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The Boltzmann Equation for a Bounded Medium I. General Theory

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THE BOLTZMANN EQUATION FOR A BOUNDED MEDIUM
I. GENERAL THEORY

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CONTENTS

A general theoretical treatment is given of the linearized Boltzmann equation for flow in a bounded medium under conditions when the collision mean free path is of the order of the dimensions of the cross-section of the specimen. The approach given may be used for any type of particle; we consider gas molecules, electrons and phonons.

Part 1 is concerned with elucidating various results for a specimen of general cross-section. Having obtained the Boltzmann equation for any type of internal scattering mechanism, we deal with the boundary conditions relating to the scatter of particles by the specimen surfaces. Employing a very general form for these, a uniqueness theorem is proved for the solution of our problem. Certain general symmetry properties of the solution are discussed, and transport considerations are dealt with. Finally, a frequently used approximate treatment of boundary scatter is placed on a firmer mathematical foundation.

Part 2 is concerned with a detailed evaluation of the solution of the Boltzmann equation and boundary conditions for the flow between parallel plates. Previous treatments of this problem have assumed a 'relaxation-time' approximation for representing the effect of interparticle collisions in the medium, together with certain simplified boundary conditions. These two assumptions effectively remove the 'coupling' which should exist between the equations relating to the different particle modes, and thus greatly simplify the solution of the problem. We retain the complete Boltzmann equation, which is equivalent to a set of coupled first-order linear differential equations, and find its general solution containing various undetermined constants, which are then calculated via our general boundary conditions. This general solution is obtained as the sum of a complementary function and a particular integral. The former involves the eigenfunctions and eigenvalues of a modified collision operator, while the form taken by the latter depends on whether or not wave number (equivalent to momentum) is conserved in interparticle collisions. If wave number is *not* conserved, the particular integral is the solution of the Boltzmann equation for an infinite medium. The complementary function is then a combination of terms, varying exponentially with respect to distance, which correspond to a decrease in the neighbourhood of the boundary; these are qualitatively of the same form as when a relaxation time is employed. On the other hand, if wave number *is* conserved, the equation for an infinite medium possesses no solution and it is then found that the particular integral corresponds to a quadratic variation with respect to distance between the boundary surfaces. When the distance between these surfaces is sufficiently greater than the collision mean free path this quadratic variation is shown to differ from the usual 'viscous flow' theory by terms which are of importance only in the neighbourhood of the boundary; these, together with the complementary function, give the boundary corrections to the usual theory. The combination of quadratic particular integral and exponential complementary function is shown to give rise to the possibility of a 'Knudsen minimum', which has so far been observed both in gases and in phonon flow in liquid helium. Throughout the paper a general anisotropic medium is assumed and we thus incidentally generalize the theory of viscous flow, previously considered only for an isotropic medium in the case of gas molecules. Finally, a consideration is given of the situation when a small proportion of collisions *not* conserving wave number occurs together with a very large proportion of collisions that *do* conserve it; this is relevant to the effect of impurities and other momentum-destroying mechanisms at low temperatures. The result for general separation of the boundaries is obtained, and it is found that if this is large enough, the total particle flow is similar to that occurring in the absence of wave number conserving processes. However, the flow variation on leaving the boundary is now accurately characterized by a relaxation length which is the geometrical mean of the relaxation lengths for the two types of collision process acting separately.

Introduction

The Boltzmann equation arises naturally as the equation governing the flow of particles through a medium in which they can undergo interparticle collisions, when they are subject to some external driving field or combination of fields. Typical situations where the equation is used are:

(*a*) the flow of gas molecules under the influence of a pressure and temperature gradient (Chapman & Cowling 1952);

(*b*) the flow of electrons in a conductor under the influence of a temperature gradient, together with an electric field (Wilson 1954);

(*c*) the flow of phonons in a conductor or insulator under the influence of a temperature gradient (Peierls 1955; Khalatnikov 1956).

As we shall be considering later a general treatment to cover these three cases, it is convenient to mention at this point certain relevant differences existing between them.

(1) Statistics: molecules, electrons and phonons obey respectively Maxwell, Fermi–Dirac and Bose–Einstein statistics.

(2) For the purpose of a Boltzmann equation the generalized co-ordinates used for a gas molecule are its position, and momentum or velocity, since in terms of these, volume in phase space is conserved during the motion. For electrons and phonons, on the other hand, it is necessary to use position and wave number in order that volume in the corresponding phase space should always be conserved. Velocity instead of wave number is only permissible if the energy is a quadratic function of the latter; this will not be the case in general for electrons in a periodic potential—see appendix D.

(3) The flow of gas molecules (through a vacuum) and of phonons through liquid helium is with respect to an isotropic medium, and thus the intrinsic properties of the relevant particles—velocity for a given momentum, collision probabilities, etc., are independent of the direction of motion of the particles. However, in the case of electron and phonon propagation in crystals, these intrinsic properties must possess anisotropy corresponding to that of the crystal lattice.

(4) The types of collision that the particles can undergo are of varied character in as far as the quantities conserved in them are concerned. Thus, gas molecules are subject only to intermolecular collisions in which number, energy and momentum are conserved. In a non-conducting medium, phonons can undergo phonon-phonon collisions in which energy and wave number are conserved for a continuum, such as liquid helium; these are termed 'normal' or *N*-processes. In a crystal lattice in addition to these, 'Umklapp', or *U*-processes can occur in which energy alone is conserved. In a conducting crystal, electrons and phonons can interact via collisions in which the total energy and number of electrons are conserved for *U*-processes, and also the total wave number for *N*-processes. Electrons can further undergo electron-electron collisions of the *N* or *U* type. If impurities or defects exist in the medium, then either electrons or phonons can interact with these, yielding collisions in which number and energy are conserved (Klemens 1955).

(5) For a specimen with width much greater than the interparticle collision mean free path, the type of particle flow depends on whether or not wave number (equivalent to momentum) is conserved in collisions. If it is not conserved, then the particle flow is constant across the width of the specimen, at more than a few mean free paths from the specimen boundaries. On the other hand, if it is conserved, as with gas flow, then a parabolic variation of particle flow across the width of the specimen occurs at more than a short distance from the boundary. The reason for this difference will become clarified in this paper.

We shall now review briefly the main considerations in setting up the Boltzmann equation, in as far as these are relevant to explaining the position of the present paper relative to previous work on the Boltzmann equation. We first note that for a bounded medium it is necessary that the distribution function for the various particles should satisfy certain (so far unspecified) boundary conditions at the specimen surface as well as the Boltzmann equation inside the medium. The latter is obtained by the requirement that, for equilibrium flow, the rate at which particles are undergoing collision transitions into some state at some point in space should equal the rate at which they are leaving that state due to their convective movement under the action of the applied fields.‡ For a bounded medium with a driving field applied along its length, this gives rise to the following three terms (as will be seen in §1·1):

(*a*) a collision term, involving, in general, an integration over a non-linear algebraic combination of the occupation numbers f of the possible particles taking part in the relevant collision process;

(*b*) a term involving the divergence of f over the cross-section;

(*c*) a convection term corresponding to the applied driving field and involving the differential coefficient of f with respect to the wave number, temperature, etc. The resulting

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‡ An alternative approach to the Boltzmann equation in a particular case, via the relevant density matrix, has been given by Kohn & Luttinger (1957).

Boltzmann equation may be simplified in different ways, depending on the relative magnitude of the following three characteristic lengths: (1) the collision mean free path, (2) a mean specimen width, (3) the distance along the specimen in which the particle equilibrium distribution radically alters owing to the external driving field. If (1) is much greater than (2), the collision term (*a*) vanishes from the Boltzmann equation; if (2) is much greater than (1), the above spatial variation term (*b*) vanishes from the equation; if (3) is much greater than (1) or (2), the collision term (*a*) becomes linear in the displacement from some equilibrium distribution, and the convective term (*c*) involves only the differential coefficient of an equilibrium distribution occupation number—which is known. Previous work on the Boltzmann equation may be conveniently divided up on the basis of which of the lengths (1), (2) and (3) were considered to be large enough for the corresponding simplification to operate, also on the basis of whether wave number is conserved in collisions, case (i), or is not, case (ii). There are four situations to consider.

(A) The problem most commonly dealt with is where the lengths (2) and (3) are both much larger than (1). This gives rise to the linear Boltzmann equation for an infinite medium, which in case (i) has been dealt with for gas flow by Enskog (1922) and others (Hirschfelder, Curtiss & Bird 1954) using a variational approach and the introduction of a viscosity. In case (ii), variational techniques have been used by Kohler (1948, 1949*a*) and Sondheimer (1950) for electron conduction, and by Leibfried & Schlömann (1954) for phonons undergoing *U*-processes. Numerical methods have also been used by Rhodes (1950).

(B) The situation when length (2) is much greater than (1) and (3) has been considered in case (i) for gas flow by Burnett (1935), who used a perturbation approach giving first-order corrections to the results obtained by Enskog (1922). A different approach in this region has been given by Grad (1949) who employed moment equations, derived from the Boltzmann equation.

(C) At the other extreme, we have lengths (1) and (3) both much greater than length (2). In this case, the particles pass freely between boundaries of the specimen and the theory may be readily calculated (Devienne 1958). Pioneering work in this region was performed for gas flow by Knudsen (1911); the situation also occurs for phonon flow in solid dielectrics (Casimir 1938) and in liquid helium at sufficiently low temperatures (Whitworth 1958).

(D) The situation in which we are principally interested, and with which this paper will be dealing, is when length (3) is much greater than (1) and (2). We see from our earlier comments that this will give rise to a linearized Boltzmann equation retaining the three terms mentioned there. Treatments of this region (intermediate between (A) and (C)) have been given previously via the introduction of a 'relaxation-time' approximation, together with simplified boundary conditions to be satisfied at the specimen's surface. This 'relaxation-time' approximation consists of assuming that the collision term (*a*) in the Boltzmann equation is proportional to the displacement of the occupation number from the equilibrium distribution for the wave number under consideration. As boundary conditions it is assumed that a certain definite fraction of those particles incident on the surface are diffusely scattered and the remainder specularly reflected; the correct boundary conditions would give a definite probability for a particle incident in any state of being scattered into any other state. As will become clear in this paper, these two approximations taken together effectively remove the 'coupling' that should exist between the Boltzmann equation for different wave numbers, in the same way as the employment of a diagonal matrix will remove the 'coupling' between a set of linear simultaneous algebraic equations, reducing them to so many separate equations. In this way, the resulting Boltzmann equation and boundary condition for any wave number involves only that wave number, and may be readily solved. This treatment has been given by Fuchs (1938) for case (ii) in electron conduction, and has since been used exclusively in this work (reviewed by Sondheimer 1952). Similarly in case (i) for gas flow, a 'relaxation-time' approach has been used by Gross, Jackson & Ziering (1957) under these circumstances. Now, to what extent is the use of a 'relaxation-time' approximation justifiable? It has been employed for the situation (A) both in cases (i) and (ii), and here we may distinguish between two classes of use. The first class covers those situations where it is known that the assumption of a relaxation time is only an approximation. The second class is exemplified by impurity scatter of electrons in an infinite isotropic medium (Wilson 1954), where it may be rigorously shown that the true solution of the Boltzmann equation possesses the same directional variation as that obtained by making a 'relaxation-time' approximation. However, this result depends on the fact that the convective term in the Boltzmann equation transforms as a particular representation of the complete rotational group, while the collision operator is invariant under this group. Thus the validity of a relaxation time for this situation does not imply that it will be valid for a bounded medium where there exists an additional term in the Boltzmann equation; a further discussion of the error involved here has been given by Ham & Mattis (1955). We may therefore conclude that a relaxation-time approach is never strictly correct for a bounded medium.

In case (i) for gas flow, the complete Boltzmann equation has been considered by Wang-Chang & Uhlenbeck (1953, 1954) and by Gross & Ziering (1958). However, they are interested only in obtaining numerical results in particular cases, with certain orders of approximation, and they employ the simplified boundary conditions mentioned above; their work is, of course, only for an isotropic medium and does not deal with case (ii). We are interested in dealing with the complete linear Boltzmann equation and boundary conditions for a bounded medium without making any approximations, and in as general a manner as possible. In part 1 we consider the equation in detail for a medium of general cross-section, while in part 2 we obtain specific results for the flow between two plane parallel boundaries. The detailed arrangement is as follows. In §1·1 we obtain the Boltzmann equations for the flow of electrons, phonons and gas molecules, and show that, subject to a certain condition in the case of electron flow, they can all be written in the same form. In §1·2 we deal with the most general type of boundary conditions, assuming that there is no exchange of energy with the specimen walls. We then proceed to show in §1·3 that the Boltzmann equation, together with these boundary conditions and certain auxiliary conditions, have a unique solution, while in §1·4 we discuss certain symmetry properties of this solution. General transport considerations, both of quantities conserved in collisions and also of entropy, are dealt with in §1·5, and in §1·6 we put on a firmer mathematical basis an approximate method frequently used for boundary scatter, whereby a relaxation time for the particle to traverse the specimen is estimated, and then added reciprocally to the interparticle collision relaxation time in order to estimate the total relaxation time (Klemens 1956).

We consider the Boltzmann equation and boundary conditions for flow between two plane parallel surfaces in §2·1, and show that the former may be looked upon as a set of coupled linear first-order differential equations, whose solution involves a complementary function and particular integral. The former is considered in §2·2, and we show how it may be obtained in terms of the eigenvalues and generalized eigenvectors of the matrix coupling the differential equations; various relevant properties of this matrix are proved in appendix B. In §2·3 we deal with the particular integral, showing that it is spatially constant if wave number is *not* conserved in interparticle collisions and that it possesses a parabolic spatial variation if wave number *is* conserved. The problem of fitting the boundary conditions is tackled in §2·4, while in §2·5 we consider the form taken by our results for the cases of physical interest. The general question of transport is dealt with in §2·6, and in §2·7 we consider various special cases of our results, showing, among other things, how our solution in the case of wave-number conservation reduces to the usual 'viscous' result when the boundary separation is sufficiently greater than the collision mean free path. Finally, in §2·8 we deal with the situation when a small number of collisions *not* conserving momentum occurs together with a large number of collisions that *do* conserve it. By means of perturbation theory we obtain the effect of the former, and consider the form taken by the general result for various boundary separations.

Applications of the present theory to a detailed consideration of the Knudsen intermediate region, electron conduction in thin metallic films and to Couette flow in gases will be given in a subsequent paper. The theory of Part 2 will also be extended to cover magnetic fields and specimens of arbitrary cross-section. It will then remain to provide a treatment in the general case when the non-linear Boltzmann equation must be employed.

PART 1. PARTICLE FLOW IN A SPECIMEN OF GENERAL CROSS-SECTION

1·1. *Boltzmann equation for a medium of finite cross-section*

We shall consider the time-independent Boltzmann equation, first for electrons and phonons, and then for gas molecules, when flow occurs along a solid specimen (for electrons and phonons) or a tube (for gas molecules) of infinite length, but finite cross-section, under the action of some 'driving force' (temperature gradient, electric field, etc.) parallel to the tube axis. In the case of electrons we shall omit any consideration of a magnetic field, the inclusion of which would introduce certain difficulties which we do not propose to deal with in this paper. As shown in Wilson (1954), the Boltzmann equation for electrons and phonons then takes the form

$$\partial f/\partial t]_{\text{coll.}} = \mathbf{v}\,.\,\nabla_{\mathbf{R}} f + (e/\hbar)\,\mathscr{E}\,.\,\nabla_{\mathbf{k}} f, \tag{1·1}$$

where $f = f(\mathbf{k}, \mathbf{R})$ is the distribution function for particles (electrons or phonons) of wave number $\mathbf{k}$ at the point $\mathbf{R}$ in the medium. $\mathscr{E}$ is the total electric field acting on the particle, e and $\mathbf{v}$ are its charge and group velocity respectively, while $\partial f/\partial t]_{\text{coll.}}$ is the rate of change of f due to collisions of all types; $\nabla_{\mathbf{R}}$ and $\nabla_{\mathbf{k}}$ are gradient operators in real and wave-number space, respectively. To simplify equation (1·1) we suppose that there exists a fictitious temperature variation, linear along the length of the specimen (the z direction) with a gradient equal to the applied temperature gradient,‡ but constant across the specimen cross-section;§ we then define $\Phi(\mathbf{k}, \mathbf{r})$ by

$$f(\mathbf{k}, \mathbf{R}) = f^0(\mathbf{k}) - w(\mathbf{k})\,\Phi(\mathbf{k}, \mathbf{r}). \tag{1·2}$$

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‡ By 'applied temperature gradient' we mean the difference in temperature beetwen corresponding points in two cross-sections separated by distance d, divided by d.

§ This does not fix the absolute value of the temperature, which is considered in §1·3.

