the lowest of these.

Most textbooks on numerical analysis describe methods for solving matrix eigenvalue problems, and working computer programs are available as publications and in computer libraries. Two points are, however, worth noting: Firstly, most methods assume orthonormal basis sets  $(\psi^{(\nu)}, \varphi^{(\nu')}) = \delta_{\nu\nu'}$ . To avoid an orthogonal transformation, it is therefore convenient—and more so here than in the foregoing Part IV—to start out with orthonormal basis sets from the beginning; e.g. with normalized Burnett functions. Secondly, quite a few methods assume the matrix  $(\psi, \mathcal{L}\varphi)$  to be symmetric (or, if complex functions are used, self-adjoint). The field term  $a \cdot \partial_c$  will, however, always induce asymmetries, regardless of the basis set, and the last-mentioned group of methods can therefore not be used in general.

The choice of basis set, and the parameters occurring in it, is governed by essentially the same considerations as in Part IV. Ideally, the size of the basis set and the basis set parameters should be varied until converged values for the lowest eigenvalue are obtained. Non-converged values are of little use, as there is no extremum theorem showing the sign of the deviation from the true value for non-self-adjoint eigenvalue problems.

## (b) Zero-field eigenvalue method

At zero field, only the collision operator J remains in the linear operator  $\mathcal{L}$ . It can be made self-adjoint by extracting a Maxwellian  $w(\alpha c)$  at the neutral gas temperature as a weight function (Robson 1976a, 1979),

$$\int \psi^{(\nu)}(c) J(w \,\psi^{(\nu')}(c)) \,\mathrm{d}c = \int \psi^{(\nu)}(c) J(w \,\psi^{(\nu')}(c)) \,\mathrm{d}c \,. \tag{252}$$

With self-adjoint operators, the approximate solution of the eigenvalue problem obtained from the use of a finite basis set or a set of trial functions will always give an *upper* limit to the lowest eigenvalue, as is well known.

The solution of equation (251), using  $w(\alpha c)$  as weight function, will thus in this case give useful information about  $\lambda_0$  even with a small basis set. Further, one is no longer restricted to the use of a linear combination of trial functions, i.e. a basis set expansion, but may alternatively use a nonlinear variational approach, as discussed by Robson (1976a, 1979).

The zero-field problem is, of course, formally the same whether the test particles are charged or not. Recently, a theory of 'hot atom reactions' has been presented by Robson *et al.* (1978), with a more elaborate discussion of what has here been classified as the 'zero-field eigenvalue method'. The theory also finds application to electron attachment in molecular gases; a comprehensive analysis of this phenomenon in the zero-field Cavalleri experiment (Huxley and Crompton 1974) has been given by Ness (1977), who considers 'diffusion cooling', 'attachment cooling' and cross effects.

## (c) Perturbation method

The reactions can quite often be classified as 'weak', in the sense that the presence of reactions does not greatly influence the form of the velocity distribution. The reaction part of the collision operator can then be treated by perturbation methods, as will be shown below, and this considerably reduces the computational efforts needed for the determination of the reaction rate.

If the influence of the reactions on the form of the velocity distribution is totally neglected, as is common practice in neutral chemistry calculations, the reaction rate is obtained directly as an integral over this unperturbed velocity distribution. A reaction theory using these assumptions, in a Burnett-function representation, has been presented by Viehland and Mason (1977).

In a more general perturbation expansion, which will allow us to proceed beyond the infinitesimally weak-reaction assumption, we may formally associate the reactive loss collision operator with a smallness parameter  $\varepsilon$  (which in the end is put equal to 1), and expand both velocity distribution and reaction rate in powers of this parameter:

$$\mathscr{L} = \boldsymbol{a} \cdot \partial_{\boldsymbol{c}} + J = \mathscr{L}^{(0)} + \varepsilon J^{(\mathrm{RL})}.$$
(253a)

$$f(\mathbf{c}) = f^{(0)}(\mathbf{c}) + \varepsilon f^{(1)}(\mathbf{c}) + \varepsilon^2 f^{(2)}(\mathbf{c}) + \dots,$$
(253b)

$$\alpha \equiv \lambda_0 = \varepsilon \alpha^{(1)} + \varepsilon^2 \alpha^{(2)} + \dots$$
 (253c)

The zeroth order contribution to the reaction rate is by definition zero. Further, the functions  $f^{(i)}(c)$  should fulfill the normalization and self-consistency condition

$$\int f^{(i)}(\boldsymbol{c}) \, \mathrm{d}\boldsymbol{c} = \delta_{i0} \,. \tag{254}$$

Insertion of the equations (253) into (247a) gives, on equating the coefficients of  $\varepsilon^{j}$  individually to zero, a system of equations of the form

$$\mathscr{L}^{(0)}f^{(j)}(\mathbf{c}) = \{\alpha^{(1)} - J^{(\mathrm{RL})}\}f^{(j-1)}(\mathbf{c}) - \sum_{i=2}^{j} \alpha^{(i)}f^{(j-i)}(\mathbf{c}).$$
(255)

Integration of this equation gives, using the normalization conditions (254) on the  $f^{(j)}$ 's and the particle-preserving property of  $\mathscr{L}^{(0)}$ , an expression for  $\alpha^{(j)}$  in terms of  $f^{(j-1)}$ :

$$\alpha^{(j)} = \int J^{(\mathrm{RL})} f^{(j-1)}(c) \,\mathrm{d}c \,. \tag{256}$$

The equations (255) and (256) are in a form equivalent to the drift and diffusion equations in Section 16, and can be solved to successively higher orders with exactly the same methods as described in Part IV. One simplification, however, is worth noting:  $J^{(RL)}$  is spherically symmetric and all the  $f^{(j)}$ 's thus have the same cylindrical symmetry, while the distribution functions occurring in the diffusion problem have different symmetries due to the vector form of the inhomogeneous term. It may be noted at this point that endothermic reactions will often take place only in the high energy tail of the velocity distribution. Here, there will be very few particles, and the reactions may easily disturb the velocity distribution appreciably, making the perturbation approach a doubtful procedure in some cases (to be tested by the calculations in the actual case). On the other hand, exothermic reactions (for nonresonant processes) tend to take place more uniformly over the whole distribution, and drastic (i.e. order-of-magnitude) changes in the distribution due to reactions are less likely to occur, increasing the chances of a successful perturbation approach.

The methods described in subsection (a) and here have been applied to the recently demonstrated phenomenon of 'attachment cooling' by Crompton *et al.* (1979). For discussions of ionization and attachment see the papers by Taniguchi *et al.* (1977; 1978*a*, 1978*b*) and Sakai *et al.* (1979) and the references quoted by them.

### 26. Systems in chemical equilibrium

The stationary transport of a multicomponent system in chemical equilibrium can be formally treated very much in the same way as the transport of a one-species system, outlined in Section 4. To attain this formal equivalence, it is only necessary to sum over all charged species to obtain the density and velocity distributions of the charges, regardless of charge carriers.

For the sake of simplicity, we consider here only the lowest level kinetic equation, i.e. the one determining the drift velocity. This equation may be obtained (compare equation 180a) by averaging equation (245) over  $\mathbf{r}$  and assuming  $\partial/\partial t = 0$ :

$$(a_i \cdot \partial_c + J_i^{(\text{PC})} + J_i^{(\text{RL})})f_i(c) + \sum_{j \neq i} J_{ij}^{(\text{RG})}f_i(c) = 0.$$
 (257)

The charge velocity distribution f(c) is given by

$$f(c) = \sum_{i} f_i(c).$$
(258)

Moment equations can be formed in the usual way by expanding f(c) in a basis set and integrating the Boltzmann equation with suitable moment functions. The dimensions of basis and moment function sets, however, will have to be increased to encompass the whole 'multispecies space'.

We thus insert into the Boltzmann equation an expansion

$$f(\boldsymbol{c}) = \sum_{\boldsymbol{v}} \xi^{(\boldsymbol{v})} \, \varphi^{(\boldsymbol{v})}(\boldsymbol{c}) \equiv \sum_{i} \sum_{\boldsymbol{v}} \xi^{(\boldsymbol{v})}_{i} \, \varphi^{(\boldsymbol{v})}_{i}(\boldsymbol{c}) \tag{259}$$

and use moment functions  $\psi^{(v)}(c) \equiv \psi_i^{(v)}(c)$  to obtain linear algebraic equations of the form

$$\sum_{\mathbf{v}'} \mathscr{L}^{\mathbf{v}\mathbf{v}'} \xi^{(\mathbf{v}')} = 0, \qquad (260a)$$

where the matrix elements  $\mathscr{L}^{vv'}$  are given by

$$\mathscr{L}^{\nu\nu'} \equiv \mathscr{L}^{\nu\nu'}_{ii'} = \delta_{ii'} \int \psi_i^{(\nu)}(a_i \cdot \partial_c + J_i^{(PC)} + J_i^{(RL)}) \varphi_i^{(\nu')} \, \mathrm{d}c + \int \psi_i^{(\nu)} J_{ii'}^{(RG)} \varphi_{i'}^{(\nu')} \, \mathrm{d}c \,.$$
(260b)

Equation (260a) should be solved with the normalization condition  $\int f(c) dc = 1$ . The only essential difference between this equation and the one-species mobility equation is the *i*-dimensional summation. The symmetry in c space is not changed and, in particular, in a spherical harmonic representation the tridiagonality in the *l* index is preserved. In a Burnett-function representation, the equations can thus be reduced in effective size and solved as outlined in Section 19.