Here $f^0(\mathbf{k})$ is the equilibrium distribution (Fermi–Dirac or Bose–Einstein) with temperature T corresponding to the value of z at the point considered, while $w(\mathbf{k}) = \partial f^0(\mathbf{k})/\partial E(\mathbf{k})$, $E(\mathbf{k})$ being the energy associated with the state $\mathbf{k}$. Φ will now be independent of z and is spatially a function only of $\mathbf{r}$, a two-dimensional vector specifying the position in the cross-section of the specimen. If v_z is the resolute of $\mathbf{v}$ in the z direction, this allows the first term on the right-hand side of equation (1·1) to be written $v_z(\partial f^0/\partial T)\,(\mathrm{d}T/\mathrm{d}z) - w\mathbf{v}\,.\,\nabla_{\mathbf{r}}\Phi$, where the spatial derivative of w may be neglected since we assume $w\Phi \ll f^0$; for the same reason the second term becomes $(e/\hbar)\,\mathscr{E}\,.\,\nabla_{\mathbf{k}} f^0$. Now, $\mathscr{E}$ here is the total electric field acting on the particle, consisting of the applied field $\mathscr{E}_1$ along the z direction, together with any field $\mathscr{E}_2$ in the cross-sectional plane of the specimen which may be set up by the electron flow. Thus, in general we must put $\mathscr{E} = \mathscr{E}_1 + \mathscr{E}_2$ in the above expression, where $\mathscr{E}_2$ satisfies the equations

$$\operatorname{div}_{\mathbf{r}} \mathscr{E}_2 = 4\pi\rho(\mathbf{r}) = (e/\pi^2)\int w(\mathbf{k})\,\Phi(\mathbf{k},\mathbf{r})\,\mathrm{d}\mathbf{k}, \tag{1·3a}$$

$$\operatorname{curl}_{\mathbf{r}} \mathscr{E}_2 = 0, \tag{1·3b}$$

$\rho(\mathbf{r})$ being the total charge density of electrons and ions at $\mathbf{r}$; also $\mathscr{E}_2$ is zero at the boundaries. Now we shall see later in § 1·4 that if the anisotropy of our medium is such that the cross-sectional plane of the specimen is a plane of symmetry, then the solution of the Boltzmann equation obtained by omitting $\mathscr{E}_2$ is such as to make the right-hand side of equation (1·3a) zero. This means that if such a symmetry plane is present, a self-consistent solution of the Boltzmann equation, together with equations (1·3a) and (1·3b) exists in which $\mathscr{E}_2$ is zero. We shall therefore assume in our future discussion the existence of such a symmetry plane, and shall consequently omit $\mathscr{E}_2$ from the Boltzmann equation. Of course, for phonon conduction in dielectric media it is unnecessary to impose any such restriction on the anisotropy.

Finally, we consider the term $\partial f/\partial t]_{\text{coll.}}$ in equation (1·1), the form of which depends on the type of collision process. Thus for simple scattering of a particle by an impurity from state $\mathbf{k}$ to $\mathbf{k}'$ with probability $L(\mathbf{k},\mathbf{k}')$, we have

$$\partial f/\partial t]_{\text{coll.}} = \int L(\mathbf{k},\mathbf{k}')\,(\Phi - \Phi')\,\mathrm{d}\mathbf{k}',$$

while for a general n-particle process this generalizes to

$$\partial f/\partial t]_{\text{coll.}} = L[\Phi]. \tag{1·4}$$

Here $[\Phi]$ is a linear combination of the $n\Phi$'s corresponding to the interacting particles and L is a (negative) collision operator which multiplies $[\Phi]$ by a term involving properties of the medium and the n interacting particles, before integrating over all values of the wave numbers of the $n-1$ particles with which the one under consideration interacts.‡

The above considerations yield our Boltzmann equation in the form

$$w\mathbf{v}\cdot\nabla_{\mathbf{r}}\Phi + L[\Phi] = U, \tag{1·5}$$

where
$$U(\mathbf{k}) = v_z(\partial f^0/\partial T)\,(\mathrm{d}T/\mathrm{d}z) + (e/\hbar)\,\mathscr{E}\,.\,\nabla_{\mathbf{k}} f^0. \tag{1·6}$$

We shall now deal with the flow through a tube of gas molecules of one type, for which the general Boltzmann equation is given by Hirschfelder *et al.* (1954) in the form

$$\partial f/\partial t]_{\text{coll.}} = \mathbf{v}\,.\,\nabla_{\mathbf{R}} f + m^{-1}\mathbf{F}\,.\,\nabla_{\mathbf{v}} f, \tag{1·7}$$

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‡ If more than one type of collision occurs, for example, electrons with phonons and impurities, then the theory remains unaltered with $L[\Phi]$ replaced by $\sum_s L_s[\Phi]_s$ where s specifies the collision type.

where $f = f(\mathbf{v}, \mathbf{R})$ is the distribution function for molecules of velocity $\mathbf{v}$ at the point $\mathbf{R}$;[‡] m is the molecular mass and $\mathbf{F}$ is the (velocity-independent) force acting on it. Usually $\mathbf{F}$ is zero, but in the case of ion motion under the action of an electric field $\mathscr{E}$ in the z direction, $\mathbf{F} = e\mathscr{E}$, where e is the ion charge; our earlier remarks show that no electric field components are set up in the cross-sectional plane. To simplify equation (1·7) we proceed in a manner similar to that used for electrons and phonons and suppose that there exists a fictitious temperature and pressure gradient along the z direction equal to the respective applied gradients. We then define $\Phi'(\mathbf{v}, \mathbf{r})$ by

$$f(\mathbf{v}, \mathbf{R}) = f^0(\mathbf{v}) - w'(\mathbf{v})\,\Phi'(\mathbf{v}, \mathbf{r}), \tag{1·8}$$

where $f^0(\mathbf{v}) = n_0(2\pi m/kT)^{\frac{3}{2}} \exp(-E/kT)$ is the Maxwell equilibrium distribution with temperature T and number n_0 corresponding to the value of z at the point considered. Also $w'(\mathbf{v}) = \partial f^0/\partial E(\mathbf{v})$, $E(\mathbf{v})$ $[=\frac{1}{2}mv^2]$ being the energy of a molecule with velocity $\mathbf{v}$, and $\mathbf{r}$ is a two-dimensional vector specifying position in the cross-section of the tube. Substituting from equation (1·8) we readily see that, confining our attention to small deviations from equilibrium, the right-hand side of equation (1·7) becomes

$$\left[v_z\left(\frac{\partial f^0}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}z} + \frac{\partial f^0}{\partial n_0}\frac{\mathrm{d}n_0}{\mathrm{d}z}\right) + \frac{\mathbf{F}}{m}\,.\,\nabla_{\mathbf{v}} f^0\right] - w'\mathbf{v}\,.\,\nabla_{\mathbf{r}}\Phi'$$

$$= \left[f^0 v_z\left\{\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}z}\left(\frac{E}{kT} - \frac{5}{2}\right) + \frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}z} - \frac{F}{kT}\right\}\right] - w'\mathbf{v}\,.\,\nabla_{\mathbf{r}}\Phi', \tag{1·9}$$

use being made of the above explicit form for f^0; here P is the gas pressure.

Finally, we consider the term $\partial f/\partial t]_{\text{coll.}}$ in equation (1·7), where we are now only concerned with two-body collisions of the molecules. For this situation $\partial f/\partial t]_{\text{coll.}}$ may be readily obtained (Hirschfelder *et al.* 1954) and shown to be capable of representation in the form (1·4) where n now equals four (corresponding to the velocities of the two molecules before and after collision), and where we replace 'wave number' by 'velocity' in the definition of L. Thus we obtain our Boltzmann equation in the form

$$w'\mathbf{v}\,.\,\nabla_{\mathbf{r}}\Phi' + L[\Phi'] = U'(\mathbf{v}), \tag{1·10}$$

where $U'(\mathbf{v})$ is given by the square bracket in equation (1·9). In order to continue our development using a single equation to represent the behaviour of molecules, electrons and phonons, it is desirable to write equation (1·10) in the form (1·5), which we do by defining the wave number $\mathbf{k}$ for molecules by

$$\mathbf{k} = m\mathbf{v}/\hbar, \tag{1·11}$$

and by specifying the motion of a molecule with $\mathbf{k}$ rather than $\mathbf{v}$. In this way equation (1·10) becomes equation (1·5) on putting

$$w'(\hbar\mathbf{k}/m) = w(\mathbf{k}), \quad U'(\hbar\mathbf{k}/m) = U(\mathbf{k}) \quad \text{and} \quad \Phi'(\hbar\mathbf{k}/m, \mathbf{r}) = \Phi(\mathbf{k}, \mathbf{r}).$$

This definition (1·11), leading to the identity of the Boltzmann equation for molecules on the one hand and phonons and electrons on the other, shows that as far as deductions from this equation are concerned, conservation of momentum and wave number will lead to the same results. We shall see in Part 2 that such conservation leads to the possibility of 'viscous flow', and this result, suitably interpreted, will apply to electrons and phonons as well as to gas molecules.

[‡] To provide a treatment identical with that given previously for phonons and electrons, we define $(1/8\pi^3)\,f(\mathbf{v}, \mathbf{R})\,\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{R}$ as the number of molecules in the range $\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{R}$.

A slightly different way of writing the Boltzmann equation (1·5) (which will be used in Part 2) is to suppose that $\mathbf{k}$ takes the set of $2\mathcal{N}$ discrete values $\mathbf{k}_p$ ($-\mathcal{N} \leqslant p \leqslant +\mathcal{N}$, except $p = 0$) rather than to suppose it to be a continuous variable.‡ We then consider any function $g(\mathbf{k})$ to be represented by g_p, and by use of a summation instead of an integration we can put $L[\Phi] = \sum_q L_{pq}\Phi_q$ for the collision integral relating to $\mathbf{k}_p$, where the summation is taken here over all values of q; that is, $-\mathcal{N} \leqslant q \leqslant +\mathcal{N}$. This gives the Boltzmann equation (1·5) in the form

$$w_p \mathbf{v}_p \,.\, \nabla_{\mathbf{r}} \Phi_p(\mathbf{r}) + \sum_q L_{pq}\Phi_q(\mathbf{r}) = U_p. \tag{1·12}$$

With this notation, the principle of microscopic reversibility takes the form $L_{pq} = L_{qp}$; that is, the matrix L_{pq} is symmetric. We also have

$$\sum_{pq} L_{pq}\Lambda_p^*\Lambda_q = \int \Lambda^* L[\Lambda]\,\mathrm{d}\mathbf{k}$$

for any complex Λ, where Λ^* is the complex conjugate. It may be shown that owing to the invariance of L with respect to interchange of particles taking part in the process, the latter term may be readily transformed to $\kappa\int L[\Lambda]\,[\Lambda]^*\,\mathrm{d}\mathbf{k}$ (Chapman & Cowling 1952, Ziman 1956) where κ is a positive numerical factor depending on the number and polarization (if this is relevant) of particles occurring in the collision process. Since L is always negative, it follows that $\int \Lambda^* L[\Lambda]\,\mathrm{d}\mathbf{k}$ is always real and less than zero, unless $[\Lambda] = 0$, when it is zero. Thus L_{pq} is a negative definite matrix in the sense that $\sum_{pq} L_{pq}\Lambda_p^*\Lambda_q < 0$, unless Λ_p satisfies

$$\sum_q L_{pq}\Lambda_q = 0, \text{ when } \sum_{pq} L_{pq}\Lambda_p^*\Lambda_q = 0.$$

Finally, we note that a relaxation-time assumption for $\partial f/\partial t]_{\text{coll.}}$ is equivalent to assuming that the matrix L_{pq} is diagonal; that is, that $L_{pq} = (w_p/\tau_p)\,\delta_{pq}$ where τ_p is the relevant relaxation time. We shall discuss this further in §2·7.

1·2. *Boundary conditions*

In the previous section we obtained the Boltzmann equation governing the change of Φ inside the medium. However, in order to include all the physical facts and to obtain a unique solution, it is necessary to specify the conditions to be satisfied by Φ at the boundary of the specimen. The simple model for a surface that we shall employ is to suppose it to act as a rigid body scattering a particle incident from some direction into some other direction, without the possibility of any exchange of energy between the particle and the surface. To deal with this, we shall consider that at any given point $\mathbf{r}$ on the surface, the wave number is called positive for those particles approaching the surface and negative for those leaving it. Further, the symbol $\mathbf{k}$ will be used in matters concerning boundary scatter to denote only positive wave numbers. Then we shall define a probability $G(\mathbf{k}, \mathbf{k}', \mathbf{r})\,\mathrm{d}\mathbf{k}$ of a particle incident at $\mathbf{r}$ with wave number $\mathbf{k}'$ being scattered into a mode with wave number lying in the elementary volume $\mathrm{d}\mathbf{k}$ about $\bar{\mathbf{k}} (= -\mathbf{k})$. It follows that, since energy is conserved in boundary collisions, $G(\mathbf{k}, \mathbf{k}', \mathbf{r})$ will be non-zero only if $E(\mathbf{k}') = E(\mathbf{k})$ and, from the definition of probability, we have

$$\int' G(\mathbf{k}, \mathbf{k}', \mathbf{r})\,\mathrm{d}\mathbf{k} = 1 \tag{1·13}$$

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‡ In fact, owing to quantization this is really a more accurate representation of the physical facts, with $\mathcal{N} \sim 10^{20}$ to 10^{25}! However, we can, of course, obtain a satisfactory representation of the situation with $\mathcal{N}$ taking more reasonable values.

for all $\mathbf{k}'$ and $\mathbf{r}$, where $\int' d\mathbf{k}$ implies that the integral is taken over all positive values of $\mathbf{k}$.

The function G must satisfy the analogue of the general principle of microscopic reversibility (Moliner & Simons 1957), which states that if $f(\mathbf{k}, \mathbf{r})$ were independent of $\mathbf{k}$,‡ then the rate of particle transitions from $\mathbf{k}'$ to $\bar{\mathbf{k}}$ would equal that from $\mathbf{k}$ to $\bar{\mathbf{k}}'$; that is

$$u(\mathbf{k}', \mathbf{r})\, G(\mathbf{k}, \mathbf{k}', \mathbf{r}) = u(\mathbf{k}, \mathbf{r})\, G(\mathbf{k}', \mathbf{k}, \mathbf{r}), \tag{1·14}$$

where $u(\mathbf{k}, \mathbf{r})$ is the magnitude of the component of $\mathbf{v}(\mathbf{k})$ normal to the surface at $\mathbf{r}$. We see from this, together with equation (1·13), that

$$\int' u(\mathbf{k}', \mathbf{r})\, G(\mathbf{k}, \mathbf{k}', \mathbf{r})\, d\mathbf{k}' = u(\mathbf{k}, \mathbf{r}) \int' G(\mathbf{k}', \mathbf{k}, \mathbf{r})\, d\mathbf{k}' = u(\mathbf{k}, \mathbf{r}). \tag{1·15}$$

Introducing now the distribution function $f(\mathbf{k}, \mathbf{R})$, we see from the definition of $G(\mathbf{k}, \mathbf{k}', \mathbf{r})$ that, at any point on the boundary, the former satisfies the relation

$$u(\mathbf{k}, \mathbf{r})\, f(\bar{\mathbf{k}}, R) = \int' G(\mathbf{k}, \mathbf{k}', \mathbf{r})\, u(\mathbf{k}', \mathbf{r})\, f(\mathbf{k}', \mathbf{R})\, d\mathbf{k}'. \tag{1·16}$$

This yields
$$\Phi(\bar{\mathbf{k}}, \mathbf{r}) = \int' G(\mathbf{k}', \mathbf{k}, \mathbf{r})\, \Phi(\mathbf{k}', \mathbf{r})\, d\mathbf{k}', \tag{1·17}$$

use being made of equations (1·14) and (1·15), since the equilibrium distribution $f^0(\mathbf{k})$, depending only on $E(\mathbf{k})$, automatically satisfies equation (1·16). The set of equations (1·17) to be satisfied at all points $\mathbf{r}$ on the surface, constitute our required boundary conditions to be imposed on the Boltzmann equation (1·5). If we use the subscript notation introduced at the end of the last section, they take the form

$$\Phi_{\bar{p}}(\mathbf{r}) = \sum_q{}' G_{pq}(\mathbf{r})\, \Phi_q(\mathbf{r}), \tag{1·18}$$

where $\mathbf{k}_{\bar{p}} = \bar{\mathbf{k}}_p$, and $G_{pq}(\mathbf{r})$ is such as to make equations (1·17) and (1·18) equivalent; the summation is over all positive values of q.

In many contexts it is found sufficiently accurate to suppose the surface to be perfectly 'white'; that is, the probability of scattering for any given incident particle is such as to yield a constant spatial density for all modes leaving the surface. It is readily seen that for this to be so

$$G(\mathbf{k}, \mathbf{k}', \mathbf{r}) = u(\mathbf{k}, \mathbf{r}) \Big/ \int' u(\mathbf{k}, \mathbf{r})\, d\mathbf{k}. \tag{1·19}$$

For the case of an isotropic medium, this is seen to be identical with the familiar Lambert's cosine law of diffuse scatter.

1·3. *A uniqueness theorem*

The interparticle and boundary collisions that we have considered in the two preceding sections both conserve particle energy (and possibly particle number). We would therefore expect the Boltzmann equation (1·5) together with the boundary conditions (1·17) to determine uniquely the function $\Phi(\mathbf{k}, \mathbf{r})$, only if the total energy (and possibly the total particle number) is specified independently, since the equations (1·5) and (1·17) are only concerned with changes in f subject to conservation of these quantities. Consideration of the

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‡ This hypothetical situation does not, of course, correspond to a solution of the time-independent Boltzmann equation.

Boltzmann equation and boundary collisions alone is perhaps analogous to consideration of equations of motion for a dynamical system in that in the latter case it is found that a unique solution is only obtained for these equations, when the energy, which is conserved throughout the motion, is independently specified.

Now how should the total energy be specified in our system? We recall that when setting up the Boltzmann equation in § 1·1 we introduced a linear temperature variation along the z direction of the specimen, equal to the applied temperature gradient; however, the absolute value of the temperature T introduced was not fixed. If we now equate the total energy of the particles inside an elemental length δz of the specimen to the total energy of particles whose distribution function is the equilibrium distribution $f^0(\mathbf{k})$ at temperature T, this will specify the total energy of our system and will simultaneously remove the arbitrariness in our original definition of T. In this way we readily obtain the auxiliary condition

$$\iint E(\mathbf{k})\, w(\mathbf{k})\, \Phi(\mathbf{k},\mathbf{r})\, \mathrm{d}\mathbf{k}\, \mathrm{d}\mathbf{r} = 0, \tag{1·20a}$$

where the $\mathbf{k}$ integration is over all wave numbers, and the $\mathbf{r}$ integration over the specimen cross-section. Similarly, if the number of particles is conserved in all collisions, specification of the total number is given by the auxiliary condition

$$\iint w(\mathbf{k})\, \Phi(\mathbf{k},\mathbf{r})\, \mathrm{d}\mathbf{k}\, \mathrm{d}\mathbf{r} = 0. \tag{1·20b}$$

We expect from our discussion that the Boltzmann equation (1·5) together with the boundary and auxiliary conditions (1·17) and (1·20) should yield a unique solution for $\Phi(\mathbf{k},\mathbf{r})$. To prove this result mathematically, we consider two functions Φ_1 and Φ_2 each satisfying the equations (1·5), (1·17) and (1·20). Then if $\Psi = \Phi_1 - \Phi_2$, Ψ will satisfy equations (1·17) and (1·20) together with

$$L[\Psi] + w\mathbf{v}\,.\,\nabla_{\mathbf{r}}\Psi = 0. \tag{1·21}$$

A uniqueness theorem will result if we can show that Ψ is necessarily zero. We therefore multiply equation (1·21) by Ψ, and integrate over all $\mathbf{k}$ and over the cross-section of the specimen. The first term becomes $\iint \Psi L[\Psi]\, \mathrm{d}\mathbf{k}\, \mathrm{d}\mathbf{r}$, which may be written $\kappa\iint L[\Psi]^2\, \mathrm{d}\mathbf{k}\, \mathrm{d}\mathbf{r}$ for positive κ—see end of § 1·1. The second term becomes

$$\iint w\Psi\mathbf{v}\,.\,\nabla_{\mathbf{r}}\Psi\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{k} = \frac{1}{2}\iint w\Psi^2\mathbf{v}\,.\,\mathrm{d}\mathbf{s}\, \mathrm{d}\mathbf{k} = \frac{1}{2}\iint w\left\{\int' u[\Psi^2(\mathbf{k},\mathbf{r}) - \Psi^2(\bar{\mathbf{k}},\mathbf{r})]\mathrm{d}\mathbf{k}\right\}\mathrm{d}E\, \mathrm{d}s, \tag{1·22}$$

where $\mathrm{d}\mathbf{s}$ is an element of the boundary of the cross-sectional area of the specimen, and where $\int' \mathrm{d}\mathbf{k}$ is an integration over all positive values of $\mathbf{k}$ of constant energy E. Making use of the boundary conditions (1·17), we obtain the right-hand side of equation (1·22) in the form

$$\frac{1}{2}\iint w\left\{\int' u(\mathbf{k}')\, \Psi^2(\mathbf{k}',\mathbf{r})\, \mathrm{d}\mathbf{k}' - \int'\!\!\int'\!\!\int' \mathrm{u}(\mathbf{k})\, G(\mathbf{k}',\mathbf{k},\mathbf{r}) \right.$$
$$\left. \times\, G(\mathbf{k}'',\mathbf{k},\mathbf{r})\, \Psi(\mathbf{k}',\mathbf{r})\, \Psi(\mathbf{k}'',\mathbf{r})\, \mathrm{d}\mathbf{k}\, \mathrm{d}\mathbf{k}'\, \mathrm{d}\mathbf{k}''\right\}\mathrm{d}E\, \mathrm{d}s. \tag{1·23}$$

Now, from equation (1·13) we may write the first integral in the bracketed term of (1·23) in the form

$$\int'\!\!\int'\!\!\int' u(\mathbf{k}')\, G(\mathbf{k},\mathbf{k}',\mathbf{r})\, G(\mathbf{k}'',\mathbf{k},\mathbf{r})\, \Psi^2(\mathbf{k}',\mathbf{r})\, \mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{k}'\,\mathrm{d}\mathbf{k}'' \\ = \int'\!\!\int'\!\!\int' u(\mathbf{k})\, G(\mathbf{k}',\mathbf{k},\mathbf{r})\, G(\mathbf{k}'',\mathbf{k},\mathbf{r})\, \Psi^2(\mathbf{k}',\mathbf{r})\, \mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{k}'\,\mathrm{d}\mathbf{k}'',$$

making use of equation (1·14). Thus the expression (1·23) becomes

$$\tfrac{1}{2}\int\!\!\int w\left\{\int'\!\!\int'\!\!\int' u(\mathbf{k},\mathbf{r})\, G(\mathbf{k}',\mathbf{k},\mathbf{r})\, G(\mathbf{k}'',\mathbf{k},\mathbf{r})\, [\Psi^2(\mathbf{k}',\mathbf{r}) \\ -\Psi(\mathbf{k}',\mathbf{r})\, \Psi(\mathbf{k}'',\mathbf{r})]\, \mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{k}'\,\mathrm{d}\mathbf{k}''\right\} \mathrm{d}E\,\mathrm{d}s.$$

Interchanging $\mathbf{k}'$ and $\mathbf{k}''$ in this expression yields an identical form, except that the first term in the square bracket becomes $\Psi^2(\mathbf{k}'',\mathbf{r})$. Adding this new expression to the above, and halving the result allows (1·23) to be written

$$\tfrac{1}{4}\int\!\!\int w\left\{\int'\!\!\int'\!\!\int' u(\mathbf{k},\mathbf{r})\, G(\mathbf{k}',\mathbf{k},\mathbf{r})\, G(\mathbf{k}'',\mathbf{k},\mathbf{r})\, [\Psi(\mathbf{k}',\mathbf{r})-\Psi(\mathbf{k}'',\mathbf{r})]^2\, \mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{k}'\,\mathrm{d}\mathbf{k}''\right\} \mathrm{d}E\,\mathrm{d}s.$$

Thus the net result of our operations on equation (1·21) yields

$$\kappa\int\!\!\int L[\Psi]^2\,\mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{r} + \int\!\!\int\!\!\int'\!\!\int'\!\!\int' \Omega(\mathbf{k},\mathbf{k}',\mathbf{k}'',\mathbf{r}) \\ \times [\Psi(\mathbf{k}',\mathbf{r})-\Psi(\mathbf{k}'',\mathbf{r})]^2\,\mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{k}'\,\mathrm{d}\mathbf{k}''\,\mathrm{d}E\,\mathrm{d}s = 0, \qquad (1{\cdot}24)$$

where $\Omega = \frac{1}{4}w(E)\, u(\mathbf{k},\mathbf{r})\, G(\mathbf{k}',\mathbf{k},\mathbf{r})\, G(\mathbf{k}'',\mathbf{k},\mathbf{r})$. Now, both L and Ω are necessarily negative, and since the remainder of the integrand in each term of equation (1·24) is a square, it follows that the equation can only be true if each bracket is individually zero for all values of the relevant wave numbers. The square bracket in the second term of equation (1·24) will vanish for all $\mathbf{k}$ if $\Psi(\mathbf{k},\mathbf{r}) = a+bE(\mathbf{k})$ for constant a and b, while it follows from equation (A 2) in appendix A that the same remarks apply to the first term if $\Psi(\mathbf{k},\mathbf{r})$ is equal to a linear combination of quantities that are conserved in an interparticle collision. It therefore follows that equation (1·24) is always satisfied by $\Psi(\mathbf{k},\mathbf{r}) = bE(\mathbf{k})$ (since energy is always conserved in interparticle collisions), and will also be satisfied by $\Psi(\mathbf{k},\mathbf{r}) = a+bE(\mathbf{k})$ if interparticle collisions conserve number. In both of these cases we see that application of the relevant equations (1·20) yields $a = b = 0$, showing that $\Psi(\mathbf{k},\mathbf{r}) = 0$, and hence that a unique solution of our problem exists.

1·4. *General properties of the solution*

Although explicit solutions of our problem have not yet been obtained, it is possible to deduce general properties of the solution under certain conditions. We give the following:

(*a*) If the cross-section of the specimen possesses a centre of symmetry O, from which $\mathbf{r}$ is measured, then

$$\Phi(\bar{\mathbf{k}},\bar{\mathbf{r}}) = -\Phi(\mathbf{k},\mathbf{r}). \qquad (1{\cdot}25)$$

(*b*) If the cross-sectional plane of the specimen is a symmetry plane and $\mathbf{k}_*$ is the reflexion of $\mathbf{k}$ in that plane

$$\Phi(\mathbf{k}_*,\mathbf{r}) = -\Phi(\mathbf{k},\mathbf{r}). \qquad (1{\cdot}26)$$

(*c*) If Φ refers to a specimen of given cross-section and given collision operator L, while $\Phi^{\dagger}$ refers to a specimen with cross-section of the same shape, but increased by a factor of N and collision operator decreased by a factor of N, then if both specimens have the same surface scatter,

$$\Phi^{\dagger}(\mathbf{k}, \mathbf{r}^{\dagger}) = N\Phi(\mathbf{k}, \mathbf{r}), \tag{1·27}$$

where $\mathbf{r}^{\dagger}$ and $\mathbf{r}$ refer to corresponding points in the two cross-sections.

These results may be proved by demonstrating in each case that the two functions to be shown equal separately satisfy the same Boltzmann equation, boundary conditions and auxiliary conditions. It will then follow from the uniqueness theorem established in the previous section that the two functions are equal. The detailed proof in each case is quite straightforward and will not be given here.

We can now easily prove that when the cross-sectional plane is a symmetry plane, the right-hand side of equation (1·3*a*) is zero, which fact was used earlier in obtaining the Boltzmann equation for electrons. For this expression is proportional to

$$\int w(\mathbf{k})\, \Phi(\mathbf{k}, \mathbf{r})\, \mathrm{d}\mathbf{k} = \frac{1}{2}\int w(\mathbf{k})\, \{\Phi(\mathbf{k}, \mathbf{r}) + \Phi(\mathbf{k}_*, \mathbf{r})\}\, \mathrm{d}\mathbf{k} = 0$$

via equation (1·26).

We have defined the temperature used in the Boltzmann equation, constant across the specimen cross-section, by the condition (1·20*a*) $\int[\int E(\mathbf{k})\, w(\mathbf{k})\, \Phi(\mathbf{k}, \mathbf{r})\, \mathrm{d}\mathbf{k}]\, \mathrm{d}\mathbf{r} = 0$. Now, in general, the $\mathbf{k}$ integral inside the square bracket will not be identically zero for all $\mathbf{r}$, and this means that the *physical* temperature at different points in a given cross-section (as measured by some minute thermometer introduced at that point) will not be the same; thus a physical temperature variation can be set up across the cross-section. However, it is readily seen by the method used in the preceding paragraph that if the cross-section of the specimen is a symmetry plane, then the above $\mathbf{k}$ integral *will* be identically zero for all $\mathbf{r}$, and hence no such temperature (or by similar argument, number) variation is produced. In particular, no temperature or density variation is set up across the tube in the case of gas flow. This latter result has been previously obtained in a special case by Gross *et al.* (1957).

It follows from equations (1·17), (1·19) and (1·26) that if the surface is perfectly 'white' and the cross-section is a symmetry plane, then

$$\begin{aligned}\Phi(\bar{\mathbf{k}}, \mathbf{r}) &= \int' u(\mathbf{k}', \mathbf{r})\, \Phi(\mathbf{k}', \mathbf{r})\, \mathrm{d}\mathbf{k}' \Big/ \int' u(\mathbf{k},\mathbf{r})\, \mathrm{d}\mathbf{k} \\ &= \frac{1}{2}\int' u(\mathbf{k}', \mathbf{r})\, \{\Phi(\mathbf{k}', \mathbf{r}) + \Phi(\mathbf{k}'_*, \mathbf{r})\}\, \mathrm{d}\mathbf{k}' \Big/ \int' u(\mathbf{k}, \mathbf{r})\, \mathrm{d}\mathbf{k} = 0.\end{aligned} \tag{1·28}$$

This result is frequently used (for example, by Fuchs 1938) as the boundary condition for a perfectly 'white' surface. The above proof shows it to be strictly correct only when the required symmetry plane is present. It may be readily seen from equation (1·22) and the accompanying discussion, that the boundary condition (1·28) applied to the Boltzmann equation determines a unique solution to our problem, without requiring any auxiliary conditions.

1·5. *Transport considerations*

We now consider the transport by the particles of those physical quantities which may be experimentally measured, and which are conserved in particle collisions. For phonons, only the energy is of interest, this being related to the thermal conductivity, while for electrons, we deal with both energy and number, the latter giving rise to the electrical conductivity. In the case of gas molecules, we are also concerned with the momentum or 'wave number', since this relates to the pressures and shear stress that arise. If $\Gamma(\mathbf{k})$ denotes any of these quantities then the total transport per second Δ_z of Γ along the specimen is given by

$$\Delta_z = (1/8\pi^3)\left[A\int f^0(\mathbf{k})\,\Gamma v_z\,d\mathbf{k} - \iint w\Gamma v_z\,\Phi(\mathbf{k},\mathbf{r})\,d\mathbf{k}\,d\mathbf{r}\right], \qquad (1\cdot29)$$

where A is the cross-sectional area of the specimen. When $\Gamma(\mathbf{k})$ represents energy or number $\Gamma(\bar{\mathbf{k}}) = +\Gamma(\mathbf{k})$, $f^0(\bar{\mathbf{k}}) = +f^0(\mathbf{k})$ and $v_z(\bar{\mathbf{k}}) = -v_z(\mathbf{k})$, showing that the first term on the right-hand side of equation (1·29) is zero; this, of course, corresponds to the fact that a non-zero transport of these quantities depends on the departure from equilibrium. If $\Gamma(\mathbf{k}) = Z(\mathbf{k})$ the resolute of $\mathbf{k}$ in the z direction, then this term is non-zero, being proportional to the force on the tube cross-section for gas molecules. However, the $\mathbf{k}$ integral in the second term is now identically zero for all $\mathbf{r}$ as may be easily shown from equation (1·26), since for gas molecules the medium is isotropic; thus the pressure at all points in the cross-section is unaltered by the departure from equilibrium. Shear stresses across the cross-section will be proportional to Δ_z, when $\Gamma(\mathbf{k}) = X(\mathbf{k})$ or $Y(\mathbf{k})$, the resolutes of $\mathbf{k}$ in the x and y directions, respectively, and by a consideration of the cross-sectional symmetry plane it is readily seen that for gas molecules the first term in equation (1·29) is zero as expected. However, the integral in the second term will be non-zero in general and thus we may expect shear stresses to be set up across the tube due to the gas flow.

Consider now the total transport per second Δ_r of Γ on to unit length of any cylinder inside the specimen. We have

$$\Delta_r = (1/8\pi^3)\left[\iiint f^0(\mathbf{k})\,\Gamma\mathbf{v}\,.\,d\mathbf{s}\,d\mathbf{k} - \iint w\Gamma\Phi(\mathbf{k},\mathbf{r})\,\mathbf{v}\,.\,d\mathbf{s}\,d\mathbf{k}\right], \qquad (1\cdot30)$$

where $d\mathbf{s}$ is an element of the boundary of the cylinder cross-section. When $\Gamma(\mathbf{k})$ represents energy or number, we see by considering $\mathbf{k}$ and $\bar{\mathbf{k}}$ that the first term on the right-hand side of equation (1·30) is zero. To evaluate the second term, we multiply the Boltzmann equation (1·5) by $\Gamma(\mathbf{k})$ and integrate over all $\mathbf{k}$ and $\mathbf{r}$. This yields

$$A\int U(\mathbf{k})\,\Gamma(\mathbf{k})\,d\mathbf{k} = \iint \Gamma w\mathbf{v}\,.\,\nabla_{\mathbf{r}}\Phi\,d\mathbf{k}\,d\mathbf{r} = \iint \Gamma w\Phi\mathbf{v}\,.\,d\mathbf{s}\,d\mathbf{k}, \qquad (1\cdot31)$$

since the expression arising from the $L[\Phi]$ term in the Boltzmann equation is zero, as shown in appendix A. If Γ represents energy or number, we see by considering $\mathbf{k}$ and $\bar{\mathbf{k}}$ that the left-hand side of equation (1·31) is zero, and hence from equation (1·30) there is no net flow of energy or number through the cylinder. If $\Gamma(\mathbf{k}) = Z(\mathbf{k})$ we see by considering the cross-sectional symmetry plane that the first term in equation (1·30) is zero. However, from equation (1·31) we see the second term to be non-zero. It is proportional to the rate at which momentum in the z direction is destroyed by boundary collisions and is thus proportional to the force in the z direction exerted by the molecules on the cylinder. If $\Gamma(\mathbf{k}) = X(\mathbf{k})$ or $Y(\mathbf{k})$, the $\mathbf{k}$ integral in the first term of equation (1·30) is proportional to the equilibrium gas pressure on the cylinder wall at the point concerned, and the $\mathbf{k}$ integral in the second term gives the change in this pressure due to the departure from equilibrium.