From the solution of equation (260a), both the partial velocity distributions  $f_i(c)$ , normalized to the mole fraction  $x_i$ , and the total velocity distribution f(c), yielding the drift velocity, are found.

The hydrodynamic limit assumption that is implicit in omitting the time derivative from equation (257) is more serious here than in the one-species transport theory. In the latter case, the hydrodynamic assumption implies time scales (and corresponding length scales) that are long compared with typical energy-relaxation times, while, in the present case, the time scales must also be long compared with the mean time between reactions; a condition which is often not fulfilled experimentally. If the reactions are slow on the energy-relaxation time scale, one may, however, break the description of the system up in two parts, firstly an uncoupled treatment of the different species as undergoing unidirectional reactions, and then a purely hydrodynamic (i.e. non-Boltzmann) description of the coupled system.

# Part VI. Concluding remarks

The reader interested in calculating drift and diffusion will find a summary of methods and results in Section 23. If calculation of higher transport coefficients is contemplated, appropriate kinetic equations may be taken from Section 4 and solved by the methods discussed in Part IV. The manifestations of their effects in experiments have to be carefully disentangled from those due to non-hydrodynamic phenomena and time-dependent transport coefficients (Section 3). The same methods apply for calculations in the presence of (1) inelastic effects due to the structure of gas atoms (the appropriate collision operator for this case is treated in Section 14); (2) mixtures of neutral gases (Note [15]); and (3) loss- or attachment-type reactions (Section 25).\* Greater modifications are needed when different charged species or ions with internal structure are present (Section 26). The calculation of reaction rates is discussed in Sections 25 and 26.

Most of the theory outlined in this paper is for an infinite medium, with no boundaries. This is an idealization, and proper analysis of experiment requires that boundaries be taken into account, which in turn requires a proper kinetic treatment of the boundary layer. Sometimes, these effects can be dealt with by using 'effective' transport coefficients; this was briefly touched upon in Section 7.

Computer simulations are an effective means of obtaining physical insight into all aspects of swarm behaviour. They can also be used to obtain accurate values of transport coefficients (Section 22).

The mathematically inclined reader will find a discussion: of the limitations of hydrodynamic theories in Section 5; of the problem of finding accurate solutions of kinetic equations in Sections 17–21; of the properties of the collision operator in Part III; of the properties of the three-dimensional translation operator and the corresponding Taylor series in Appendix 3.

The appended Notes will give some idea of how the work stands in relation to special treatments of the problems considered here and in the broader context of kinetic theory.

The problem we have treated in this paper is that of calculating the transport properties from given cross sections, which may be specified by giving an interaction potential. The inverse problem, that of finding the potentials or cross sections from given transport properties, is perhaps of greater practical interest. While the solution of the direct problem is unique, that of the inverse problem is not. The ambiguities in the solution of the inverse problem are resolved in various ways (Elford 1972, Section 2.2c; Huxley and Crompton 1974, Ch. 13; Milloy *et al.* 1974, 1977; Viehland *et al.* 1976; Gatland *et al.* 1978; Maitland *et al.* 1978). It will be seen from these discussions that the greater the accuracy in solving the direct problem the better it is for the solution of the inverse problem, although some ambiguity will always be present.

The problems that need further elaboration are the problems involving boundaries, charged particles with internal structure and many species of reacting charged particles. Methods which may be used in these investigations have been pointed out.

Further afield, many problems have been treated in the presence of weak high frequency fields. These treatments can be generalized to the situation where a strong

\* The kinetic theory part of the treatment of positrons in gases (Massey 1976; Campeanu and Humberston 1977) may well be improved by use of these methods.

electrostatic field is present along with a superimposed weak oscillating electric field, by replacing the collision operator J occurring in these treatments by the operator  $a \cdot \partial_c + J$ . Similarly, the treatments of processes involving large density gradients can also be generalized. In all such cases, attention has to be paid to the time scales in the processes involved to ensure that the hydrodynamic or quasi-hydrodynamic description can be applied.

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### Notes

[1] History. Kinetic theory is particularly well served by studies of a historical nature. Among the works of a general nature we mention those by Brush (1972) and Truesdell (1968). Of more immediate interest will be the historical remarks by Uhlenbeck and Ford (1963), Chapman and Cowling (1970) and Koga (1970). Specifically for the subject of this paper, systematic historical comments may be found in the texts by Huxley and Crompton (1974) and McDaniel and Mason (1973). For greater detail about recent history, see Kumar and Robson (1973) and Lin *et al.* (1979b). A shorter review covering many of the points discussed in the present paper was given by Skullerud (1977).

[2] Computer simulations or Monte Carlo methods. These methods first came into prominence in connection with the kinetic theory of liquids and that is still the most common association in kinetic theory (Watts and McGee 1976; Berne 1977). The technical problems in simulating gases and swarms are, however, somewhat different. The first such simulation seems to have been made by Yarnold (1947), in connection with a discharge-related problem. An important early application by R. W. Hamming was reported in Wannier's (1953) paper. Itoh and Musha (1960) were the first to simulate electron drift. The null-collision method was introduced by Skullerud (1968, 1973), and improved by Lin and Bardsley (1977). For a comparison between the Boltzmann equation and Monte Carlo calculations in specific cases, see Taniguchi *et al.* (1977) and Reid and Hunter (1979). Other references are given in Section 22. That the computer simulations may be regarded as a way of solving the Boltzmann equation itself has been argued by Bird (1970) in the context of rarefied gas dynamics.

There are three distinct sets of ideas involved in the topics mentioned above: the first is that of the molecular dynamics simulations of liquid theory which give information on both the equilibrium and nonequilibrium properties; the second concerns the so-called 'straight' Monte Carlo simulations, which sample the equilibrium configuration space and yield only the equilibrium properties; and the third is that of the simulations used for the problems considered in this paper which give the transport properties for dilute systems.

[3] Accuracy of present day experiments. Discussions of the problems involved in estimating accuracies have been given by Elford (1972) and Huxley and Crompton (1974, Ch. 10, 11, 12). From these and other sources we surmise that the best experiments may be relied upon to provide the drift to 0.5% and the diffusion to 1%. Measurements themselves may be repeatable to within 0.1% for the drift. We thus consider it reasonable that in theoretical calculations one should aim for a precision of 0.1% in drift and 1% in diffusion.

[4] Kinetic theory models. In other areas of kinetic theory there is a lively tradition of solving model problems with mathematical rigour. Some references are given in Section 5. For a refreshing discussion see Blatt (1975). However, there is little of that in connection with the present problem. Here the models are used more as an aid to physical reasoning and to provide estimates and insights not easily found otherwise.

[5] Cold gas approximation. In this approximation the gas atoms are initially at rest but are free to recoil. It is evident that the two assumptions are not compatible. However, if we consider the motion of only one test particle in an infinite gas, the

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perturbation would be very small indeed. The test particle may set a gas molecule in motion but is not likely to meet with it again. Such approximations must have occurred earlier in kinetic theory, but the first systematic discussion is by Wannier (1953). It does not seem to have been used much until recently (Paveri-Fontana 1970, 1974; Skullerud and Forsth 1979). In the case  $\sigma(g, \chi) \sim g^{\gamma}$ ,  $\gamma < 0$ , after a scale transformation the kinetic equations (Section 4) in the limit  $E \to \infty$  are the same as those for limit  $T_0 \to 0$ . However, the limit  $T_0 \to 0$  does not necessarily imply the limit  $E \to \infty$  and some further clarification is needed for the case of general cross sections.

[6] Swarm experiments. Systematic and comprehensive expositions have been given in the books by McDaniel and Mason (1973) and Huxley and Crompton (1974). A shorter review is made by Elford (1972) and a simpler account may be found in the text by McDaniel (1964), Chapter 11.

[7] Expansions in terms of density gradients and Fourier series. Expansions in terms of density gradients are implicit in the works of Wannier (1953) and Kihara (1953). The first systematic use of Fourier expansion in this context was by Parker and Lowke (1969). Both approaches are discussed by Kumar and Robson (1973). For extensive discussions and applications of the continuity equation, see Huxley and Crompton (1974).