Finally, we deal with entropy. This physical quantity is not conserved in collisions, neither between particles nor at the boundary, and it is therefore necessary to take into account its rate of production, together with its transport. If we consider unit length of the specimen, then using the standard statistical definition of entropy, it may be shown (Moliner & Simons 1957) that for any cross-section, the net flow out of the volume along the z direction is proportional to $\iint U\Phi\,\mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{r}$ and that the flow into the volume perpendicular to this direction is proportional to $\frac{1}{2}\iint w\Phi^2\mathbf{v}.\mathrm{d}\mathbf{s}\,\mathrm{d}\mathbf{k}$; the rate of production of entropy inside the volume is proportional to $\iint \Phi L[\Phi]\,\mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{r}$. It readily follows from multiplying the Boltzmann equation by Φ and integrating over $\mathbf{k}$ and $\mathbf{r}$ that the rate of entropy production inside the volume equals the total rate of flow out of it, while the discussion in § 1·3 shows that the rate of entropy production due to boundary collisions is positive.

1·6. *A mean-free-path treatment of boundary effects*

It was mentioned in the introduction that in the presence of boundary scatter the Boltzmann equation for an infinite medium $L[\Phi] = U$ has at times been considered to be modified to the form

$$L[\Phi]+w\Phi/\tau_2 = U, \tag{1·32}$$

where τ_2 is some relaxation time for scatter of the particles by the boundaries alone. It is obvious that if this is sufficiently accurate, and also if $L[\Phi]$ can be represented by $w\Phi/\tau_1$, then the result for an infinite solid may be modified for a bounded medium by replacing τ_1 by τ where

$$\tau^{-1} = \tau_1^{-1}+\tau_2^{-1}; \tag{1·33}$$

this is just the well-known result concerning the addition of the reciprocals of the relevant relaxation times. The present basis for the equations (1·32) and (1·33) would appear to be rough physical arguments, whereby one assumes that the essentially discontinuous changes undergone by a particle at the boundary at intervals of time τ_2 can in some way be represented by a continuous change, the rate of which will then be given by the second term on the left-hand side of equation (1·32). But how should τ_2 be computed; is it just the time for traversal of the specimen by particles of given wave number, averaged over all points at which the particles may leave the boundaries? The position is further complicated by the fact that the boundary conditions must to some extent enter into the calculation of τ_2. For if the walls were perfectly 'white' we might assume that τ_2 should correspond to a single transversal of the specimen, but as the proportion of specular reflexion increases, we must suppose that τ_2 increases in some way as well, since each collision with the boundary does not now completely destroy the motion of the particle parallel to the direction of the temperature gradient. Finally, we might expect the value of τ_2 to depend in some way on the collisions undergone by the particle inside the specimen. In general, these collisions alter the direction of motion of a given particle, and thus affect the time for it to transverse the specimen.

It would therefore seem that the rough physical argument on which equation (1·32) is based requires backing by a more fundamental mathematical argument, which should include some detailed prescription for the calculation of τ_2.

Now, we have seen earlier that the flow of particles in a finite specimen is accurately represented by a function $\Phi(\mathbf{k},\mathbf{r})$ satisfying equation (1·5). Also we have from equation (1·29) that the net transport Δ_z of energy or number along the specimen may be written

$$\Delta_z = \iint \Pi(\mathbf{k})\,\Phi(\mathbf{k},\mathbf{r})\,\mathrm{d}\mathbf{k}\,\mathrm{d}\mathbf{r}, \tag{1·34a}$$

where $\Pi(\mathbf{k})$ depends on the property considered, but is independent of $\mathbf{r}$. Thus if A is the cross-sectional area of the specimen,

$$\Delta_z = A\int \Pi(\mathbf{k})\,\overline{\Phi}(\mathbf{k})\,\mathrm{d}\mathbf{k}, \tag{1·34b}$$

where
$$\overline{\Phi}(\mathbf{k}) = A^{-1}\int \Phi(\mathbf{k},\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{1·35}$$

this representing the average of $\Phi(\mathbf{k},\mathbf{r})$ across the specimen cross-section. It is obvious that equation (1·34b) is the form for Δ_z that would be employed for conduction over an area A of an infinite medium, if $\overline{\Phi}(\mathbf{k})$ now represents the spatially independent solution of the Boltzmann equation for such a medium. Thus if equation (1·32) is to be correct, then the spatially independent Φ appearing in it must be $\overline{\Phi}(\mathbf{k})$ defined above, and we would therefore wish to show that $\overline{\Phi}(\mathbf{k})$ satisfies an equation of the form (1·32). To do this, we integrate the Boltzmann equation (1·5) over the cross-sectional area of the specimen, when dividing by A we obtain

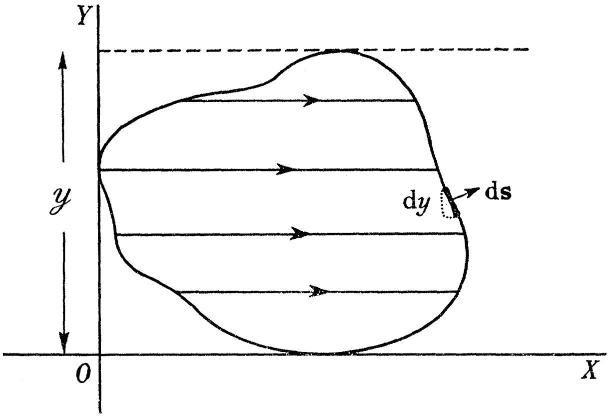

FIGURE 1

$$U - L[\overline{\Phi}] = (wv/A)\int \mathrm{div}_{\mathbf{r}}\,(\mathbf{j}\Phi)\,\mathrm{d}\mathbf{r} = (wv/A)\int \Phi\mathbf{j}\,.\,\mathrm{d}\mathbf{s}, \tag{1·36}$$

where $\mathbf{j}$ is a unit vector in the direction of $\mathbf{v}$. To develop further the right-hand side of equation (1·36), we introduce plane Cartesian x and y co-ordinates to specify position in the cross-section of the specimen shown in figure (1), where the x axis is taken parallel to the projection of $\mathbf{j}$ (for the particle under consideration) on the plane of the cross-section. Then if γ is the angle made by $\mathbf{j}$ with the specimen axis, we have $\mathbf{j}\,.\,\mathrm{d}\mathbf{s} = +\mathrm{d}y\sin\gamma$ for an element of boundary which the particle is approaching and $\mathbf{j}\,.\,\mathrm{d}\mathbf{s} = -\mathrm{d}y\sin\gamma$ for an element which the particle is leaving. Thus if v' $(=v\sin\gamma)$ is the resolute of $\mathbf{v}$ in the cross-section of the specimen, the right-hand side of equation (1·36) becomes $(wv'/A)\int\Phi^*(\mathbf{k},y)\,\mathrm{d}y$ where $\Phi^*(\mathbf{k},y)$ is the change in Φ between the boundaries at any y. We can now define the average change in Φ between the boundaries by $\hat{\Phi} = \mathscr{Y}^{-1}\int_0^{\mathscr{Y}}\Phi^*\,\mathrm{d}y$ where $\mathscr{Y}$ is the maximum width of the cross-section in a direction parallel to the y axis; also a mean value $\hat{\mathscr{X}}$ of the width $\mathscr{X}(y)$ of the cross-section in the x direction is defined by $\hat{\mathscr{X}} = \mathscr{Y}^{-1}\int_0^{\mathscr{Y}}\mathscr{X}\,\mathrm{d}y = A/\mathscr{Y}$. Hence, we obtain for the right-hand side of equation (1·36)

$$(wv'/\hat{\mathscr{X}})\,\hat{\Phi}. \tag{1·37}$$

To introduce $\overline{\Phi}$, we formally define the dimensionless quantity

$$\alpha(\mathbf{k}) = \overline{\Phi}(\mathbf{k})/\hat{\Phi}(\mathbf{k}), \tag{1·38}$$

and thus from the expression (1·37) obtain the Boltzmann equation (1·36) in the form

$$L[\overline{\Phi}] + w\overline{\Phi}/\tau_2 = U, \tag{1·39}$$

where

$$\tau_2 = \alpha\tau' \quad \text{and} \quad \tau' = \hat{\mathscr{X}}/v'. \tag{1·40}$$

τ' is independent of the particle interactions and boundary conditions; it corresponds physically to a certain well-defined average time for a particle of given wave number to cross the specimen.

We have now obtained in equation (1·39) an expression formally identical with the required form (1·32), but at the expense of having to introduce the quantity $\alpha(\mathbf{k})$, the exact calculation of which via equation (1·38) requires the solution of our original Boltzmann equation (1·5); thus it might at first appear that our treatment has been of little value. However, we shall now see that under certain circumstances the parameter $\alpha(\mathbf{k})$ can be estimated without solving our Boltzmann equation, the results of our considerations being such as to clarify the earlier qualitative comments on the modification of τ_2 by the particle interactions and boundary conditions.

Let us suppose at first that the boundaries are perfectly 'white'. Then the simplest case arises in the limit of no-particle interactions inside the medium, the value of $\alpha(\mathbf{k})$ corresponding to a linear change in Φ across the specimen. Under these circumstances

$$\alpha(\mathbf{k}) = \frac{A^{-1}\int_0^{\mathscr{Y}}\int_0^{\mathscr{X}} x\,\mathrm{d}x\,\mathrm{d}y}{\mathscr{Y}^{-1}\int_0^{\mathscr{Y}} \mathscr{X}\,\mathrm{d}y} = \frac{1}{2}\frac{\left[\int_0^{\mathscr{Y}} \mathscr{X}^2\,\mathrm{d}y/\mathscr{Y}\right]}{\left[\int_0^{\mathscr{Y}} \mathscr{X}\,\mathrm{d}y/\mathscr{Y}\right]^2} = \frac{1}{2}\frac{\widehat{\mathscr{X}^2}}{\hat{\mathscr{X}}^2}. \tag{1·41}$$

It is obvious that $\alpha(\mathbf{k})$ now depends only on the cross-sectional shape and the orientation of the x and y axes with respect to it; in fact $\alpha(\mathbf{k}) = \alpha(\phi)$ where $\mathbf{k}$ has spherical polar coordinates (k, θ, ϕ) with respect to the z direction. We know that $(\widehat{\mathscr{X}^2}/\hat{\mathscr{X}}^2) \geqslant 1$, and we would expect it to be close to 1 for reasonably symmetric cross-sections. For a circular cross-section α is independent of ϕ and may be shown to equal 0·54, while for a square α depends on ϕ, but if averaged over ϕ yields $\bar{\alpha} = 0·60$. For a rectangle $\bar{\alpha}$ increases, as the ratio of the sides increases, becoming 0·7 and 1·2 for ratios of 10 and 100, respectively. We therefore conclude in general terms that when there are no interactions $\alpha(\mathbf{k}) \sim 0·5$ to 0·6 for symmetrical shapes, increasing perhaps to unity for very asymmetrical cross-sections. We may mention in passing that if this approach is quantitatively followed up in the limit of no interactions, the results of Casimir (1938) for this situation are readily obtained.

If we now suppose particle interactions to be present the problem is obviously more complicated. We consider the situation when the interactions do not conserve momentum and in the limit of specimen width much greater than the mean free path due to interactions. If we assume that the particle interaction effect can be completely represented by a relaxation time (despite the possible objections to this mentioned earlier), then the variation of Φ across the specimen will consist of an initial rapid increase from zero, to a maximum value which will be maintained over the remainder of the cross-section; this gives $\alpha(\mathbf{k}) = 1$ independent of $\mathbf{k}$. It appears therefore that under these circumstances $\alpha(\mathbf{k})$ varies by a factor of up to 2, as we consider the transition from the limit of free-particle flow to the limit of very strong interactions, and it may be verified by detailed considerations that it varies monotonically as the interactions increase. Results similar to some of these have been obtained by Herring (1954).

Consider now the situation when the boundary scatter is partially specular. It is clear that this will not substantially alter $\hat{\Phi}$ since that represents the *change* in Φ from one boundary to the other. However $\overline{\Phi}$, representing an *absolute* value of Φ, will be increased and thus $\alpha(\mathbf{k})$ will increase. This in turn implies the increase in τ_2 that we would expect. It is possible to evaluate $\alpha(\mathbf{k})$ in detail for a given interparticle relaxation time and given proportion of specular surface scatter c; this gives in the limit of very small interparticle relaxation time $\alpha \sim (1-c)^{-1}$.

Our final conclusion is therefore that it is reasonable to use equations (1·32) and (1·33) for estimating approximately the combined effects of interparticle and boundary scatter, but that the points mentioned above should be taken into account when computing τ_2.

Part 2. Particle flow between infinite parallel plates

2·1. *Boltzmann equation and boundary conditions*

We now consider in detail the solution of the Boltzmann equation (1·5), together with its boundary and auxiliary conditions (1·17) and (1·20), for the case of particle flow between two infinite parallel plates. We suppose the plates to be separated by a distance $2a$, and specify position by means of Cartesian axes, with the x axis perpendicular to the plates and the z axis along the direction of the driving force, as in part 1; the origin is taken midway between the plates as shown in figure 2. The situation is a particular case of that considered in part 1, with the simplification that Φ will now be independent of y, neglecting edge effects; thus, employing the suffix notation introduced at the end of § 1·1, we shall be considering $\Phi_p(x)$. This function satisfies the Boltzmann equation (1·12), which now takes the form

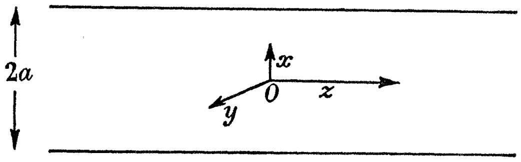

Figure 2

$$\sigma_p \frac{\mathrm{d}\Phi_p(x)}{\mathrm{d}x} + \sum_q L_{pq}\,\Phi_q(x) = U_p, \tag{2·1}$$

where
$$\sigma_p = w_p v_p^{(x)}, \tag{2·2}$$

$v_p^{(x)}$ being the resolute of $\mathbf{v}_p$ along the x direction. We note that the following relations exist between quantities with subscripts p and $\bar{p}$:

$$\sigma_{\bar{p}} = -\sigma_p, \quad U_{\bar{p}} = -U_p, \quad L_{\bar{p}\bar{q}} = L_{pq}. \tag{2·3}$$

In order to specify the boundary conditions in the form given by equation (1·18), we now establish the convention that positive and negative values of p should correspond to particles with $v_p^{(x)}$ respectively positive and negative. This gives the boundary conditions at the upper and lower plates

$$\Phi_{\bar{p}}(+a) = \sum_q{}' G_{pq}(+a)\,\Phi_q(+a) \quad \text{and} \quad \Phi_p(-a) = \sum_q{}' G_{pq}(+a)\,\Phi_{\bar{q}}(-a). \tag{2·4}$$

It follows from equations (1·14) and (2·2) that

$$\sigma_p G_{pq}(+a) = \sigma_q G_{qp}(+a). \tag{2·5}$$

Finally, we see that the auxiliary equations (1·20) now become

$$\sum_p E_p w_p \left[\int_{-a}^{+a} \Phi_p(x)\,\mathrm{d}x\right] = 0 \quad \text{and} \quad \sum_p w_p \left[\int_{-a}^{+a} \Phi_p(x)\,\mathrm{d}x\right] = 0. \tag{2·6}$$

The form of the Boltzmann equation (2·1) shows it to consist of a set of coupled first-order linear differential equations for the unknown $\Phi_p(x)$. We may therefore attempt to solve it by the elementary technique of obtaining a complementary function and a particular integral. The former is the general solution of equation (2·1) with the right-hand side put equal to zero and must contain $2\mathscr{N}$ arbitrary constants corresponding to the $2\mathscr{N}$ Φ's involved; the latter is *any* solution of equation (2·1). It then follows from the theory of differential equations that the general solution of our equation is the sum of the complementary function and the particular integral, and the conditions (2·4) and (2·6) may then be employed to determine the values of the $2\mathscr{N}$ arbitrary constants, and hence the unique solution of our problem. We shall follow this programme from a mathematical viewpoint in the next three sections, before considering in §2·5 the application of our results to cases of physical interest.