[8] Path integral methods. These methods have their origin in the work of Wiener on Brownian motion and are used mainly in quantum statistical methods (see e.g. Wiegel 1975). In kinetic theory (Reif 1965) they arise from the integral equation for the distribution function and have similarities with simulation methods (Fahr and Müller 1967). The path integral methods are to be distinguished from free path methods also used in kinetic theory.

[9] Integral equation approach. The idea that the integro-differential equation of Boltzmann can be converted to an integral equation and solved in that form goes back to Hilbert. In the present context, the books by Reif (1965) and Koga (1970) and the papers by Paveri-Fontana (1970), Cavalleri and Paveri-Fontana (1972) and Braglia (1977, 1978) may be consulted.

[10] Generalized Einstein relations. Huxley and Crompton (1974) have argued that the Einstein relation between mobility and diffusion at zero field should be properly called the Nernst-Townsend relation. Wannier (1953) suggested that a similar relation should hold in the presence of fields. A clear statement of the generalized relations along with a thermodynamic derivation was given by Robson (1972). Since then they have been widely used in solid state physics (Robson 1973b; Chattopadhyay and Nag 1977) and kinetic theory (Skullerud 1976; Robson 1976b). Considerable effort has been denoted to understanding them from a theoretical point of view (Wannier 1973; Kumar 1977; Viehland and Mason 1978; and references quoted by Skullerud 1976). These relations are exact only for the constant mean free time model. Our point of view regarding them is expressed at the end of Section 3.

[11] Derivation of kinetic equations. The Boltzmann equation can be decomposed into simpler equations in a number of ways, depending on the strength of the external field, as discussed by Chapman and Cowling (1970). All such methods are variants of the original Chapman–Enskog method and are sometimes called the Chapman– Enskog method. There is no fixed usage for the latter term, although specific meaning is attached to it in the context of the theory of neutral gases (see e.g. Uhlenbeck and Ford 1963). The assumptions regarding the hydrodynamic regime are similar to those involved in the theory of neutral gases. The main point of the derivation given here is the use of equations (3) and (31b), for which see Note [7]. The derivation may be combined with other assumptions about the distribution function, with consequent complications in the equations; an example is discussed in Section 23. Limitations of such theories are discussed in Section 5. They are not rigorous in the mathematical sense, although in kinetic theory and chemical literature they are sometimes described as rigorous.

For discussions involving 'time-scales', see Schruben and Condiff (1973) and van de Water (1977).

[12] Transport cross sections and collision frequencies. The quantity

$$\sigma^{(1)}(g) = 2\pi \int \sigma(g,\chi) (1 - \cos \chi) \, \mathrm{d}(\cos \chi)$$

is called the momentum transfer cross section, and  $n_0 g \sigma^{(1)}(g)$  is the corresponding momentum transfer collision frequency. Similar interpretations may be made for the quantities  $\sigma^{(l)}(g)$  for l > 1. As pointed out at the end of Section 8, we prefer to deal with these because they occur naturally in our work and because of their relationship to orthogonal polynomials. In the literature, related quantities

$$Q_{i}(g) = 2\pi \int_{-1}^{+1} \sigma(g,\chi) (1 - \cos^{l}\chi) d(\cos \chi)$$

are often used. The integrals  $\Omega^{(l,s)}$  of kinetic theory are defined in terms of  $Q_l(g)$ . The relation between  $\sigma^{(l)}$  and  $Q_l$  is straightforward (Kumar 1967),

$$\sigma^{(l)}(g) = \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} Q_l(g), \qquad P_l(x) = \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} x^{l-2r}.$$

For another point of view concerning the use of these quantities and the evaluation of related integrals, see Suchy and Rawer (1971), Thiel and Suchy (1977), Weinert (1978) and Weinert *et al.* (1978).

[13] Fokker-Planck expansion. There is considerable literature on the Fokker-Planck expansion in plasma physics (see e.g. Allis 1956) and in stochastic theories (see e.g. papers in the collection by Wax 1954). In plasma physics the change in velocity  $\Delta c$  (cf. equation 55) is considered small by virtue of the long-range nature of the Coulomb force and the resulting small-angle deflections in the particle trajectories. Expansions up to second order in  $\Delta c$  are used throughout irrespective of the mass of the particle. The general expansion is sometimes also called the Kramers-Moyal expansion after Kramers (1940) and Moyal (1949). The related literature is reviewed by Braglia (1978).

The presentation in Section 10 is not closely connected with such theories or special approximations used in them. It is a straightforward expansion of the (foreign gas) collision operator in powers of the mass ratio  $m_0/(m+m_0)$ . Complete formulae were first derived by one of us (H.R.S.) starting from cartesian tensors in cartesian coordinates. The derivation given in the present text is somewhat more compact. The actual expressions obtained in the two cases have different appearance. At the

time of writing we have not been able to show their equivalence but results up to fourth order are found to agree.

[14] Differential operators for spherical harmonic decomposition. Earlier calculations of these operators occur in connection with the electron problem. The expansion is motivated in analogy with the Fokker-Planck expansion, with the change in energy  $\Delta \varepsilon$  playing the role of  $\Delta c$  in the Fokker-Planck case. To give proper meaning to the 'order' of the expansion, certain 'consistency' considerations have to be introduced. The temperature dependence is not treated separately and no reference is made to the cold gas limit. The related literature is reviewed by Braglia (1978); see also Lo Surdo (1971). It will be seen that our motivation is quite different and we circumvent the problems of previous derivations.

[15] Mixtures of neutral gases and Blanc's Law. The work in the text is easily generalized to the case when the charged test particles move in a mixture of neutral gases. The single species collision operator is replaced by

$$J(f) = \sum_{i} x_i J_i(f),$$

where  $x_i$  is the mole fraction of the *i*th neutral species and  $J_i(f)$  describes the collisions between the charged particle and the *i*th neutral species. If  $K_i$  denotes the mobility in the pure neutral gas *i*, then Blanc's law (McDaniel and Mason 1973) states that the mobility K in the mixture is given by

$$K^{-1} = \sum_{i} x_i K_i^{-1}.$$

The general nature of the deviation from the law at low fields was pointed out by Robson (1973a).

Milloy and Robson (1973) and Whealton *et al.* (1974) extended the momentum transfer theory of Mason and Hahn (1972) to obtain corrections to Blanc's law which agree with the results from both a low-field solution (Whealton and Mason 1974) and a high-field solution (Viehland and Mason 1975) of the Boltzmann equation. These approximate analytic formulae involve the logarithmic derivative of the mobility, which is familiar from the generalized Einstein relations [10] and other similar results (Viehland *et al.* 1974).

[16] Theory of electron swarms. In view of the simplicity of the collision operator for this case it is convenient to use differential equations with various numerical methods (Huxley and Crompton 1974). Usually the first two terms in the spherical harmonic expansion suffice. Calculations with three terms have been reported by Ferrari (1975, 1977). Other theories are reviewed by Braglia (1978). In the presence of inelastic interactions and highly anisotropic differential cross sections, such methods are no longer useful and recourse to more general methods is needed (Lin *et al.* 1979b). Thus one might say that the gap that was apparent earlier between the methods used in the theory of electron and ion swarms has been bridged.

[17] Moment equations. These equations have a long history in kinetic theory. They are completely equivalent to the equations obtained by polynomial methods (see e.g. Chapman and Cowling 1970). To look upon these as matrix equations is a relatively recent approach and so is the use of weight functions that are different from

the equilibrium Maxwellian (Weitzsch 1961; Everett 1963; Suchy 1964; Weinert and Suchy 1977; and other papers quoted in the text).

[18] Momentum transfer theory. This theory is significant in having produced formulae which are simple and at least qualitatively correct for arbitrary fields and various ion-neutral interactions. One takes the moment equations from the constant mean free time model (Section 18d), but inserts collision frequencies with an energy dependence prescribed by the actual law of force operating between the ion and gas molecules. The resulting equations are easy to work with and produce reasonable results. While these are considerable advantages in a complex situation, the theory is not suitable when high accuracy is desired. It has been extensively used (Mason and Hahn 1972; Hahn and Mason 1973; McDaniel and Mason 1973; Milloy and Robson 1973; Whealton *et al.* 1974; Robson 1976b).

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## Appendix 1. Notation and Frequently Used Formulae

As far as possible we have tried to assign to the symbols the meanings conventionally associated with them. It should help in recognizing them, although such associations are not uniform throughout the literature. The symbols are defined where they first appear. At a subsequent appearance there is a reference to some equation where the symbol was previously used, or to the defining equation itself. Sometimes the definitions are repeated so that a long search should not be necessary at any point. A description of conventions used and a list of frequently used formulae follows.

A group of equations occurring together should be read as a whole: the first equation usually contains abbreviations which are explained in subsequent equations.