2·2. *The general solution of* $\sigma_p \mathrm{d}\Phi_p/\mathrm{d}x + \sum_q L_{pq}\Phi_q = 0$

We now proceed to obtain the general solution of the equation

$$\mathrm{d}\Phi_p(x)/\mathrm{d}x + \sum_q M_{pq}\Phi_q(x) = 0, \tag{2·7}$$

where

$$M_{pq} = \sigma_p^{-1} L_{pq}. \tag{2·8}$$

To solve this equation, we assume a solution of the form

$$\Phi_p(x) = \mathrm{e}^{-\lambda x} \sum_{n=0}^{Q} A_p^{(n)} x^n, \tag{2·9}$$

where Q, λ and the set of vectors $A_p^{(n)}$ $(0 \leqslant n \leqslant Q)$ are so far left undetermined. The fact that we shall presently show a solution of this form, containing $2\mathscr{N}$ undetermined constants, to satisfy the equation (2·7), will prove that it is the required general solution. Now, substituting our trial function (2·9) into the equation (2·7) yields

$$x^Q\left[\sum_q M_{pq} A_q^{(Q)} - \lambda A_p^{(Q)}\right] + \sum_{n=0}^{Q-1} x^n \left[\sum_q M_{pq} A_q^{(n)} - \lambda A_p^{(n)} + (n+1)\, A_p^{(n+1)}\right] = 0. \tag{2·10}$$

In order for this equation to be true for all x, it is necessary that the coefficients of x^n be identically zero for all relevant n. This gives

$$\sum_q M_{pq} A_q^{(Q)} - \lambda A_p^{(Q)} = 0 \tag{2·11 a}$$

and

$$\sum_q M_{pq} A_q^{(n)} - \lambda A_p^{(n)} = -(n+1)\, A_p^{(n+1)} \tag{2·11 b}$$

for $0 \leqslant n \leqslant Q-1$. From equation (2·11 *a*) we see that λ must be an eigenvalue of the matrix M_{pq}, while, $A_p^{(Q)}$ is a corresponding eigenvector. In the general case of degeneracy of an eigenvalue, there may exist several linearly independent eigenvectors, $B_p^{(t)}$ $(1 \leqslant t \leqslant T)$ and the most general form for $A_p^{(Q)}$ will then be given by

$$A_p^{(Q)} = \sum_{t=1}^{T} \nu_t B_p^{(t)}, \tag{2·12}$$

involving the T (so far) undetermined constants ν_t. Consider now the first of the equations (2·11 b), with $n = Q-1$: it may be written

$$\sum_q J_{pq} A_q^{(Q-1)} = -QA_p^{(Q)} = -Q\sum_{t=1}^{T} \nu_t B_p^{(t)}, \tag{2·13}$$

where

$$J_{pq} = M_{pq} - \lambda\delta_{pq}. \tag{2·14}$$

Now, equation (2·13) will possess a solution for $A_p^{(Q-1)}$ only if the right-hand side is orthogonal to all solutions η_p of the adjoint homogeneous equation

$$\sum_q J_{qp}\eta_q = 0; \tag{2·15}$$

that is, only if

$$\sum_p \eta_p A_p^{(Q)} = 0 \tag{2·16}$$

for all η_p. This question is examined in detail in appendix B where it is shown that the condition (2·16) gives rise to a set of T linear relations between the ν_t's of the form

$$\sum_{t=1}^{T} K_{st}\nu_t = 0, \tag{2·17}$$

where $K_{st} = \sum_p \sigma_p B_p^{(s)} B_p^{(t)}$, which must be satisfied if equation (2·13) is to possess a solution for $A_p^{(Q-1)}$. The possibility of satisfying equation (2·17) for non-zero ν_t is dealt with in appendix B, and it is proved there that if $\lambda \neq 0$ no such ν_t exist. Thus if $\lambda \neq 0$ equation (2·13) does not possess a solution. Hence in our trial solution (2·9) we must put $Q = 0$ for $\lambda \neq 0$ in order that no equation of the form (2·13) should result for which there is no solution. So if corresponding to $\lambda \neq 0$, there are H different eigenvectors B_{ps} $(1 \leqslant s \leqslant H)$, each 'normalized' in some way, say $\sum_p B_{ps} = 1$, we shall have a solution of equation (2·7) of the form

$$\Phi_p(x) = \sum_{s=1}^{H} l_s B_{ps}\,\mathrm{e}^{-\lambda_s x} \tag{2·18}$$

involving H arbitrary constants l_s. This solution will cover degeneracy of any eigenvalue λ by allowing the required λ_s to be equal.

Now if $\lambda = 0$, it is shown in appendix B that it *may* be possible to find non-zero ν_t satisfying equation (2·17). This will be so if the T relations of this equation are equivalent to some smaller number, say $T-S$, independent relations. In this case, we may express $T-S$ of the ν_t's in terms of the remaining S by relations of the form

$$\nu_t = \sum_{r=T-S+1}^{T} \alpha_{t,r}\nu_r \quad (1 \leqslant t \leqslant T-S),$$

which then gives the right-hand side of equation (2·13) as

$$-Q\sum_{r=T-S+1}^{T} \nu_r \left[\mathscr{B}_p^{(r)} + \sum_{t=1}^{T-S} \alpha_{t,r}\mathscr{B}_p^{(t)}\right]^{\ddagger}$$

which may be written $-Q\sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)}$ where

$$\mathscr{C}_p^{(t)} = \mathscr{B}_p^{(t+T-S)} + \sum_{s=1}^{T-S} \alpha_{s,\,t+T-S}\mathscr{B}_p^{(s)}; \tag{2·19}$$

[‡] Script capitals are used for symbols relating to eigenvectors with zero eigenvalue.

equation (2·13) will then possess a solution for completely arbitrary μ_t. We see that the $\mathscr{C}_p^{(t)}$ are those linear combinations of the $\mathscr{B}_p^{(t)}$ which allow the equation

$$\sum_q J_{pq} \mathscr{D}_q^{(t)} = -Q\mathscr{C}_p^{(t)} \tag{2·20}$$

to possess a solution for $\mathscr{D}_p^{(t)}$. Then, corresponding to $A_p^{(Q)} = \sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)}$ we will now have $A_p^{(Q-1)} = \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)}$. Further, since $\sum_q J_{pq} \mathscr{B}_q^{(t)} = 0$, it follows that a more general expression for $A_p^{(Q-1)}$ is given by

$$A_p^{(Q-1)} = \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)}. \tag{2·21}$$

We now consider the second of the equations (2·11 *b*) with $n = Q-2$, which for $\lambda = 0$ may be written

$$\sum_q M_{pq} A_q^{(Q-2)} = -(Q-1)\, A_p^{(Q-1)}. \tag{2·22}$$

In order for this to possess a solution it is necessary that the right-hand side should satisfy the orthogonality condition $\sum_q \eta_p A_p^{(Q-1)} = 0$, and it is shown in appendix B that this cannot be satisfied for any non-zero μ_t. Thus in our trial solution (2·9) we must put $Q = 1$ for $\lambda = 0$ in order that no equations of the form (2·22) should result, for which there is no solution. Hence for $\lambda = 0$ we shall have a solution of equation (2·7) of the form

$$\Phi_p(x) = x \sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)} + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)}, \tag{2·23}$$

where we suppose $\mathscr{C}_p^{(t)}$ to be 'normalized', which may be added to the solution (2·18) to give a more general solution containing $H+S+T$ arbitrary constants

$$\Phi_p(x) = \sum_{\substack{s=1 \\ \lambda_s \neq 0}}^{H} l_s B_{ps}\, \mathrm{e}^{-\lambda_s x} + x \sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)} + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)}. \tag{2·24}$$

But is this the most general solution of equation (2·7)? To answer this in the affirmative, we follow Friedman (1956) and define for any matrix M_{pq} a generalized eigenvector of rank n with eigenvalue λ, ${}_nB_p$ (if it exists) by the conditions

$$\sum_q (J_{pq})^n\, {}_nB_q = 0 \quad \text{and} \quad \sum_q (J_{pq})^{n-1}\, {}_nB_q \neq 0; \tag{2·25}$$

with this nomenclature an 'ordinary' eigenvector is, of course, an eigenvector of rank unity. It is shown by Friedman that for any eigenvalue there always exists a chain of generalized eigenvectors with the rank n taking successive integral values from 1 up to some maximum m. Now, if we operate with the matrix J_{pq} on the equation (2·20) we obtain

$$\sum_q (J_{pq})^2 \mathscr{D}_q^{(t)} = -Q \sum_q J_{pq} \mathscr{C}_q^{(t)} = 0, \tag{2·26}$$

showing that $D_p^{(t)}$ is a generalized eigenvector of rank two. Thus the proof given in appendix B of the non-existence of solutions of equation (2·13) for $\lambda \neq 0$ is equivalent to proving that no generalized eigenvectors of rank greater than unity exist for $\lambda \neq 0$; in fact, it is under the latter title that the proof in appendix B is given. Similarly, the proof that equation (2·22) possesses no solution for $\lambda = 0$ effectively proves that no eigenvectors of rank greater than two exist for $\lambda = 0$. Now, it is shown by Friedman (1956) that the totality of generalized eigenvectors span the vector space associated with the matrix M_{pq}, their number being equal to the order of the matrix, which in our case is $2\mathscr{N}$. It is obvious that the number of arbitrary constants in the solution (2·24) equals the total number of generalized eigenvectors, and thus equals $2\mathscr{N}$, showing that the solution (2·24) is the most general solution of equation (2·7).

We can further simplify our complementary function by making use of the fact, proved in appendix B, that if λ is a non-zero eigenvalue with eigenvector χ_p, then $-\lambda$ is also an eigenvalue with eigenvector $\psi_p = \chi_{\bar{p}}$. Applying this result to the first term of equation (2·24) gives the complementary function in the form

$$\Phi_p(x) = \sum_{\substack{s=1\\ \lambda_s \neq 0}}^{\frac{1}{2}H} [l_s B_{ps}\,\mathrm{e}^{-\lambda_s x} + m_s B_{\bar{p}s}\,\mathrm{e}^{+\lambda_s x}] + x\sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)} + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)}. \tag{2·27}$$

2·3. *A particular integral of* $\sigma_p\,\mathrm{d}\Phi_p/\mathrm{d}x + \sum_q L_{pq}\Phi_q = U_p$

It is shown in appendix B that the solutions of $\sum_q L_{pq}\mathscr{B}_q = 0$ (if any) can be chosen to satisfy either $\mathscr{B}_{\bar{p}} = +\mathscr{B}_p$ or $\mathscr{B}_{\bar{p}} = -\mathscr{B}_p$. If no solutions exist satisfying $\mathscr{B}_{\bar{p}} = -\mathscr{B}_p$, we shall term L_{pq} a U-matrix, while if any such solutions do exist we shall term it an N-matrix; the reason for this nomenclature will become apparent in § 2·5. We shall now see that the form taken by a particular integral of equation (2·1) depends on whether L_{pq} is a U- or N-matrix.

Case A: L_{pq} is a U-matrix. It is obvious that if we can solve the equation

$$\sum_q L_{pq}\Theta_q = U_p, \tag{2·28}$$

where Θ_p is now independent of x, then this value of Θ_p will constitute a particular integral of equation (2·1), since for such a Θ_p the first term of this equation is zero. Now, the condition for equation (2·28) to possess a solution is that U_p should be orthogonal to *all* solutions $\mathscr{B}_p$ of the adjoint homogeneous equation, which now takes the form $\sum_q L_{pq}\mathscr{B}_q = 0$, since $L_{pq} = L_{qp}$; that is, we require

$$\sum_p U_p \mathscr{B}_p = 0. \tag{2·29}$$

We can readily see that this condition (2·29) will always be satisfied since $U_{\bar{p}} = -U_p$ and $\mathscr{B}_{\bar{p}} = +\mathscr{B}_p$, as L_{pq} is a U-matrix. Thus a particular integral is given by the solution of equation (2·28) and we see from the latter two relations (2·3) that this may be chosen to satisfy $\Theta_{\bar{p}} = -\Theta_p$.

Case B: L_{pq} is a N-matrix. In this case we see that the condition (2·29) will not be satisfied, since at least one $\mathscr{B}_p$ exists for which $\mathscr{B}_{\bar{p}} = -\mathscr{B}_p$. Thus equation (2·28) does not possess a solution and we must therefore employ another method for obtaining a particular integral. In order to deal with this, let us consider the method used in the previous section for obtaining the complementary function. We assumed a solution of the form (2·9) and found that this satisfied equation (2·7) as long as solutions could be found for the equations (2·11). Now, suppose that we use the same trial solution (2·9) for the complete Boltzmann equation (2·1), in order to find a particular integral. Then, if we choose $\lambda = 0$,‡ it is readily seen that for this trial solution to satisfy our Boltzmann equation, we must satisfy conditions identical with (2·11) except that for $n = 0$ we have

$$\sum_q M_{pq} A_q^{(0)} = -A_p^{(1)} + \sigma_p^{-1} U_p, \tag{2·30}$$

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‡ It is obvious that for $\lambda \neq 0$, the exponential term will remain in the equation, thus preventing a solution from being obtained.

differing by $\sigma_{p}^{-}\,U_p$ from the corresponding equation (2·11 *b*). Now, since we are interested in obtaining *any* solution of equation (2·1), we wish to find the smallest value of Q for which a trial solution of the form (2·9) can be found, with vectors $A_p^{(n)}$ satisfying the equations (2·11) and (2·30). We know from the discussion given earlier in this section that no solution exists when $Q=0$. If $Q=1$, it is shown in appendix C that the relevant equations for $A_p^{(n)}$ have no solution, while for $Q=2$, on the other hand, it is shown that a solution always exists. Thus our particular integral $\Theta_p(x)$ is given by

$$\Theta_p(x) = A_p^{(2)}x^2 + A_p^{(1)}x + A_p^{(0)}, \tag{2·31}$$

where we see from equations (2·11) and (2·30) that the relevant $A_p^{(n)}$ must satisfy the relations

$$\sum_q L_{pq}A_q^{(2)} = 0, \tag{2·32a}$$

$$\sum_q L_{pq}A_q^{(1)} = -2\sigma_p A_p^{(2)}, \tag{2·32b}$$

$$\sum_q L_{pq}A_q^{(0)} = U_p - \sigma_p A_p^{(1)}. \tag{2·32c}$$

Equations (2·32 *a*, *b*) yield immediately that $A_p^{(2)}$, $A_p^{(1)}$ are respectively first- and second-rank eigenvectors of the matrix M_{pq} corresponding to eigenvalue zero; these we have considered in the last section. Equation (2·32 *c*) is, however, a new equation, the solution of which depends on the orthogonality condition

$$\sum_p (U_p - \sigma_p A_p^{(1)})\,\mathscr{B}_p^{(t)} = 0 \tag{2·33}$$

being satisfied for all $\mathscr{B}_p^{(t)}$. It is shown in appendix C that this condition, together with the equations (2·32), yields unique values for $A_p^{(0)}$, $A_p^{(1)}$, $A_p^{(2)}$, the latter two being given by

$$A_p^{(2)} = \sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)}, \tag{2·34a}$$

$$A_p^{(1)} = \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)} + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)}. \tag{2·34b}$$

Here μ_t and ν_t satisfy the equations

$$\sum_{t=1}^{S} H_{rt}\mu_t = \sum_p U_p \mathscr{C}_p^{(r)}, \tag{2·35a}$$

$$\sum_{t=1}^{T} K_{rt}\nu_t = \sum_p U_p \mathscr{B}_p^{(r)} - \sum_{t=1}^{S} I_{rt}\mu_t, \tag{2·35b}$$

where

$$H_{rt} = \sum_p \sigma_p \mathscr{C}_p^{(r)}\mathscr{D}_p^{(t)}, \quad I_{rt} = \sum_p \sigma_p \mathscr{B}_p^{(r)}\mathscr{D}_p^{(t)}. \tag{2·36}$$

Further, it may be shown that the A's satisfy the relations

$$A_{\bar{p}}^{(0)} = -A_p^{(0)}, \quad A_{\bar{p}}^{(1)} = +A_p^{(1)}, \quad A_{\bar{p}}^{(2)} = -A_p^{(2)}.$$

2·4. *Fitting the boundary and auxiliary conditions*

We see from equations (2·27), (2·28) and (2·31) that the general solution of our Boltzmann equation (2·1) is

$$\Phi_p(x) = \sum_{\substack{s=1\\ \lambda_s \neq 0}}^{\frac{1}{2}H} [l_s B_{ps}\,\mathrm{e}^{-\lambda_s x} + m_s B_{\bar{p}s}\,\mathrm{e}^{+\lambda_s x}] + x\sum_{=1}^{S} \mu_t \mathscr{C}_p^{(t)} + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)} + \Theta_p(x), \tag{2·37}$$

where $\Theta_p(x)$ is obtained from either equation (2·28) or (2·31) as the case may be. The solution (2·37) possesses $2\mathscr{N}(=H+S+T)$ undetermined constants, which according to the results of § 1·3 should be uniquely determined by application of the boundary and auxiliary conditions (2·4) and (2·6); this we now consider. If we put $\mathscr{G}_{pq}=G_{pq}(+a)$, and write

$$*W_p = W_p-\sum_q{}'\mathscr{G}_{pq}W_{\bar{q}}, \quad *W_{\bar{p}} = W_{\bar{p}}-\sum_q{}'\mathscr{G}_{pq}W_q, \tag{2·38}$$

for any vector W_p, the boundary conditions (2·4) applied to equation (2·37) yield

$$\sum_{\substack{s=1\\ \lambda_s\neq 0}}^{\frac{1}{2}H}[l_s{*B_{\bar{p}s}}\,\mathrm{e}^{-\lambda_s a}+m_s{*B_{ps}}\,\mathrm{e}^{+\lambda_s a}]+\sum_{t=1}^{S}\mu_t(a{*\mathscr{C}_{\bar{p}}^{(t)}}+{*\mathscr{D}_{\bar{p}}^{(t)}})+\sum_{t=1}^{T}\nu_t{*\mathscr{B}_{\bar{p}}^{(t)}}+{*\Theta_{\bar{p}}}(+a) = 0 \tag{2·39a}$$

and

$$\sum_{\substack{s=1\\ \lambda_s\neq 0}}^{\frac{1}{2}H}[l_s{*B_{ps}}\,\mathrm{e}^{+\lambda_s a}+m_s{*B_{\bar{p}s}}\,\mathrm{e}^{-\lambda_s a}]-\sum_{t=1}^{S}\mu_t(a{*\mathscr{C}_{p}^{(t)}}-{*\mathscr{D}_{p}^{(t)}})+\sum_{t=1}^{T}\nu_t{*\mathscr{B}_{p}^{(t)}}+{*\Theta_{p}}(-a) = 0. \tag{2·39b}$$