Vectors and tensors are denoted by bold face type and used in the conventional way. The second order unit tensor is 1. If c is a vector,  $\hat{c}$  is the unit vector in the direction of c. Sometimes  $\hat{c}$  is used for the spherical polar angular variables  $(\theta, \varphi)$ 

of  $c \equiv (c, \theta, \varphi)$ . The volume element  $d\hat{c}$  is  $d(\cos \theta) d\varphi$ . We reserve c for charged particle velocity,  $c_0$  for neutral particle velocity, g and g' for relative velocities and W for the drift velocity.

Spherical harmonics  $Y_m^{(l)}(\hat{e})$ , irreducible tensors  $\Psi_m^{(nl)}$  etc., Racah coefficients  $\overline{W}$  and Wigner coefficients  $(l_1 m_1 l_2 m_2 | l_3 m_3)$ , and the corresponding coupling and recoupling schemes for irreducible tensors, all follow the conventions used in the book by Fano and Racah (1959). These have been summarized, for instance, by Kumar (1966, 1967). In these references the Gothic symbol  $\mathfrak{Y}_m^{(l)}$  was used, for which we have written  $Y_m^{(l)}$  in this paper. The convention of round and square bracket superscripts for tensors is explained in the references above and is summarized by

$$\Psi_m^{(nl)} = (\Psi_m^{[nl]})^*.$$
(A1)

The rank of the tensor is associated with l (=0, 1, 2, 3, ...); for each l, the index m takes the values l, l-1, ..., -l.

Collision operator J and translation operator T. Any symbol with leading letter J (or T) denotes an operator or matrix element related to the collision (or translation) operator. Subscripts, superscripts and other indices are added to emphasize different properties of the operators or to specify the derived quantities. The symbol T is also used for the temperature and, in other papers, for the Talmi coefficients. The latter do not occur in this paper and no confusion should arise.

Distribution function f. Any symbol with leading letter f denotes a function of c or an expansion coefficient related to the distribution function. Bold-face f is used when such a quantity is a tensor. Indices are attached to emphasize certain properties or to specify the derived quantities. Note that  $f^{(0)}(c)$  is the space-averaged distribution function in equations (33);  $f_l^{(0)}(c)$  is a function of the scalar variable c occurring in the spherical harmonic decomposition (Section 16); while  $f_0(c_0)$  is the distribution function for the neutral gas and a function of the neutral velocity vector  $c_0$ .

Differential cross section  $\sigma(g, \chi)$ . Derived quantities  $\sigma_l(g)$  and  $\sigma^{(l)}(g)$  are defined by equations (58) and (59). The symbols  $\sigma(l_1 l_2 l_3)$  and  $\bar{\sigma}(l'1l)$  are constants not related to cross sections (see below).

Weight functions W(c), w(c). These are functions of the three-dimensional vector c. They are not to be confused with the magnitude of vectors W used for the drift velocity.

The Maxwellian is denoted by

$$w(\alpha, c) = (\alpha^2/2\pi)^{3/2} \exp(-\frac{1}{2}\alpha^2 c^2), \qquad \int w(\alpha, c) \, \mathrm{d}c = 1.$$
 (A2)

Burnett functions  $\phi_m^{(nl)}(c)$ . For these, see Kumar (1966, 1967) or, closer at hand, Section 2 of the second accompanying paper (Kumar 1980b). Frequently used formula are:

$$\phi^{(\mathbf{v})}(c) \equiv \phi_m^{(\mathbf{v}l)}(c), \qquad \mathbf{v} \equiv (\mathbf{v}, l, m); \tag{A3}$$

$$\phi_m^{(vl)}(c) = R_{vl}(c) Y_m^{(l)}(\hat{c}), \qquad (A4)$$

$$R_{vl}(c) = N_{vl}(c/\sqrt{2})^l S_{l+\frac{1}{2}}^{(v)}(\frac{1}{2}c^2), \qquad (A5)$$

$$N_{\nu l}^{2} = 2\pi^{3/2} \Gamma(\nu+1) / \Gamma(\nu+l+\frac{3}{2}), \qquad (A6)$$

the  $S_{l+*}^{(\nu)}(\frac{1}{2}c^2)$  being Sonine polynomials.

Another frequently used normalizing constant is

$$\overline{N}_{\nu l}^2 = 2\pi^{3/2} / \Gamma(\nu+1) \, \Gamma(\nu+l+\frac{3}{2}). \tag{A7}$$

The Legendre polynomial  $P_l(x)$  is given by

$$\mathbf{P}_{l}(x) = \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} x^{l-2r}, \qquad a_{rl} = \left(-\right)^{r} 2^{-l} {l \choose r} {2l-2r \choose l}, \tag{A8}$$

where  $\left[\frac{1}{2}l\right]$  is the largest integer less than or equal to  $\frac{1}{2}l$ .

The coupling rule for spherical harmonics is

$$Y_{m_1}^{[l_1]}(\hat{c}) Y_{m_2}^{[l_2]}(\hat{c}) = \sum_{l} \sigma(l_1 l_2 l) (l_1 m_1 l_2 m_2 | lm) Y_m^{[l]}(\hat{c}),$$
(A9)

$$\sigma(l_1 \, l_2 \, l_3) = \left(\frac{(2l_1+1)(2l_2+1)}{4\pi(2g+1)}\right)^{\frac{1}{2}} \frac{\tau(g)}{\tau(g-l_1)\,\tau(g-l_2)\,\tau(g-l_3)},\tag{A10}$$

$$\tau(g) = g!/(2g!)^{\frac{1}{2}}, \qquad 2g = l_1 + l_2 + l_3;$$
(A11)

$$\sigma(l_1 l_2 l_3) = 0$$
, if  $l_1 + l_2 + l_3$  odd. (A12)

An alternative expression is

$$\sigma(l_1 l_2 l_3) = i^{l_1 + l_2 - l_3} \left( \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l_3 + 1)} \right)^{\frac{1}{2}} (l_1 0 l_2 0 | l_3 0),$$
(A13)

but

$$\bar{\sigma}(l\,1\,l') = \mathbf{i}^{(l-l'+3)}(l'\,0\,1\,0\,|\,l0). \tag{A14}$$

The addition theorem for spherical harmonics has the form

$$P_{l}(\hat{a} \cdot \hat{b}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{m}^{[l]}(\hat{a}) Y_{m}^{(l)}(\hat{b}).$$
(A15)

The 'plane-wave' expansion is given by

$$\exp(2\boldsymbol{a} \cdot \boldsymbol{b}) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \overline{N}_{nl}^{2} (ab)^{2n+l} Y_{m}^{[l]}(\hat{\boldsymbol{a}}) Y_{m}^{(l)}(\hat{\boldsymbol{b}}).$$
(A16)

# Appendix 2. Collision Operator for Stationary Cold Gas

(

(a) Fokker-Planck Expansion

We introduce the Fourier transforms

$$\hat{f}(\boldsymbol{k}) = \int \exp(-i\boldsymbol{k} \cdot \boldsymbol{c}) f(\boldsymbol{c}) \, \mathrm{d}\boldsymbol{c} \,, \tag{A17}$$

$$f(\boldsymbol{c}) = (2\pi)^{-3} \int \exp(i\boldsymbol{k} \cdot \boldsymbol{c}) \hat{f}(\boldsymbol{k}) \, \mathrm{d}\boldsymbol{k} \,, \tag{A18}$$

$$J(f) = (2\pi)^{-6} \int \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{c}) \,\hat{J}(\mathbf{k}, \mathbf{k}') \,\hat{f}(\mathbf{k}') \,\mathrm{d}\mathbf{k} \,\mathrm{d}\mathbf{k}' \,, \tag{A19}$$

$$\hat{J}(\boldsymbol{k},\boldsymbol{k}') = \int \exp(-i\boldsymbol{k}\cdot\boldsymbol{c}) J(\exp(i\boldsymbol{k}'\cdot\boldsymbol{c})) \,\mathrm{d}\boldsymbol{c} \,. \tag{A20}$$

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For the stationary cold gas, we have

$$\hat{J}(\boldsymbol{k},\boldsymbol{k}') = \int \delta(\boldsymbol{c}_0) \exp(\mathrm{i}(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{c}) \{1-\exp(\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{c}-\boldsymbol{c}'))\} \,\mathrm{d}\mathscr{V}, \qquad (A21)$$

with

$$\mathrm{d}\mathscr{V} = g\,\sigma(g,\chi)\,\mathrm{d}\hat{g}'\,\mathrm{d}g\,\mathrm{d}G\,. \tag{A22}$$

The integration over dG in equation (A21) may be carried out immediately. We introduce a vector  $\mathbf{h} \equiv (h, \kappa, \omega)$  by

$$\boldsymbol{c} - \boldsymbol{c}' = \mu_0(\boldsymbol{g} - \boldsymbol{g}') = \mu_0 \boldsymbol{h}, \qquad (A23a)$$

$$h^2 = 2g^2(1 - \cos \chi), \qquad \cos \kappa = \hat{g} \cdot \hat{h} = h/\sqrt{2g},$$
 (A23b)

and make the plane-wave expansion of the exponential in the braces in equation (A21):

$$\exp(i\mu_0 \,\boldsymbol{k} \cdot \boldsymbol{h}) = \sum_{nlm} \mu_0^{2n+l} (\frac{1}{2}h)^{2n+l} Y_m^{(l)}(\hat{\boldsymbol{h}}) Z_m^{[nl]}(i\boldsymbol{k}) \,. \tag{A24}$$

This may be taken as a definition of the quantity Z. The mass dependence of equation (A21) arises entirely through the term in the braces and is made fully explicit here.