There will be $\mathscr{N}$ equations of the form (2·39*a*) and $\mathscr{N}$ of the form (2·39*b*) corresponding to the $\mathscr{N}$ modes leaving each of the upper and lower surfaces, respectively, and thus we might expect the boundary conditions in themselves to be sufficient to determine the $2\mathscr{N}$ arbitrary constants in our general solution. To see why the auxiliary conditions are in fact necessary, we note first that any first-rank eigenvector $\mathscr{B}_p^{(r)}$ appearing in the solution (2·37) is conserved in interparticle collisions (see appendix A). If this quantity is also conserved in boundary collisions, it may be readily shown that $*\mathscr{B}_p^{(r)}=0$, and hence ν_r will not be determined by equations (2·39). Instead, we have a corresponding auxiliary condition

$$\sum_p\mathscr{B}_p^{(r)}w_p\left[\int_{-a}^{+a}\Phi_p(x)\,\mathrm{d}x\right] \equiv \sum_{\substack{s=1\\ \lambda_s\neq 0}}^{\frac{1}{2}H}[(l_s+m_s)\,\lambda_s^{-1}(\mathrm{e}^{+\lambda_s a}-\mathrm{e}^{-\lambda_s a})\,(\sum_p w_p\mathscr{B}_p^{(r)}B_{ps})]$$
$$+2a\left[\sum_{t=1}^{S}\mu_t\,(\sum_p w_p\mathscr{B}_p^{(r)}\mathscr{D}_p^{(t)})+\sum_{t=1}^{T}\nu_t(\sum_p w_p\mathscr{B}_p^{(r)}\mathscr{B}_p^{(t)})\right]+\sum_p w_p\mathscr{B}_p^{(r)}\int_{-a}^{+a}\Theta_p(x)\,\mathrm{d}x = 0, \tag{2·40}$$

which taken together with the equations (2·39) (which remain consistent although $*\mathscr{B}_p^{(r)}=0$) gives the correct number of equations to obtain the undetermined constants. As a first step towards finding these constants, we add equations (2·39*a*) and (2·39*b*) which gives the following $\mathscr{N}$ equations

$$\sum_{\substack{s=1\\ \lambda_s\neq 0}}^{\frac{1}{2}H}n_s[{*B_{ps}}\,\mathrm{e}^{+\lambda_s a}+{*B_{\bar{p}s}}\,\mathrm{e}^{-\lambda_s a}]+\sum_{t=1}^{S}\mu_t[a({*\mathscr{C}_{\bar{p}}^{(t)}}-{*\mathscr{C}_{p}^{(t)}})+({*\mathscr{D}_{\bar{p}}^{(t)}}+{*\mathscr{D}_{p}^{(t)}})]$$
$$+\sum_{t=1}^{T}\nu_t({*\mathscr{B}_{\bar{p}}^{(t)}}+{*\mathscr{B}_{p}^{(t)}})+{*\Theta_{\bar{p}}}(+a)+{*\Theta_p}(-a) = 0, \tag{2·41}$$

where $n_s=l_s+m_s$. It may be easily shown that the coefficient of μ_t in the second summation of equation (2·41) is zero if $\mathscr{C}_{\bar{p}}^{(t)}=+\mathscr{C}_p^{(t)}$ and that the coefficient of ν_t in the third summation is zero if $\mathscr{B}_{\bar{p}}^{(t)}=-\mathscr{B}_p^{(t)}$. Also, it readily follows from the remarks at the end of cases *A* and *B* of §2·3 that we always have $\Theta_{\bar{p}}(+a)=-\Theta_p(-a)$, whence we see that the terms in $*\Theta_p$ are zero in equation (2·41), as is also the contribution to equation (2·40) arising from the Θ_p term. Since it may be shown that the number of constants with non-zero coefficient in equations (2·40) and (2·41) is less than or equal to the number of independent equations, it follows that such constants must be zero. Hence we see that

$$m_s=-l_s, \quad \mu_t=0 \quad \text{if} \quad \mathscr{C}_{\bar{p}}^{(t)}=-\mathscr{C}_p^{(t)} \quad \text{and} \quad \nu_t=0 \quad \text{if} \quad \mathscr{B}_{\bar{p}}^{(t)}=+\mathscr{B}_p^{(t)}.$$

Thus the solution (2·37) may now be written

$$\Phi_p(x) = \sum_{\substack{s=1\\ \lambda_s\neq 0}}^{\frac{1}{2}H} l_s[B_{ps}\,\mathrm{e}^{-\lambda_s x} - B_{\bar{p}s}\,\mathrm{e}^{+\lambda_s x}] + x\sum_{t=1}^{S}\mu_t\mathscr{C}_p^{(t)} + \sum_{t=1}^{S}\mu_t\mathscr{D}_p^{(t)} + \sum_{t=1}^{T}\nu_t\mathscr{B}_p^{(t)} + \Theta_p(x). \quad (2{\cdot}42)$$

This solution contains $\mathscr{N}$ arbitrary constants which may be determined by applying the boundary conditions (2·4) at *one* surface, that is, by use of equations equivalent to *either* (2·39 *a*) *or* (2·39 *b*). Since the deductions about the arbitrary constants made so far are such as to automatically satisfy the auxiliary conditions (2·40), these latter are now superfluous. Applying therefore our boundary condition (2·39 *b*) at the plane $x = -a$ we now have

$$\sum_{\substack{s=1\\ \lambda_s\neq 0}}^{\frac{1}{2}H} l_s[{}^*B_{ps}\,\mathrm{e}^{+\lambda_s a} - {}^*B_{\bar{p}s}\,\mathrm{e}^{-\lambda_s a}] + \sum_{t=1}^{S}\mu_t({}^*\mathscr{D}_p^{(t)} - a\,{}^*\mathscr{C}_p^{(t)}) + \sum_{t=1}^{T}\nu_t\,{}^*\mathscr{B}_p^{(t)} = -{}^*\Theta_p(-a) \quad (2{\cdot}43)$$

for p positive—a set of $\mathscr{N}$ linear equations to determine the $\mathscr{N}$ unknown constants. If L_{pq} is an N-matrix, the right-hand side of equation (2·43) may be somewhat simplified as follows. We know that $A_p^{(2)}$ is a definite linear combination of first-rank eigenvectors with zero eigenvalue, and hence by incorporating suitable terms from the complementary function into the particular integral, it may be seen from equation (2·31) that the latter can be written

$$\Theta_p(x) = A_p^{(2)}(x^2 - a^2) + A_p^{(1)}x + A_p^{(0)}. \quad (2{\cdot}44)$$

This gives the right-hand side of equation (2·43) as

$$-{}^*\Theta_p(-a) = {}^*A_p^{(1)}a - {}^*A_p^{(0)}.$$

We now consider deductions concerning the arbitrary constants that can be made from equation (2·43), when additional symmetry is present in the medium to which our equations refer. The basis of our examination is as follows: we know that $\Theta_p(x)$ is composed of one or more vectors Π_p (depending on whether L_{pq} is a U- or N-matrix) which are obtained from equations of the form $\sum_q L_{pq}\Pi_q = F_p$ for a given F_p. Now, if the matrices L_{pq} and M_{pq} are both invariant under a particular symmetry group, and if the vector F_p transforms as a definite representation of that group, we may deduce that Π_p transforms likewise. Hence if all the Π_p's contributing to $\Theta_p(x)$ transform in the same way, we can deduce that $\Theta_p(x)$ transforms in that way. Further, assuming that $\mathscr{G}_{pq}$ is invariant under the same symmetry group as is M_{pq},‡ we see from equation (2·38) that ${}^*\Theta_p(x)$ will transform in the same way as $\Theta_p(x)$. Thus the right-hand side of equation (2·43) transforms as a particular representation of the group under which M_{pq} is invariant. As far as the left-hand side of equation (2·43) is concerned, we make use of the fact that the first-rank eigenvectors B_{ps} of M_{pq} all transform according to some representation of the group under which M_{pq} is invariant, while the defining equation (2·20) for the second-rank eigenvectors corresponding to $\lambda = 0$ enables us to find under which representation these transform. As above, we assume $\mathscr{G}_{pq}$ to be invariant to the group concerned, and thus all terms, such as ${}^*B_{ps}$ on the left-hand side of equation (2·43) transform as some representation of this group. Now, we have shown above that the right-hand side of equation (2·43) transforms according to a *particular* representation of the group, and hence for equation (2·43) to be satisfied, it is necessary that all the

‡ This will generally be the case unless some additional directional properties are impressed on the specimen surface by, say, ruling grooves parallel to an arbitrary direction.

undetermined quantities, such as l_s, shall be zero, which have as coefficient a vector not transforming in the same way as the right-hand side.

We shall apply these ideas to the cases where the following are symmetry planes; (a) $y = 0$, (b) $z = 0$; we shall also consider the case of isotropy. If $y = 0$ or $z = 0$ is a symmetry plane, then L_{pq} and M_{pq} are both invariant under the inversion group where this applies to reflexion across the plane (this would not be true for M_{pq} if the symmetry plane were $x = 0$). By applying the method outlined above, it follows that when $y = 0$ is a symmetry plane, all constants on the left-hand side of equation (2·43) are zero, whose coefficients transform as the minus representation of the inversion group, while when $z = 0$ is a symmetry plane all constants are zero whose coefficients transform as the plus representation of the group. This method may also be used when the x axis is an axis of n-fold symmetry; we shall now consider the limiting case of this, when the medium is isotropic. Here L_{pq} and M_{pq} are both invariant to the axial rotation group applied about the x axis. If ϕ measures azimuth about this axis, it can be shown that Θ_p is always proportional to $\cos\phi$, and we can then deduce that the only non-zero undetermined constants are those whose coefficient is an eigenvector possessing a $\cos\phi$ variation. If we specify a state by spherical polar co-ordinates (k, θ, ϕ) relative to the x axis we can deduce that when L_{pq} is a U-matrix, Θ_p varies as $\sin\theta\cos\phi$, since U_p then varies in this way and L_{pq} is invariant to the complete rotation group.

Finally, it can be readily shown that the solution (2·42) satisfies the three general relations given in §1·4.

2·5. *Application to the physical situation*

Having dealt with our problem from a mathematical standpoint in the last three sections, we now return to a consideration of physical applications of the results obtained. It is obvious from our treatment that a specification of the quantities $\mathscr{B}_p$ which are conserved in inter-particle collisions, and which therefore satisfy $\sum_q L_{pq}\mathscr{B}_q = 0$ is fundamental to determining the nature of the solution. Possible quantities that $\mathscr{B}_p$ can be are: the energy E_p, the number N_p (which is, of course, unity for each particle) and the x, y and z resolutes of the wave number, X_p, Y_p, Z_p, respectively. There are four sets of these quantities that occur in practice.

(1) $\mathscr{B}_p = E_p$. This occurs with phonons and electrons undergoing those Umklapp processes in which the total number of particles alters.

(2) $\mathscr{B}_p = E_p, N_p$. This occurs with Umklapp processes in which the total number of particles is conserved, and also in the more important case of scatter of phonons and electrons by lattice imperfections of one type or another.

(3) $\mathscr{B}_p = E_p, X_p, Y_p, Z_p$. This occurs with phonons and electrons undergoing non-Umklapp processes conserving wave number in which the total number of particles alters.

(4) $\mathscr{B}_p = E_p, N_p, X_p, Y_p, Z_p$. This occurs with non-Umklapp processes in which the total number of particles is unaltered, and also in the very important case of intermolecular collisions in gas flow.

We shall now generalize the term ‘Umklapp’ or U-process to cover any collision in which wave number is not conserved (cases (1) and (2) above) and ‘non-Umklapp’ or N-process to cover any collision in which it is conserved (cases (3) and (4)). By comparison with §2·3 we see that for a U-process, L_{pq} will be a U-matrix, and for a N-process it will be a N-matrix.

In order to apply our solution (2·42) we shall first consider the form taken by the complementary function, before dealing with the particular integral and general solution. To tackle the complementary function, we must investigate what second-rank eigenvectors exist in each of the four cases given above. To do this, we obtain in each case the zero elements of the relevant K_{st} matrix (defined below equation (2·17)) to see what solutions there are of equation (2·17) and hence to derive the possible linear combinations of first-rank eigenvectors $\mathscr{C}_p^{(t)}$ (defined in equation (2·19)) which allow equation (2·20) to possess a solution for the corresponding second-rank eigenvector $\mathscr{D}_p^{(t)}$. It is clear that $K_{st}=0$ if the two vectors $\mathscr{B}_p^{(s)}, \mathscr{B}_p^{(t)}$ contributing towards it transform in the same way under the inversion group, where this replaces p by $\bar{p}$, and further elements may also be zero if additional symmetry is present. Since the detailed calculation is quite straightforward, the results will be tabulated for the above four cases:

(1) $T=1, S=1: \mathscr{B}_p^{(1)}=E_p=\mathscr{C}_p^{(1)}$.

(2) $T=2, S=2: \mathscr{B}_p^{(1)}=E_p=\mathscr{C}_p^{(1)}, \mathscr{B}_p^{(2)}=N_p=\mathscr{C}_p^{(2)}$.

(3) $T=4, S=2: \mathscr{B}_p^{(1)}=E_p, \mathscr{B}_p^{(2)}=X_p, \mathscr{B}_p^{(3)}=Y_p, \mathscr{B}_p^{(4)}=Z_p$;

general anisotropy: $\mathscr{C}_p^{(1)}=Y_p-(K_{13}/K_{12})\,X_p, \quad \mathscr{C}_p^{(2)}=Z_p-(K_{14}/K_{12})X_p$,

isotropy: $\mathscr{C}_p^{(1)}=Y_p, \quad \mathscr{C}_p^{(2)}=Z_p$.

(4) $T=5$ (*a*) $S=1$ for general anisotropy, (*b*) $S=3$ if $y=0$ *and* $z=0$ *or* if $x=0$ are symmetry planes:

$$\mathscr{B}_p^{(1)}=E_p, \quad \mathscr{B}_p^{(2)}=N_p, \quad \mathscr{B}_p^{(3)}=X_p, \quad \mathscr{B}_p^{(4)}=Y_p, \quad \mathscr{B}_p^{(5)}=Z_p;$$

(*a*) $\mathscr{C}_p^{(1)}=\kappa_3 X_p+\kappa_4 Y_p+Z_p$,

where $\kappa_3=[(K_{14}K_{25}-K_{24}K_{15})/(K_{13}K_{24}-K_{14}K_{23})]$

and $\kappa_4=[(K_{13}K_{25}-K_{23}K_{15})/(K_{14}K_{23}-K_{13}K_{24})]$.

(*b*) $\mathscr{C}_p^{(1)}=Y_p, \mathscr{C}_p^{(2)}=Z_p, \mathscr{C}_p^{(3)}=E_p-(K_{13}/K_{23})\,N_p$.

(*b*) applies, of course, for isotropy, and in particular to molecular flow.

In many of these results we are concerned with evaluating the ratio of non-zero elements of the relevant K_{st}-matrix. The general element we are concerned with is of the form $K=\sum_p \sigma_p \mathscr{G}_p \mathscr{H}_p$ where $\mathscr{G}_p=E_p$ or N_p and $\mathscr{H}_p=X_p$, Y_p or Z_p. To evaluate such an expression it is necessary to return to our original formulation, making use of the continuous variable $\mathbf{k}$, rather than the suffix p in order to specify a particle. In terms of $\mathbf{k}$, and making use of equation (2·2) we have

$$K \propto \int w(E)\,v_x(\mathbf{k})\,\mathscr{G}(E)\,\mathscr{H}(\mathbf{k})\,\mathrm{d}\mathbf{k}, \tag{2·45}$$

where the integration is taken over the relevant volume in $\mathbf{k}$ space. This result may be readily transformed to

$$K \propto \left[\int \mathscr{H}(\mathbf{k})\,\mathscr{K}(E)\,\mathrm{d}S_x-\beta\int \mathscr{K}(E)\,\mathrm{d}\mathbf{k}\right], \tag{2·46}$$

where $$\mathscr{K}(E)=\int_0^E w(\epsilon)\,\mathscr{G}(\epsilon)\,\mathrm{d}\epsilon,$$

$\mathrm{d}\mathbf{S}$ is an element of the boundary area in $\mathbf{k}$ space, and $\beta=1$ if $\mathscr{H}_p=X_p$, $\beta=0$ if $\mathscr{H}_p=Y_p$ or Z_p. If $\beta=1$, it is easily seen that the first term in (2·46) may be neglected if $\mathscr{K}(E)$ over the boundary area is much less than the average value of $\mathscr{K}(E)$ throughout the relevant volume in **k** space. This will be so for gas molecules, phonons at sufficiently low temperatures, and for electrons if the Fermi surface does not cut the first Brillouin zone.