We may now write

$$\hat{J}(\boldsymbol{k},\boldsymbol{k}') = \sum_{nlm} \mu_0^{2n+l} Z_m^{[nl]}(\mathrm{i}\boldsymbol{k}) \, \hat{\Psi}_m^{(nl)}(\boldsymbol{k}-\boldsymbol{k}') \qquad (nlm \neq 000) \,, \tag{A25}$$

$$\hat{\Psi}_{m}^{(nl)}(\boldsymbol{k}) = -\int \exp(-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{g}) (\frac{1}{2}h)^{2n+l} Y_{m}^{(l)}(\hat{\boldsymbol{h}}) g \,\sigma(g,\chi) \,\mathrm{d}\hat{\boldsymbol{g}}' \,\mathrm{d}\boldsymbol{g} \,. \tag{A26}$$

Substituting this into equation (A19) and noting that the k' integration defines a convolution, we have

$$J(f) = \sum_{nlm} \mu_0^{2n+l} \mathbb{Z}_m^{[nl]} (\Psi_m^{(nl)}(c) f(c)).$$
 (A27)

The tensor differential operator  $\mathbb{Z}$  is obtained by replacing ik by d/dc in the expression for Z defined by equation (A24). We do not require the explicit form here. The tensor  $\Psi$  is obtained from equation (A26) as

$$\Psi_{m}^{(nl)}(c) = (2\pi)^{-3} \int \exp(ik \cdot c) \widehat{\Psi}_{m}^{(nl)}(k) \, \mathrm{d}k = -\int (\frac{1}{2}h)^{2n+l} Y_{m}^{(l)}(\hat{h}) g \,\sigma(g,\chi) \, \mathrm{d}\hat{g}' |_{c=g}.$$
(A28)

The integration in equation (A28) is performed by taking the z axis along  $g \ (\equiv c)$  and noting that in this coordinate system the azimuth of h and g' is the same. The result is

$$-2\pi \operatorname{Y}_{m}^{(l)}(\hat{c}) \int (\frac{1}{2}h)^{2n+l} \operatorname{P}_{l}(\cos \kappa) \, c \, \sigma(c, \chi) \, \mathrm{d}(\cos \chi) \,. \tag{A29}$$

The angular integration can be separated by expanding

$$\sigma(c,\chi) = \sum_{\lambda=0}^{\infty} \left\{ (2\lambda+1)/4\pi \right\} \sigma_{\lambda}(c) \operatorname{P}_{\lambda}(\cos\chi)$$
(A30)

and introducing the variables

$$x = \cos \chi, \qquad y = \cos \kappa = \{\frac{1}{2}(1-x)\}^{\frac{1}{2}} = h/\sqrt{2}c.$$
 (A31)

We note further that

$$\delta(1-x) = \sum_{\lambda=0}^{\infty} \frac{1}{2} (2\lambda + 1) P_{\lambda}(x)$$
 (A32)

and, at x = 1, y = 0 so that from equations (A28) and (A29) we have

$${}^{\circ}\Psi_{m}^{(nl)}(\boldsymbol{c}) = Y_{m}^{(l)}(\hat{\boldsymbol{c}}) {}^{\circ}\Psi_{nl}(\boldsymbol{c}), \qquad (A33)$$

$${}^{\circ}\Psi_{nl}(c) = \sum_{\lambda} c^{2n+l+1} \sigma^{(\lambda)}(c) a_{nl}^{\lambda}, \qquad (A34)$$

$$a_{nl}^{\lambda} = \frac{1}{2}(2l+1)\int_{-1}^{+1} y^{2n+l} \mathbf{P}_{l}(y) \mathbf{P}_{\lambda}(x) \,\mathrm{d}x, \qquad y = \{\frac{1}{2}(1-x)\}^{\frac{1}{2}}, \tag{A35}$$

where we have added the superscript 'o' at this point to emphasize that these quantities are for the stationary cold gas. The coefficients  $a_{nl}^{\lambda}$  are discussed in the next subsection of this appendix. The quantity  $\sigma^{(\lambda)}$  was defined in equation (59) of the text; see also Note [12].

Now we find the scalar form of the operator in equation (A27), that is, we carry out the summation over the index m and show that, for an arbitrary function f(c), we have

$$\sum_{m=-l}^{l} \mathbb{Z}_{m}^{[nl]} \big( \mathbf{Y}_{m}^{(l)}(\hat{c}) f(c) \big) = S^{nl} \big( f(c) \big) .$$
 (A36)

It is more convenient to first show the adjoint relation

$$\sum_{m=-l}^{l} \mathbf{Y}_{m}^{(l)}(\hat{\boldsymbol{c}}) \, \widetilde{\mathbb{Z}}_{m}^{[nl]}(\boldsymbol{\varphi}(\boldsymbol{c})) = \widetilde{S}^{nl}(\boldsymbol{\varphi}(\boldsymbol{c})) \,. \tag{A37}$$

Note that the operator relation corresponding to equation (A24) is

$$\exp(\boldsymbol{V}.\partial_c) = \sum_{nlm} (\frac{1}{2}V)^{2n+l} Y_m^{(l)}(\hat{\boldsymbol{V}}) \mathbb{Z}_m^{[nl]}.$$
(A38)

Since  $\tilde{T} = T^{-1}$  we have

$$\mathbb{Z}_{m}^{[nl]} = (-)^{l} \mathbb{Z}_{m}^{[nl]}.$$
(A39)

In equation (A37) let  $\varphi = \exp(i\mathbf{k} \cdot \mathbf{c})$  and use the relation (A39) and the fact that from equation (A24) we have

$$Z_m^{[nl]}(\mathbf{i}k) = \overline{N}_{nl}^2(\mathbf{i}k)^{2n+l} Y_m^{[l]}(\hat{k}).$$
 (A40)

The summation over m in equation (A37) is now an application of the addition theorem of spherical harmonics. One gets

$$\widetilde{S}^{nl}(\exp(i\boldsymbol{k}.\boldsymbol{c})) = (-)^{l} \{(2l+1)/4\pi\} \overline{N}^{2}_{nl} \mathbf{P}_{l}(\hat{\boldsymbol{c}}.\hat{\boldsymbol{k}})(ik)^{2n+l} \exp(i\boldsymbol{k}.\boldsymbol{c}).$$
(A41)

The operator form is obtained by noting that

$$(\mathbf{i}k)^{l} \mathbf{P}_{l}(\hat{\mathbf{c}} \cdot \hat{\mathbf{k}}) = \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl}(\hat{\mathbf{c}} \cdot \mathbf{i}k)^{l-2r} (\mathbf{i}k)^{2r}$$
(A42)

and replacing ik by d/dc. Since  $\hat{c} \cdot d/dc = d/dc$  we have

$$\widetilde{S}^{nl} = (-)^{l} \{ (2l+1)/4\pi \} \, \overline{N}_{nl}^{2} \sum_{r=0}^{\lfloor \frac{1}{2} l \rfloor} a_{rl} (\mathrm{d}/\mathrm{d}c)^{l-2r} \, \nabla^{2(n+r)} \,. \tag{A43}$$

It is important to note that terms in  $\hat{c}$  in equation (A42) come from the spherical harmonic in equation (A28) which is not operated upon. Hence they have to be kept to the left of differential operators in the substitution  $i\mathbf{k} \rightarrow d/d\mathbf{c}$ .

From the adjoint relations

$$\left[ \hat{\boldsymbol{c}} \cdot (\mathrm{d}/\mathrm{d}\boldsymbol{c}) \right]^{\sim} = -(\mathrm{d}/\mathrm{d}\boldsymbol{c}) \cdot \hat{\boldsymbol{c}} = (\mathrm{d}/\mathrm{d}\boldsymbol{c} + 2/c), \qquad \left[ \nabla_{\boldsymbol{c}}^2 \right]^{\sim} = \nabla_{\boldsymbol{c}}^2, \qquad (A44)$$

where  $\llbracket A \rrbracket^{\sim} \equiv \tilde{A}$ , one gets

$$S^{nl} = \frac{2l+1}{4\pi} \overline{N}_{nl}^{2} \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} \nabla_{c}^{2(n+r)} \left(\frac{\mathrm{d}}{\mathrm{d}c} + \frac{2}{c}\right)^{l-2r}.$$
 (A45)

The forms given in equations (81) and (83) are obtained by substituting equations (A36) and (A45) in (A27), and similarly for the adjoint operator.