To complete the detailed formulation of the complementary function, it is now necessary to obtain all the λ_s and B_{ps}; this we must defer until we deal with a definite situation in which L_{pq} is specified. Meanwhile we may note that the complementary function (2·27) involves terms of the form $\exp(\lambda_s x)$. On physical grounds we might therefore expect the various λ_s to be real, since otherwise the solution might possess an oscillatory behaviour inside the medium. Although the matrix M_{pq} is not Hermitian, it can nevertheless be shown that its eigenvalues are real; this is proved in appendix B.

We now consider the form taken by the particular integral in the four cases given above. For cases (1) and (2) L_{pq} is a U-matrix and thus the particular integral is given by the solution of equation (2·28). We note that this equation is the Boltzmann equation for an infinite medium, and thus our particular integral is the spatially constant solution for such a medium. For cases (3) and (4) given above, L_{pq} is a N-matrix and thus the particular integral is given by equation (2·44) where $A_p^{(2)}$, $A_p^{(1)}$, $A_p^{(0)}$ are determined via equations (2·32), (2·34) and (2·35). Applying equation (2·35b) to case (3) we readily see that $\nu_2 = \nu_3 = \nu_4 = 0$ and that ν_1, μ_1, μ_2 are determined by

$$\left.\begin{aligned} K_{21}\nu_1 + I_{21}\mu_1 + I_{22}\mu_2 &= \sum_p U_p X_p, \\ K_{31}\nu_1 + I_{31}\mu_1 + I_{32}\mu_2 &= \sum_p U_p Y_p, \\ K_{41}\nu_1 + I_{41}\mu_1 + I_{42}\mu_2 &= \sum_p U_p Z_p. \end{aligned}\right\} \tag{2·47}$$

If additional symmetry is present, further terms in equation (2·47) may be zero. Thus if $x = 0$ is a symmetry plane,

$$K_{13} = K_{14} = I_{21} = I_{22} = 0 = \sum_p U_p X_p.$$

If $y = 0$ is a symmetry plane,

$$K_{13} = I_{21} = I_{32} = I_{41} = 0 = \sum_p U_p X_p,$$

while if $z = 0$ is a symmetry plane,

$$K_{41} = I_{22} = I_{32} = I_{41} = 0 = \sum_p U_p X_p = \sum_p U_p Y_p.$$

This latter applies to the isotropic case, where we thus have

$$\nu_1 = \mu_1 = 0, \quad \mu_2 = \sum_p U_p Z_p \Big/ \sum_p \sigma_p Z_p \mathscr{D}_p^{(2)}.$$

In case (4) with general anisotropy there is a single second-rank eigenvector as considered above, and application of equation (2·35b) yields $\nu_3 = \nu_4 = \nu_5 = 0$. ν_1, ν_2 and μ_1 are given by

$$\left.\begin{aligned} K_{31}\nu_1 + K_{32}\nu_2 + I_{31}\mu_1 &= \sum_p U_p X_p, \\ K_{41}\nu_1 + K_{42}\nu_2 + I_{41}\mu_1 &= \sum_p U_p Y_p, \\ K_{51}\nu_1 + K_{52}\nu_2 + I_{51}\mu_1 &= \sum_p U_p Z_p. \end{aligned}\right\} \tag{2·48}$$

Again, these simplify if additional symmetry is present. If sufficient symmetry is present to give the three second-rank eigenvectors mentioned earlier, we find that when $x = 0$ is a symmetry plane $\nu_1 = \nu_2 = \nu_3 = \nu_4 = \nu_5 = \mu_3 = 0$, while μ_1 and μ_2 are given by

$$\left.\begin{aligned} I_{41}\mu_1 + I_{42}\mu_2 &= \sum_p U_p Y_p, \\ I_{51}\mu_1 + I_{52}\mu_2 &= \sum_p U_p Z_p. \end{aligned}\right\} \tag{2·49}$$

If $y = 0$ and $z = 0$ are symmetry planes it may be seen that

$$\mu_1 = 0 \quad \text{and} \quad \mu_2 = \sum_p U_p Z_p \Big/ \sum_p \sigma_p Z_p \mathscr{D}_p^{(2)}.$$

Thus for the isotropic case, we obtain the same particular integral for cases (3) and (4);

$$\Theta_p(x) = \Lambda Z_p(a^2 - x^2) + \Lambda \zeta_p x + \xi_p, \tag{2·50}$$

where $$\sum_q L_{pq}\zeta_q = 2\sigma_p Z_p, \quad \sum_q L_{pq}\xi_q = U_p - \Lambda\sigma_p\zeta_p \tag{2·51 a}$$

and $$\Lambda = \left(\sum_p U_p Z_p\right) \Big/ \left(\sum_p \sigma_p \zeta_p Z_p\right). \tag{2·51 b}$$

Now it will be shown in §2·6 that when at more than a few collision mean free paths (λ_s^{-1}) from either boundary, the solution (2·42) reduces to the particular integral Θ_p. In the case of U-processes this is what we should expect since Θ_p there represents the solution for an infinite medium. In the case of N-processes we shall be left with the solution (2·44) and it may be shown that on the assumption of a relaxation length $\mathscr{L}$, the ratio of the contributions from the term in x to that in $(x^2 - a^2)$ is of the order of $(\mathscr{L}/a)$, while the ratio of the contributions from the constant term to that in $(x^2 - a^2)$ is of the order of $(\mathscr{L}/a)^2$. Thus when we are well away from the boundary, the predominant contribution to $\Theta_p(x)$ will arise from the term in $(x^2 - a^2)$ and we shall see in §2·6 that this quadratic variation is equivalent to the quadratic variation given by the usual viscous flow theory. For both U-processes and N-processes the exponential terms in the complementary function will yield the correction to the result for an infinite medium which arises in the neighbourhood of the boundaries; for N-processes the constant term and linear term in $\Theta_p(x)$ will also contribute to this correction.

We can now see in a qualitative fashion how the 'Knudsen minimum' effect, observed for N-processes both in gas flow and in phonon flow through liquid helium, follows from our results. The solution (2·42) for N-processes may be regarded as consisting of the imposition of a term corresponding to 'viscous flow' upon a term which effectively corresponds to the complete solution for U-processes. In this latter case, the effect of the exponential terms is to decrease the flow as we leave the boundary, below the value obtained when there are no interparticle interactions. Thus in the case of N-processes, we have this initial decrease in flow as a increases from zero, followed by an increase as the quadratic 'viscous' term counteracts the decrease due to the exponential terms.

In order to evaluate the complete solution (2·42) in detail, it is necessary to deal with a specified collision operator allotting to $\mathscr{N}$ a value for which we can perform the resulting numerical work in obtaining the eigenvalues, eigenvectors and inverse. It is hoped to follow this approach in a subsequent paper, both for electron flow in thin films and for gas flow in narrow tubes.

2·6. *Transport considerations*

We now return to an evaluation of the transport of the various physical quantities Γ_p, which are conserved in interparticle collisions, in the x, y and z directions, making use of the solution (2·42) of our Boltzmann equation. A general consideration of transport was given in §1·5, and we shall now confine our attention to those situations in which a non-zero transport results only by virtue of the deviation from the equilibrium distribution. By introducing $\sigma_p = \sigma_p^{(x)} = w_p v_p^{(x)}$, $\sigma_p^{(y)} = w_p v_p^{(y)}$, $\sigma_p^{(z)} = w_p v_p^{(z)}$, it may be readily seen from equation (1·29) that the total transport per second per unit length in the y direction of Γ, along the z direction, is given in the present notation by

$$\Delta_z = (-1/8\pi^3) \sum_p \sigma_p^{(z)} \Gamma_p \left[\int_{-a}^{+a} \Phi_p(x)\, dx\right]$$

$$= (-1/8\pi^3) \Bigg\{ \sum_{\substack{s=1 \\ \lambda_s \neq 0}}^{\frac{1}{2}H} l_s \lambda_s^{-1} (e^{+\lambda_s a} - e^{-\lambda_s a}) \left[\sum_p \sigma_p^{(z)} B_{ps} (\Gamma_p + \Gamma_{\bar{p}})\right]$$

$$+ 2a \sum_{t=1}^{S} \mu_t \Big(\sum_p \sigma_p^{(z)} \Gamma_p \mathscr{D}_p^{(t)}\Big) + \sum_{t=1}^{T} \nu_t \Big(\sum_p \sigma_p^{(z)} \Gamma_p \mathscr{B}_p^{(t)}\Big) + \sum_p \sigma_p^{(z)} \Gamma_p \big(A_p^{(0)} + \tfrac{1}{3} a^2 A_p^{(2)}\big) \Bigg\}. \qquad (2·52)$$

Here the result is given when L_{pq} is a N-matrix. If it is a U-matrix the result is obtained by letting $A_p^{(2)} = A_p^{(1)} = 0$ and $A_p^{(0)} = \Theta_p$. If $\Gamma_{\bar{p}} = -\Gamma_p$ as is the case for $\Gamma_p = X_p$, Y_p or Z_p, it is readily seen that $\Delta_z = 0$, this agreeing with the results of §1·5. On the other hand, if $\Gamma_{\bar{p}} = +\Gamma_p$, as is the case if $\Gamma_p = E_p$ or N_p, then in general all the terms in equation (2·52) will contribute; this will remain true whatever symmetry is present.

Considering now the transport in the y direction, we readily see that Δ_y, defined analogously to Δ_z, is given by equation (2·52) with $\sigma_p^{(y)}$ substituted for $\sigma_p^{(z)}$, and that if $\Gamma_{\bar{p}} = -\Gamma_p$ it is zero. If $\Gamma_{\bar{p}} = +\Gamma_p$, then for general anisotropy all terms will contribute to Δ_y, but if either the $y = 0$ or $z = 0$ planes are symmetry planes it is easily shown that $\Delta_y = 0$; in particular this result holds if the medium is isotropic.

Finally, we consider transport in the x direction. Here we define $\Delta_x(x)$ as the total transport of Γ per second per unit area in the y–z plane along the x direction; this will be a function of x. We shall have

$$\Delta_x(x) = (-1/8\pi^3) \sum_p \sigma_p \Gamma_p \Phi_p(x) \qquad (2·53a)$$

$$= (-1/8\pi^3) \Bigg\{ \sum_{\substack{s=1 \\ \lambda_s \neq 0}}^{\frac{1}{2}H} l_s \Big[e^{-\lambda_s x} \sum_p \sigma_p \Gamma_p B_{ps} + e^{+\lambda_s x} \sum_p \sigma_p \Gamma_{\bar{p}} B_{ps}\Big]$$

$$+ x \sum_{t=1}^{S} \mu_t \Big[\sum_p \sigma_p \Gamma_p \mathscr{C}_p^{(t)}\Big] + \sum_{t=1}^{S} \mu_t \Big[\sum_p \sigma_p \Gamma_p \mathscr{D}_p^{(t)}\Big] + \sum_{t=1}^{T} \nu_t \Big[\sum_p \sigma_p \Gamma_p \mathscr{B}_p^{(t)}\Big] + \sum_p \sigma_p \Gamma_p \Theta_p(x) \Bigg\}. \qquad (2·53b)$$

Now, since $\Gamma_{\bar{p}} = \pm \Gamma_p$ and since $\lambda_s \neq 0$ in the first summation over s, it follows from equation (B1) that this term is zero. Also the second term is zero from the requirement that equation (2·20) should have a solution. As far as the remaining terms are concerned, we consider first the case of U-processes when $\Gamma_p = E_p$ or N_p. Then from earlier results $\nu_t = 0$ and also $\mathscr{C}_{\bar{p}}^{(t)} = +\mathscr{C}_p^{(t)}$ and $\mathscr{D}_{\bar{p}}^{(t)} = -\mathscr{D}_p^{(t)}$. Hence since $\Gamma_{\bar{p}} = +\Gamma_p$, the only non-zero terms for general anisotropy on the right-hand side of equation (2·53b) are

$$\sum_{t=1}^{S} \mu_t \Big(\sum_p \sigma_p \mathscr{D}_p^{(t)} \Gamma_p\Big) + \sum_p \sigma_p \Gamma_p \Theta_p.$$

This is independent of x as expected from the results of § 1·5, and must be zero by a consideration of its value at the boundaries $x = \pm a$, where we know that no net flow of energy or particles occurs in the x direction. In the case of N-processes, the possible non-zero terms remaining in equation (2·53 b) are

$$\Delta_x(x) = \sum_{t=1}^{S} \mu_t [\sum_p \sigma_p \mathscr{D}_p^{(t)} \Gamma_p] + \sum_{t=1}^{T} \nu_t [\sum_p \sigma_p \mathscr{B}_p^{(t)} \Gamma_p] + x^2 \sum_p \sigma_p A_p^{(2)} \Gamma_p + x \sum_p \sigma_p A_p^{(1)} \Gamma_p + \sum_p \sigma_p A_p^{(0)} \Gamma_p. \tag{2·54 a}$$

Of these, we see from the requirement that equations (2·32 b, c) should possess a solution, that $\sum_p A_p^{(2)} \sigma_p \Gamma_p = 0$ and $\sum_p A_p^{(1)} \sigma_p \Gamma_p = \sum_p U_p \Gamma_p$. This gives

$$\Delta_x(x) = \sum_{t=1}^{S} \mu_t [\sum_p \sigma_p \mathscr{D}_p^{(t)} \Gamma_p] + \sum_{t=1}^{T} \nu_t [\sum_p \sigma_p \mathscr{B}_p^{(t)} \Gamma_p] + x \sum_p U_p \Gamma_p + \sum_p A_p^{(0)} \sigma_p \Gamma_p. \tag{2·54 b}$$

Considering first the case that $\Gamma_{\bar{p}} = +\Gamma_p$, we have that the third term in equation (2·54 b) is always zero. The remaining terms are independent of x, as expected from the results of § 1·5, and since number and energy are conserved on the boundary their sum must be zero. Taking now the case when $\Gamma_{\bar{p}} = -\Gamma_p$, we have from previous results that the first, second and fourth terms in (2·54 b) are zero, leaving $\Delta_x(x) = x \sum_p U_p \Gamma_p$. Hence the net flow Δ_x of Γ on to the plates is $2a \sum_p U_p \Gamma_p$, this agreeing with equations (1·30) and (1·31). If symmetry planes are present, this may be zero if $\Gamma_p = X_p$ or Y_p, but not if $\Gamma_p = Z_p$.

It is interesting, as well as a check on our results, to consider the production and transport of entropy, making use of the discussion at the end of § 1·5, and evaluating the relevant quantities over a rectangular parallelepiped with base of unit area, lying between the plates, using our known solution (2·42) for $\Phi_p(x)$. Details will not be given of this calculation, the algebra of which is somewhat involved. It transpires, as we should expect, that $\Delta_z = \Delta_x + R$, where $\Delta_z = \sum_p U_p \int_{-a}^{+a} \Phi_p(x)\,\mathrm{d}x$ is the net flow of entropy out of the volume along the z direction, $\Delta_x = \sum_p \sigma_p \Phi_p^2(+a)$ is the net flow into the volume due to its production at the boundary plates, and

$$R = \int_{-a}^{+a} [\sum_{pq} L_{pq} \Phi_p(x)\, \Phi_q(x)]\,\mathrm{d}x$$

is the rate of entropy production inside the volume due to interparticle collisions.

2·7. *The solution in special cases*

We consider in this section our previous results in the following four special cases: (A) the distance between the boundary plates is much less than the collision mean free path, (B) the distance between the plates becomes very large, (C) the collision operator satisfies the relation $L_{pq} = L_{\bar{p}\bar{q}}$ $(q \neq p)$, (D) a relaxation time exists; that is $L_{pq} = w_p \tau_p^{-1} \delta_{pq}$. We shall reserve for § 2·8 a discussion of the situation when there is a large number of N-processes together with very few U-processes.

Case A. In accordance with remarks made in the introduction, we see that for this case, the Boltzmann equation (2·1) now takes the form

$$\sigma_p \frac{\mathrm{d}\Phi_p(x)}{\mathrm{d}x} = U_p, \tag{2·55}$$

with the collision term omitted. This equation has the general solution

$$\Phi_p(x) = \sigma_p^{-1} U_p x + W_p, \tag{2·56}$$

where the W_p are the required $2\mathcal{N}$ arbitrary constants. These are determined by the boundary and auxiliary conditions (2·4) and (2·6) which now become

$$a\,{}^*(\sigma_{\bar{p}}^{-1}\,U_{\bar{p}}) + {}^*W_{\bar{p}} = 0, \quad -a\,{}^*(\sigma_p^{-1}\,U_p) + {}^*W_p = 0, \tag{2·57}$$

and

$$\sum_p w_p E_p W_p = 0, \quad \sum_p w_p W_p = 0, \tag{2·58}$$

respectively. This situation corresponds, in gases, to free molecular flow, and we have here given more general boundary conditions than are usually taken into account. Since for practical purposes the previous theory in this region is satisfactory (see, for example, Devienne 1958), it will not be considered any further, except to mention that the above equations (2·56), (2·57), (2·58) may be shown to arise from the corresponding equations of the general case by expanding all terms of the form $\exp(\lambda_s x)$ as a power series in x and rejecting powers of x higher than the first.

Case B. We first proceed to show that as we leave the boundary, the complementary function (2·27) decreases, and tends to zero as the distance from the boundary tends to infinity. This reduces the general solution (2·42) to the particular integral $\Theta_p(x)$, given by equations (2·28) or (2·44) as the case may be.