(b) Coefficients  $a_{nl}^{\lambda}$ 

These coefficients are pure numbers defined by equations (A35). Since the coefficient of  $P_{\lambda}(x)$  is a polynomial in x of degree n+l, it follows that

$$a_{nl}^{\lambda} = 0$$
 for  $\lambda > n+l$ . (A46)

From the coefficient of the highest power one may derive

$$a_{nl}^{n+l} = (-)^{n+l} 2^{-l} {2l \choose l} / {2n+2l \choose n+l}, \qquad a_{0l}^{l} = (-2)^{-l}.$$
 (A47a, b)

It is evident from equation (A35) that

$$a_{00}^{\lambda} = \delta_{\lambda 0} \,. \tag{A48}$$

When l = 0, the use of the identity (Erdélyi *et al.* 1953, p. 214)

$$(1-x)^{n} = 2^{n} \sum_{r=0}^{n} (-)^{r} \frac{2r+1}{n+r+1} \frac{\binom{2n}{n-r}}{\binom{2n}{n}} P_{r}(x)$$
(A49)

in equation (A35) gives

$$a_{n0}^{\lambda} = (-)^{\lambda} \frac{2\lambda + 1}{n + \lambda + 1} \frac{\binom{2n}{n - \lambda}}{\binom{2n}{n}}, \qquad n \ge \lambda.$$
(A50)

The general coefficient may be expressed as a linear combination of the coefficients with l = 0. Using the relation

. . . .

$$y^{l} \mathbf{P}_{l}(y) = \sum_{r=0}^{\lfloor \frac{1}{2}l \rfloor} a_{rl} y^{2(l-r)}$$
(A51)

in equation (A35), we have

$$a_{nl}^{\lambda} = \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} a_{n+l-r,0}^{\lambda}, \qquad a_{rl} = (-)^{r} 2^{-l} {l \choose r} {2l-2r \choose l}.$$
(A52a, b)

The coefficients satisfy the recursion relations

$$a_{nl}^{\lambda} = \frac{2l-1}{l} a_{n+1,l-1}^{\lambda} - \frac{l-1}{l} a_{n+1,l-2}^{\lambda}, \qquad (A53a)$$

$$2a_{n+1,l}^{\lambda} = a_{n,l}^{\lambda} - \frac{\lambda+1}{2\lambda+3}a_{nl}^{\lambda+1} - \frac{\lambda}{2\lambda-1}a_{nl}^{\lambda-1}.$$
 (A53b)

These may be verified by reducing the index n in equation (A35) with the help of the following identities obtained from the recursion relations for the Legendre polynomials:

$$y^{l} \mathbf{P}_{l}(y) = y^{2} \left( \frac{2l-1}{l} y^{l-1} \mathbf{P}_{l-1}(y) - \frac{l-1}{l} y^{l-2} \mathbf{P}_{l-2}(y) \right),$$
(A54a)

$$2y^{2} P_{\lambda}(x) = (1-x)P_{\lambda}(x) = P_{\lambda}(x) - \frac{\lambda+1}{2\lambda+1}P_{\lambda+1}(x) - \frac{\lambda}{2\lambda+1}P_{\lambda-1}(x).$$
 (A54b)

The coefficients satisfy the sum rule

$$\sum_{\lambda=0}^{\infty} a_{nl}^{\lambda} = 0, \qquad n+l \neq 0;$$
(A55a)

$$= 1, \qquad n = l = 0;$$
 (A55b)

which may be verified by using equations (A15) and (A35).

To find numerical values of the coefficients, one would naturally use equations (A46)-(A48) and (A50) where applicable. For other coefficients there are three possibilities: (i) direct evaluation of the integral in equations (A35); (ii) use of equations (A50) and (A52); (iii) use of the recursion relations (A53). The sum rules (A55) provide a useful check on the calculations.

## (c) Differential Operators for Spherical Harmonic Decomposition

The argument here is similar to that in subsection (a) of this appendix. We present it in an abbreviated form. Consider the Fourier transform

$$\mathscr{F} \equiv \int \exp(-ikc^2) c^{l+1} J_l^0(f) dc^2.$$
 (A56)

From equations (101) and (60) this can be written as a three-dimensional integral:

$$\mathscr{F} = 2 \int f_m^{(l)}(\boldsymbol{c}) \,\delta(\boldsymbol{c}_0) \{ \mathbf{Y}_m^{[l]}(\hat{\boldsymbol{c}}) \, \boldsymbol{c}^l \exp(-\mathbf{i}k\boldsymbol{c}^2) \\ - \mathbf{Y}_m^{[l]}(\hat{\boldsymbol{c}}') \, \boldsymbol{c}'^l \exp(-\mathbf{i}k\boldsymbol{c}^2) \} g \,\sigma(g,\chi) \,\mathrm{d}\boldsymbol{G} \,\mathrm{d}\boldsymbol{g} \,\mathrm{d}\hat{\boldsymbol{g}}' \,. \tag{A57}$$

The delta function is removed by G integration giving

$$G = \mu g, \qquad c = g, \qquad c' = \mu g + \mu_0 g'.$$
 (A58)

The integration over the azimuth of  $\hat{g}'$  can be performed by taking g along the z axis and noting that the azimuth of c' and g' are the same in this coordinate system. Then we have

$$\mathbf{Y}_{m}^{[l]}(\hat{\boldsymbol{c}}') \rightarrow 2\pi \, \mathbf{Y}_{m}^{[l]}(\hat{\boldsymbol{c}}) \, \mathbf{P}_{l}(\hat{\boldsymbol{c}} \cdot \hat{\boldsymbol{c}}'),$$

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and the integration over angles of g can be performed, leaving only the integration over  $dg \equiv dc'$  and  $d(\cos \chi)$ .

From equations (A58) we have

$$c'^2 = c^2 \eta^2$$
,  $\hat{c} \cdot \hat{c}' = \xi/\eta$ ,  $\hat{g} \cdot \hat{g}' \equiv \cos \chi \equiv x$ , (A59a)

$$\eta^2 = \mu^2 + \mu_0^2 + 2\mu\mu_0 x, \qquad \xi = \mu + \mu_0 x.$$
 (A59b)

In terms of these variables equation (A57) becomes

$$\mathscr{F} = \int \exp(-ikc^2) c^{l+1} f(c) \left[ 1 - 2\pi \eta^l \mathbf{P}_l(\xi/\eta) \exp\{ikc^2(1-\eta^2)\} \right]$$

$$\times c \,\sigma(c,\chi) \, \mathrm{d}x \, \mathrm{d}c^2 \,. \tag{A60}$$

Expanding the exponential in the square brackets, noting that  $\mu + \mu_0 = 1$  implies  $1 - \eta^2 = 2\mu\mu_0(1-x)$ , and introducing the function

$$\Phi_{nl}(c) = \int_{-1}^{+1} (1-x)^n \{\delta_{n0} - 2\pi\eta^l \mathbf{P}_l(\xi/\eta)\} c^{2n+1} \sigma(c,\chi) \,\mathrm{d}x\,, \tag{A61}$$

we may write

$$\mathscr{F} = \sum_{n=0}^{\infty} \frac{(2\mu\mu_0)^n}{n!} (ik)^n \int \exp(-ikc^2) \Phi_{nl}(c) c^{l+1} f(c) dc^2.$$
(A62)

Comparing this with equation (A56) we recognize that

$$J_{l}^{0}(f) = c^{-(l+1)} \sum_{n=0}^{\infty} \frac{(2\mu\mu_{0})^{n}}{n!} \left(\frac{\mathrm{d}}{\mathrm{d}(c^{2})}\right)^{n} \left(\Phi_{nl}(c) c^{l+1} f(c)\right)$$
(A63)

To put equation (A61) in a more useful form, we note that the first term contributes  $2\pi c \sigma_0(c) \delta_{n0}$ . Since at x = 1 we have  $\eta^l P_l(\xi/\eta) = 1$ , we may write this term as

$$2\pi c \,\sigma_0(c) \,\int_{-1}^{+1} \,(1-x)^n \,\delta(1-x) \,\eta^l \,\mathbf{P}_l(\xi/\eta) \,\mathrm{d}x$$

Substituting in equation (A61) and using the relations (A30), (A31) and (A32) we get

$$\Phi_{nl}(c) = c^{2n+1} \sum_{\lambda=0}^{\infty} \sigma^{(\lambda)}(c) b_{nl}^{\lambda}.$$
(A64)

The coefficients  $b_{nl}^{\lambda}$  are discussed in the next subsection.

### (d) Coefficients $b_{nl}^{\lambda}$

These coefficients are defined by

$$b_{nl}^{\lambda} = \frac{1}{2}(2\lambda+1) \int_{-1}^{+1} (1-x)^n \eta^l \mathbf{P}_l(\xi/\eta) \mathbf{P}_{\lambda}(x) \, \mathrm{d}x \,, \tag{A65}$$

where  $\xi$  and  $\eta$  are given by equations (A59b). In contrast to the coefficients  $a_{nl}^{\lambda}$  discussed in subsection (b) of this appendix, these coefficients depend upon the masses and, in general, are polynomials in  $\mu$  and  $\mu_0$ . There are, however, many similarities.

Using equation (A54b) we may alter the index *n* as for  $a_{nl}^{\lambda}$  to give the recursion relation, similar to (A53b),

$$b_{n+1,l}^{\lambda} = b_{nl}^{\lambda} - \frac{\lambda+1}{2\lambda+3} b_{nl}^{\lambda+1} - \frac{\lambda}{2\lambda-1} b_{nl}^{\lambda-1}.$$
 (A66)

In place of the relation (A54a) we have

$$\eta^{l} \mathbf{P}_{l}(\xi/\eta) = \xi \left(\frac{2l-1}{l}\right) \eta^{l-1} \mathbf{P}_{l-1}(\xi/\eta) - \eta^{2} \left(\frac{l-1}{l}\right) \eta^{l-2} \mathbf{P}_{l-2}(\xi/\eta), \quad (A67a)$$

$$\xi(1-x)^n = (1-x)^n - \mu_0(1-x)^{n+1}, \qquad \eta^2(1-x)^n = (1-x)^n - 2\mu\mu_0(1-x)^{n+1}, \quad (A67b)$$

and then follows the more complicated recursion relation

$$b_{nl}^{\lambda} = \frac{2l-1}{l} \left( b_{n,l-1}^{\lambda} - \mu_0 \, b_{n+1,l-1}^{\lambda} \right) - \frac{l-1}{l} \left( b_{n,l-2}^{\lambda} - 2\mu\mu_0 \, b_{n+1,l-2}^{\lambda} \right). \tag{A67c}$$

Note that this does not reduce to equation (A53a) for any simple choice of  $\mu$ 's.

In general the relation between the two coefficients is complicated. However, it is seen from the definitions that

$$b_{n0}^{\lambda} = 2^{n} a_{n0}^{\lambda} = (-)^{\lambda} 2^{n} \frac{2\lambda + 1}{n + \lambda + 1} \frac{\binom{2n}{n - \lambda}}{\binom{2n}{n}}.$$
 (A68)

The coefficients  $b_{nl}^{\lambda}$  may be expressed in terms of coefficients with l = 0 by using

$$\eta^{l} \mathbf{P}_{l}(\xi/\eta) = \sum_{r=0}^{\left[\frac{1}{2}l\right]} a_{rl} \eta^{2r} \xi^{l-2r}$$
(A69)

and the binomial expansion for the  $\xi$  and  $\eta$  factors with

$$\eta^2 = 1 - 2\mu\mu_0(1-x), \qquad \xi = 1 - \mu_0(1-x),$$
 (A70)

to obtain

$$b_{nl}^{\lambda} = \sum_{r=0}^{\left\lceil \frac{1}{2}l \right\rceil} \sum_{s=0}^{r} \sum_{t=0}^{l-2r} a_{rl} {s \choose s} {l-2r \choose t} (-2\mu\mu_0)^s (-\mu_0)^t b_{n+s+t,0}^{\lambda}.$$
(A71)

For numerical computations it might be better to evaluate the integral (A65) or work with the recursion relations (A66) and (A67c).

From a consideration of the highest power of x in the coefficient of  $P_{\lambda}(x)$  in equation (A65) one obtains

$$b_{nl}^{n+l} = (-2)^n \mu_0^l {\binom{2l}{l}} / {\binom{2n+2l}{n+l}};$$
 (A72a)

$$b_{0l}^{l} = \mu_{0}^{l}; \qquad b_{nl}^{\lambda} = 0, \quad \lambda > n+l.$$
 (A72b, c)

We have the limiting cases

$$b_{nl}^{\lambda} = \frac{1}{2}(2\lambda+1)\int_{-1}^{+1} (1-x)^n \mathbf{P}_l(x) \mathbf{P}_{\lambda}(x) \, \mathrm{d}x \,, \qquad \mu = 0; \qquad (A73a)$$

$$= \frac{1}{2}(2\lambda + 1) \int_{-1}^{+1} (1 - x)^n P_{\lambda}(x) dx \ (\equiv b_{n0}^{\lambda}), \quad \mu_0 = 0;$$
 (A73b)

and the sum rule (cf. equations A55)

$$\sum_{\lambda=0}^{\infty} b_{nl}^{\lambda} = 0, \qquad n+l \neq 0; \qquad (A74a)$$

$$= 1, \quad n = l = 0.$$
 (A74b)

### (e) Matrix Elements in Burnett-function Representation

As pointed out in Section 12c for the cold gas a Burnett-function representation is necessarily a two-temperature representation. A gas temperature  $T_0$  of zero cannot be used to define a weight function for Burnett functions.

Specifically, we have the weight function

$$\overline{w}(\alpha,c) = (\alpha^2/2\pi)^{3/2} \exp(-\frac{1}{2}\alpha^2 c^2), \qquad \alpha^2 = m/kT,$$

and the functions  $\phi^{(v)}(c)$  orthogonal with respect to it and normalized to unity. The matrix element is given by

$$[J(0)]_{\mathbf{v}\mathbf{v}'} = \int \delta(\boldsymbol{c}_0) \,\overline{w}(\alpha, c) \,\phi^{[\mathbf{v}']}(\alpha \boldsymbol{c}) \left\{ \phi^{(\mathbf{v})}(\alpha \boldsymbol{c}) - \phi^{(\mathbf{v})}(\alpha \boldsymbol{c}') \right\} \,\mathrm{d}\mathscr{V} \,. \tag{A75}$$

The integration proceeds as indicated in subsection (c) of this appendix. We have

$$[J(0)]_{vv'} = \delta_{ll'} \delta_{mm'} [J_l^0]_{vv'}, \qquad (A76a)$$

with

$$\begin{bmatrix} J_l^{\ 0} \end{bmatrix}_{\nu\nu'} = \sum_{\lambda,\nu_1} d_{\nu\nu_1}^{l\lambda} V_{\nu_1\nu'}^{\lambda l}, \qquad (A76b)$$

$$d_{\nu\nu_{1}}^{l\lambda} = \frac{N_{\nu l}}{N_{\nu_{1}l}} {\nu_{1} \choose \nu_{1}} \frac{2\lambda + 1}{2} \int_{-1}^{+1} (1 - \eta^{2})^{\nu - \nu_{1}} \eta^{2\nu_{1} + l} P_{l}(\xi/\eta) P_{\lambda}(x) dx, \qquad (A76c)$$

$$V_{\nu_1\nu'}^{\lambda l} = \int_0^\infty \overline{w}(\alpha, g) R_{\nu' l}(\alpha g) R_{\nu_1 l}(\alpha g) g^3 \sigma^{(\lambda)}(g) dg.$$
(A76d)

The quantities  $\xi$  and  $\eta$  were defined in equations (A59b) and definitions of the others may be found in Appendix 1.

The integrals  $V_{\nu\nu'}^{\lambda l}$  of equation (A76d) contain all the information on the cross sections and the parameter  $\alpha$  coming from the weight function. They are reduced to the interaction integrals  $V_{\nu\nu'}^{l}$  occurring in other works if  $\lambda = l$  (cf. Kumar 1980a).

The coefficients d defined by equation (A76c) are independent of cross sections and the parameter  $\alpha$ . They depend only on the masses and are in fact polynomials in  $\mu$  and  $\mu_0$ . Other expressions for these coefficients may be developed along the lines of subsections (b) and (d) of this appendix. It follows from those arguments that the sum over both  $v_1$  and  $\lambda$  in equation (A76b) is limited to  $0 < v_1 < v$  and  $0 < \lambda < v + v_1 + l$ .

It may be useful to point out that, after the integration over centre-of-mass velocity, the azimuth of g' and angles of g, and application of the argument given below equation (A63) one obtains as an intermediate step between equations (A75) and (A76) the expression

$$\begin{bmatrix} J_l^0 \end{bmatrix}_{\nu\nu'} = \int_0^\infty \mathrm{d}g \int_{-1}^{+1} \mathrm{d}x \ \overline{w}(\alpha, g) R_{\nu'l}(\alpha g) R_{\nu l}(\alpha g \eta) P_l(\xi/\eta) g^3 \\ \times \{\sigma_0 \,\delta(1-x) - 2\pi \,\sigma(g, \chi)\}.$$
(A77)

The g and x integrations are then separated by expressing  $R_{vl}(\alpha g\eta)$  in terms of  $R_{v1}(\alpha g)$ .

# Appendix 3. Tensor Decomposition of Translation Operator

The translation operator T is defined by

$$Tf(c) = f(c+V) = \exp(V \cdot \partial_c) f(c).$$
(A78)

It is the generator of the three-dimensional Taylor expansion. Its adjoint defined by equation (68) and its inverse are the same operators

$$\bar{T} = T^{-1} = \exp(-V \cdot \partial_c). \tag{A79}$$

The tensor decomposition is not diagonal in l and is given by (cf. equations 92, 94 and 102)

$$T(f_m^{(l)}(c)) = \sum_{n_1 l_1 l_2} (4\pi)^{\frac{1}{2}} V^{2n_1 + l_1} Y_m^{l_1 l_2(l)} T(n_1 l_1 l_2 l | f).$$
(A80)

The scalar operator  $T(n_1 l_1 l_2 l|.)$  depends only on c. Its adjoint  $\tilde{T}(n_1 l_1 l_2 l|.)$  is defined by equation (103). The tensor decomposition of  $T^{-1}$  is obtained by replacing V by -V on the right-hand side of equation (A80).

We have the identity

$$\int \varphi_{m'}^{[l']}(c) \left( T f_m^{(l)}(c) \right) dc = \int f_m^{(l)}(c) \left( T^{-1} \varphi_{m'}^{[l']}(c) \right) dc.$$
 (A81)

Using equation (A80) on both sides and adjusting the Wigner coefficients occurring in the tensors using the relation

$$(l_1 m_1 l - m | l' - m') = (-)^{l_1 - m_1} (l_1 m_1 l' m' | lm) \hat{l}' / \hat{l},$$
(A82)

with  $\hat{l} = (2l+1)^{\frac{1}{2}}$ , we obtain for the scalar operators

$$\int \varphi(c) T(n_1 l_1 l' l | f) c^2 dc = (-)^{l_1} (\hat{l'}/\hat{l}) \int f(c) T(n_1 l_1 l l' | \varphi) c^2 dc.$$
(A83)

Comparing this with the definition (103) of the adjoint we have

$$\hat{l} \tilde{T}(n_1 l_1 l' l | \varphi) = (-)^{l_1} \hat{l}' T(n_1 l_1 l l' | \varphi).$$
(A84)

This was used in equation (104).

Recursion relations for the operators may be obtained from the identities

$$\nabla_V^2 T = \nabla_c^2 T = T \nabla_c^2, \tag{A85a}$$

$$\partial_V T = \partial_c T = T \partial_c. \tag{A85b}$$

$$\mathrm{d}T/\mathrm{d}V = T\dot{V}.\partial_c. \tag{A85c}$$

We give only the relation that follows from the identity (A85a) and allows us to completely reduce the  $n_1$  dependence of the operators:

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$$T(n_1 l_1 l_2 l | f) = (\overline{N}_{0l_1}^2 2^{-2n_1} \overline{N}_{n_1 l_1}^{-2}) T(0 l_1 l_2 l | \nabla_l^{2n_1} f),$$
(A86a)

$$\nabla_l^2 f = \left(\frac{1}{c^2} \frac{\mathrm{d}}{\mathrm{d}c} c^2 \frac{\mathrm{d}}{\mathrm{d}c} - \frac{l(l+1)}{c^2}\right) f.$$
(A86b)

Equations (A85b) and (A85c) yield a step-down relation in  $l_1$  but this changes the other l values.

The  $n_1 = l_1 = 0$  term on the right-hand side of equation (A80) just picks the first term in the Taylor expansion (A78). Hence

$$T(00l_2l|f) = \delta_{ll_2}f(c).$$
(A87)

From equations (A86a) and (A87)

$$T(n_1 0 l_2 l | f) = 2^{-2n_1} \{ n_1! \Gamma(n_1 + \frac{3}{2}) / \Gamma(\frac{3}{2}) \} \delta_{ll_2} \left( \nabla_l^{2n_1} f(c) \right).$$
(A88)

The formulae for  $l_1 = 1$ ,  $n_1 = 0$ , which may be obtained from the general formula (A91) below or from equations (A78) and (A80) using the gradient formula, are given by

$$T(0\,1\,l+1\,l|f) = \left(\frac{l+1}{3(2l+1)}\right)^{\frac{1}{2}} \left(\frac{\mathrm{d}}{\mathrm{d}c} - \frac{l}{c}\right) f.$$
 (A89a)

$$T(0\,1\,l\,l-1\,|\,f) = \left(\frac{l}{3(2\,l+1)}\right)^{\frac{1}{2}} \left(\frac{d}{dc} + \frac{l+1}{c}\right) f.$$
 (A89b)

These are related by equation (A84) since  $[d/dc]^{\sim} = -(d/dc + 2/c)$  (cf. equations A44).

The tensor operator  $\mathbb{Z}_{m}^{[nl]}$  used in Section 10 and Appendix 2a is related to the translation operator by equation (A38). Its action on irreducible tensors  $f_{m}^{(l)}$  may also be expressed in terms of the scalar operators  $T(n_{1} l_{1} l_{2} l|)$  and tensors  $Y_{m}^{(l)}(\hat{c})$  by means of equations (A38) and (A80). Similarly, the relationship of the operators  $S^{nl}$  of Section 10 to  $T(n_{1} l_{1} l_{2} l|)$  may also be found.

We now give the general formula for the operators  $T(n_1 l_1 l_2 l|.)$ . In place of giving the actual derivation we have to be content to simply note that the action of the translation operator on a scalar function and on a spherical harmonic  $c^l Y_m^{(l)}(\hat{c})$  can be calculated directly. Then the general formula may be developed by using the relation

$$T\left(f(c) \mathbf{Y}_{m}^{(l)}(\hat{\boldsymbol{c}})\right) = \left(T\left(c^{-l} f(c)\right)\right) \left(T\left(c^{l} \mathbf{Y}_{m}^{(l)}(\hat{\boldsymbol{c}})\right)\right).$$
(A90)

It is evident that tensor recouplings are needed and the final result involves Wigner and Racah coefficients:

$$T(n_1 l_1 l_2 l | f) = \sum_{n'l' l_1'} \delta(2n_1 + l_1 - (2n' + l' + l_1')) \times \{l_1 l_2 l | l' l_1'\} c^{l-l_1} T_{n'l'}(c^{-l} f(c)).$$
(A91)

The *c* dependence in equation (A91) is contained in the last two terms. The operator  $T_{n'l'}$  is given by

$$T_{n'l'}(c^{-l}f(c)) = \hat{l'}c^{-l'} \sum_{r=l'}^{n'+l'} \frac{\overline{N}_{n'-l',l'}^2}{(n'+l'-r)!} c^{2r} \left(\frac{\mathrm{d}}{\mathrm{d}(c^2)}\right)^{n'+r} \left(c^{-l}f(c)\right).$$
(A92)

The effect of tensor recouplings is represented in the coefficients

$$\{l_{1} l_{2} l | l' l_{1}'\} = (4\pi)^{-\frac{1}{2}} (\hat{l}_{1} \hat{l}_{2} / \hat{l}') \sigma(l' l_{1}' l_{1}) \sigma(l - l_{1}' l' l_{2}) \sigma l_{1} l - l_{1} l) \times \overline{W} \begin{pmatrix} l_{1} l_{2} l \\ l - l_{1}' l_{1}' l' \end{pmatrix} \overline{N}_{0l_{1}}^{2} \overline{N}_{0,l-l_{1}}^{2} \overline{N}_{0l}^{-2},$$
(A93)

where  $\overline{W}$  is a Racah coefficient,  $\hat{l} = (2l+1)^{\frac{1}{2}}$  and the other quantities are defined in Appendix 1. The factors involving  $\pi$  eventually cancel out in equation (A91) but it is as well to carry them in the present form since they provide a check on the calculations.

From the first two  $\sigma$ 's in equation (A93) the coefficient vanishes unless  $l_1 + l_2 + l$  is even; the same is therefore true for  $T(n_1 l_1 l_2 l | f)$ .

The sum in equation (A91) is limited by the  $\delta$  function, with

$$2n', l', l'_1 \leqslant 2n_1 + l_1, \tag{A94}$$

and it is therefore a sum of finite terms. The number of terms in the sum is further restricted by the requirements of the Wigner and Racah coefficients.

Finally we note that from equations (A91) and (A92) we have

$$T(n_1 l_1 l_2 l | c^{l+2N}) \sim c^{l_2+2N'}$$

where  $2N' = 2N - 2n_1 + l - l_1 - l_2$ . Since  $l + l_1 + l_2$  is even and we have  $l \leq (l_1 + l_2)$ , we conclude that  $N' \leq N$ . It follows that, for a polynomial  $\varphi_N(c^2)$  of degree N in  $c^2$ ,

$$T(n_1 l_1 l_2 l | c^l \varphi_N(c^2)) = c^{l_2} \overline{\varphi}_{N'}(c^2),$$
(A95)

where  $\overline{\varphi}_{N'}(c^2)$  is another polynomial in  $c^2$  of degree N' and N'  $\leq N$ . This property was used following equation (118) in considering calculation of moments.

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