Application of the boundary conditions, equivalent to equation (2·43), to the solution (2·42), yields as an order-of-magnitude result

$$\sum_{s=1}^{\mathcal{N}} l'_s [B_{ps} - B_{\bar{p}s}\,\mathrm{e}^{-2\lambda_s a}] \approx -\Theta_p(-a), \tag{2·59}$$

where $l'_s = l_s\,\mathrm{e}^{+\lambda_s a}$. It therefore follows that $\sum_{s=1}^{\mathcal{N}} l'_s B_{ps}$ must be finite. At a distance x' from the boundary $x = -a$, we have from equation (2·42)

$$\Phi_p(x) \approx \Theta_p(x) + \sum_{s=1}^{\mathcal{N}} l'_s [B_{ps}\,\mathrm{e}^{-\lambda_s x'} - B_{\bar{p}s}\,\mathrm{e}^{-\lambda_s (2a-x')}], \tag{2·60}$$

where the summation represents the complementary function (2·27). Now, it is clear that if $x' \leqslant a$, then the second term in this summation cannot be greater than the order of magnitude of the first term, and thus the complementary function, $\Pi_p\,(x') \approx \sum_{s=1}^{\mathcal{N}} l'_s B_{ps}\,\mathrm{e}^{-\lambda_s x'}$. Hence, since $\sum_{s=1}^{\mathcal{N}} l'_s B_{ps}$ is finite, it follows that $\Pi_p(x') \to 0$ as $x' \to \infty$. This conclusion depends on the fact that the discrete λ_s are all non-zero, except for those λ_s corresponding to physical quantities conserved in interparticle collisions. However, if $\mathcal{N} \to \infty$, then a continuous spectrum of λ about $\lambda = 0$ may occur and this could prevent $\sum_{s=1}^{\mathcal{N}} l'_s B_{ps}\,\mathrm{e}^{-\lambda_s x'}$ tending to zero as $x' \to \infty$. To show that our previous result does still remain valid, let us suppose λ to be continuous with $\nu(\lambda)\,\mathrm{d}\lambda$ values in the range $\mathrm{d}\lambda$. Then the above considerations give

$$\Pi_p(x') \approx \int_0^\infty g_p(\lambda)\,\mathrm{e}^{-\lambda x'}\,\mathrm{d}\lambda, \tag{2·61}$$

where $g_p(\lambda) = \nu(\lambda)\, l'(\lambda)\, B_p(\lambda)$. We see that the right-hand side of the relation (2·61) is $\mathscr{L}(g)$, the Laplace transform of $g_p(\lambda)$, and since it is known that $\int_0^\infty g_p(\lambda)\,\mathrm{d}\lambda$ is finite, it follows that $\mathscr{L}(g)$ exists for all positive x'. It may then be shown (Doetsch 1943) that $\lim\limits_{x'\to\infty} \mathscr{L}(g) = 0$, and hence we see that $\lim\limits_{x'\to\infty} \Pi_p(x') = 0$, giving the required result. The rate at which $\Pi_p(x')$ decreases for increasing x' depends, of course, on $g_p(\lambda)$, and thus requires investigation in each individual case.

From the discussion at the end of the last section, we see that it now remains to be shown that if L_{pq} is an N-matrix, then the quadratic term of $\Theta_p(x)$ as given by equation (2·44) is equivalent to the result obtained for gas flow via the introduction of viscosity and to the result which would be obtained for other particles using the same method; this we proceed to demonstrate.

The calculation of gas flow generally proceeds in the following stages which we shall explain in general terms to include all types of particles. We consider first an infinite volume of particles whose net wave number, conserved in collisions, is non-zero. Then the distribution function f for the particles will be given by

$$f(X_p, Y_p, Z_p, E_p, N_p) = f^0(\mathscr{V}_x X_p + \mathscr{V}_y Y_p + \mathscr{V}_z Z_p + \mathscr{V}_E E_p + \mathscr{V}_N N_p), \tag{2·62}$$

where the $\mathscr{V}$'s are constants, $\mathscr{V}_x, \mathscr{V}_y, \mathscr{V}_z$ being related to the components of the total non-zero wave number, and $\mathscr{V}_E = 1/kT$. f^0 corresponds to the equilibrium distribution function: Maxwell, Fermi–Dirac or Bose–Einstein as the case may be, and $\mathscr{V}_N = 0$ if number is *not* conserved in collisions. We now suppose that the flow of particles is occurring under circumstances in which the mean wave number of a particle, averaged over all particles at the point under consideration, is non-zero, but in which there exists a variation in this mean wave number from point to point in the x direction, which mean can be considered as constant over distances of the order of a mean free path. In the case of gases, this corresponds to the existence of a gradient in the x direction for the velocity of gas flow in the z direction. It is readily shown by the approach given in § 1·1 that this gradient in mean wave number will give rise to a departure Φ'_p from the equilibrium distribution (2·62) which satisfies the Boltzmann equation

$$\sum_q L_{pq}\Phi'_q = kT\sigma_p\left(X_p\frac{\mathrm{d}\mathscr{V}_x}{\mathrm{d}x} + Y_p\frac{\mathrm{d}\mathscr{V}_y}{\mathrm{d}x} + Z_p\frac{\mathrm{d}\mathscr{V}_z}{\mathrm{d}x}\right). \tag{2·63}$$

In the case of gas flow in the z direction, we have $(\mathrm{d}\mathscr{V}_x/\mathrm{d}x) = (\mathrm{d}\mathscr{V}_y/\mathrm{d}x) = 0$, but for an anisotropic medium it may be necessary to relate these differential coefficients linearly to $\mathrm{d}\mathscr{V}_z/\mathrm{d}x$ in order that a solution to equation (2·63) should exist. Now, Φ'_p having been obtained from equation (2·63), the next step in gas flow is to calculate the rate of transfer of z momentum in the x direction; this immediately gives the shearing stress acting in the z direction on planes perpendicular to the x direction. It follows from equation (2·63) that Φ'_p is proportional to $\mathrm{d}\mathscr{V}_z/\mathrm{d}x$ and since the rate of momentum transfer, considered in §§ 1·5 and 2·6, is linear in Φ'_p, we see that the shear stress is proportional to $\mathrm{d}\mathscr{V}_z/\mathrm{d}x$. We may therefore obtain from our calculation a coefficient of viscosity η, in terms of which it is possible to evaluate the total gas flow by the usual macroscopic theory.

To show the connexion between this approach, and the one leading to our result (2·44), we first notice that the introduction of a viscosity is an unnecessary step in the usual calculation of gas flow. To see why this is so, we consider the problem of flow between two parallel plates, comparing our formulation in terms of $\Phi_p(x)$ and the 'usual' formation in terms of the $\mathscr{V}$'s together with a Φ'_p. It is readily seen from equation (1·2) that

$$\Phi_p(x) = -kT[\mathscr{V}_x X_p + \mathscr{V}_y Y_p + \mathscr{V}_z Z_p] + \Phi'_p, \tag{2·64}$$

when $\mathscr{V}_x \ll (\partial f^0/\partial \mathscr{V}_x)/(\partial^2 f^0/\partial \mathscr{V}_x^2)$, etc., and we suppose $\Phi'_p \ll \Phi_p(x)$. Now, from equation (2·53*a*) it follows that the rate of transport of Z_p in the x direction per unit area in the yz plane is given by

$$\Delta_x = (-1/8\pi^3) \sum_p \sigma_p Z_p \Phi'_p \tag{2·65}$$

since the contribution from the first term in equation (2·64) is zero. Thus

$$\delta x \frac{\mathrm{d}\Delta_x}{\mathrm{d}x} = -\frac{\delta x}{8\pi^3} \sum_p \sigma_p Z_p \frac{\mathrm{d}\Phi'_p}{\mathrm{d}x}, \tag{2·66}$$

and this represents the rate of loss of Z_p by a rectangular parallelepiped of unit base and thickness δx. This loss in the x direction is balanced by the applied driving force, and we see from equations (2·1) and (A 3) that

$$(-\delta x/8\pi^3) \sum_p U_p Z_p = (-\delta x/8\pi^3) \sum_p \sigma_p Z_p (\mathrm{d}\Phi'_p/\mathrm{d}x). \tag{2·67 a}$$

Thus it is seen from equation (2·66) that the relation

$$\sum_p U_p Z_p = \sum_p \sigma_p Z_p (\mathrm{d}\Phi'_p/\mathrm{d}x) \tag{2·67 b}$$

corresponds physically to equating the z-momentum input due to the applied driving force to that lost in the x direction; this is the basic physical fact employed in finding the flow, when using a viscosity formulation. Now, the solution of equation (2·63) for gas flow yields

$$\Phi'_p = kT(\mathrm{d}\mathscr{V}_z/\mathrm{d}x)\, \psi_p,$$

where $\sum_q L_{pq} \psi_q = \sigma_p Z_p$. Thus from equation (2·67 *b*) we have

$$\frac{\mathrm{d}^2 \mathscr{V}_z}{\mathrm{d}x^2} = \frac{\sum_p U_p Z_p}{kT \sum_p \sigma_p Z_p \psi_p}, \tag{2·68}$$

which yields

$$\Phi_p(x) = [\sum_p U_p Z_p / 2 \sum_p \sigma_p Z_p \psi_p](a^2 - x^2) Z_p, \tag{2·69}$$

by the use of equation (2·64) and the boundary conditions $\mathscr{V}_z(+a) = \mathscr{V}_z(-a) = 0$. It is readily seen from equations (2·50) and (2·51) that the result (2·69) is equivalent to the first term of the former, as is required.

In the general anisotropic case, the 'viscosity' result depends on the solution of equation (2·63), followed by an application of the conservation of wave-number condition (2·67 *b*), which latter may also have to be applied with Z_p replaced by X_p and Y_p, if these occur in the solution of equation (2·63). It can be seen that equation (2·63) is equivalent to equation (2·32 *b*), while the generalized equation (2·67 *b*) is equivalent to equation (2·33). Thus, just as equations (2·32 *b*) and (2·33) lead to the results obtained in detail in §2·5, so similarly equations (2·63) and (2·67 *b*) may be shown to yield the same results as far as the essential parabolic variation is concerned.

Case C. It is proved in appendix B that if $L_{pq} = L_{p\bar{q}}$ $(p \neq q)$, then

$$(M_{pp} - \lambda_s)\, B_{ps} = (M_{pp} + \lambda_s)\, B_{\bar{p}s}. \tag{2·70}$$

Thus if $\lambda_s = 0$, $\mathscr{B}_{\bar{p}s} = +\mathscr{B}_{ps}$, and so L_{pq} must be a U-matrix. The particular integral Θ_p is therefore given by the solution of equation (2·28), and it is readily shown that since $L_{pq} = L_{p\bar{q}}\,(p \neq q)$,

$$\Theta_p = U_p/L_{pp}. \tag{2·71}$$

Further, the second-rank eigenvectors $\mathscr{D}_p^{(1)}$, $\mathscr{D}_p^{(2)}$ of case (2) in §2·5 are given by

$$\mathscr{D}_p^{(1)} = \sigma_p E_p/L_{pp}, \quad \mathscr{D}_p^{(2)} = \sigma_p/L_{pp}. \tag{2·72}$$

This situation occurs, for instance, with certain types of impurity scatter of phonons or electrons (Klemens 1955), and it is clear that the use of equations (2·70), (2·71) and (2·72) greatly simplify the general solution (2·42).

Case D. The assumption of a relaxation time τ is made in many collision problems in order to simplify them; we shall now see some of its deficiencies. For this case we have $L_{pq} = w_p \tau_p^{-1} \delta_{pq}$ with $\tau_{\bar{p}} = +\tau_p$. This gives $M_{pq} = (\tau_p v_p^{(x)})^{-1} \delta_{pq}$, showing that the eigenvalues λ_s of M_{pq} are the $2\mathscr{N}$ quantities $(\tau_s v_s^{(x)})^{-1}$ $(-\mathscr{N} \leqslant s \leqslant +\mathscr{N})$, and it is obvious that these occur in pairs of $+\lambda_s$ and $-\lambda_s$. The corresponding first-rank eigenvectors are given by $B_{ps} = \delta_{ps}$, and since our matrix M_{pq} is diagonal, the existence of second-rank eigenvectors is precluded. This in turn means that our method for obtaining the particular integral in the case of momentum conservation cannot now be employed. It is also obvious from the form taken by B_{ps} that our relaxation-time assumption does not allow the possibility of quantities such as E_p, N_p, X_p, Y_p and Z_p being eigenvectors with zero eigenvalue, and thus we cannot find a relaxation-time formulation in which these quantities are conserved in collisions. This latter point is substantiated by the fact that the expression $\sum\limits_{pq} L_{pq}\,\Phi_q\,\Gamma_p$, giving the total time rate of change of the quantity Γ, is shown to be zero in appendix A for arbitrary Φ_p if Γ_p is conserved in collisions. Now, however, it takes the form $\sum\limits_{p} \tau_p^{-1} w_p\,\Phi_p\,\Gamma_p$, when the relaxation-time formulation is employed, and this cannot be zero for arbitrary Φ_p. Thus our relaxation-time assumption cannot reproduce certain important properties of the true collision matrix. Nevertheless, we may employ it as far as possible, to evaluate the solution (2·42). This yields results equivalent to those of Fuchs (1938) on the assumption of a perfectly rough surface, with a plane of symmetry perpendicular to the flow direction.

2·8. *A few U-processes with many N-processes*

We consider now the situation when the collision matrix is given by

$$L_{pq} = \delta L'_{pq} + \epsilon L''_{pq}. \tag{2·73}$$

Here $L'_{pq} \approx L''_{pq}$, with L'_{pq} an N-matrix and L''_{pq} a U-matrix; δ and ϵ are quantities independent of p, satisfying $\delta \gg \epsilon$. For an infinite medium, this situation has been considered previously in particular cases by Leibfried & Schlömann (1954) and by Ziman (1956). They obtained a solution by assuming that the large $\delta L'_{pq}$ term determined the *form* of the particle distribution as being some linear combination of the quantities X_p, Y_p, Z_p conserved by it, while the much smaller $\epsilon L''_{pq}$ term determined the precise linear combination via a variational calculation; we shall presently see how their results are modified by the presence of boundaries. We shall also be able to discuss in a semi-quantitative manner the effect of introducing a very large number of N-processes into a bounded medium previously possessing a much smaller number of U-processes, and shall see that there are two opposing effects, one tending to increase, and the other to decrease the total particle flow. Finally, by considering the limit of our results as $\epsilon \to 0$, it will be seen how the general solution (2·42) for U-processes tends to the corresponding solution for N-processes.

We first deal with the particular integral Θ_p as given by equation (2·28), when L_{pq} takes the form (2·73). Since $\epsilon \ll \delta$, we may write

$$\Theta_p = c_x X_p + c_y Y_p + c_z Z_p + W_p, \tag{2·74}$$

where $W_p \ll \Theta_p$, and where c_x, c_y, c_z are constants to be obtained. Substituting for Θ_p from equation (2·74) into equation (2·28) gives

$$\epsilon\big(c_x \sum_q L''_{pq} X_q + c_y \sum_q L''_{pq} Y_q + c_z \sum_q L''_{pq} Z_q\big) + \delta \sum_q L'_{pq} W_q = U_p, \tag{2·75}$$

neglecting the second-order quantity $\epsilon \sum_q L''_{pq} W_q$. We may now expand W_p in terms of all the eigenvectors $\Psi'^{(n)}_p$ $(1 \leqslant n \leqslant 2\mathcal{N})$ with eigenvalue ψ'_n of the matrix L'_{pq}, omitting X_p, Y_p and Z_p since we are only working in first-order perturbation. That is, we put $W_p = \sum_n d_n \Psi'^{(n)}_p$, when substituting into equation (2·75), multiplying by X_p, Y_p and Z_p in turn, and summing over p, we obtain

$$\left.\begin{aligned} c_x \sum_{pq} L''_{pq} X_p X_q + c_y \sum_{pq} L''_{pq} X_p Y_q + c_z \sum_{pq} L''_{pq} X_p Z_q &= \epsilon^{-1} \sum_p U_p X_p, \\ c_x \sum_{pq} L''_{pq} Y_p X_q + c_y \sum_{pq} L''_{pq} Y_p Y_q + c_z \sum_{pq} L''_{pq} Y_p Z_q &= \epsilon^{-1} \sum_p U_p Y_p, \\ c_x \sum_{pq} L''_{pq} Z_p X_q + c_y \sum_{pq} L''_{pq} Z_p Y_q + c_z \sum_{pq} L''_{pq} Z_p Z_q &= \epsilon^{-1} \sum_p U_p Z_p, \end{aligned}\right\} \tag{2·76}$$

from which c_x, c_y and c_z may be found; they are all proportional to ϵ^{-1}. The results thus obtained are equivalent to those of Leibfried & Schlömann (1954) and Ziman (1956) found by a variational approach. Our present technique allows us to obtain formally the first-order correction W_p, since from equation (2·75)

$$\sum_q L'_{pq} W_q = \delta^{-1}\big[U_p - \epsilon\big(c_x \sum_q L''_{pq} X_q + c_y \sum_q L''_{pq} Y_q + c_z \sum_q L''_{pq} Z_q\big)\big]$$

and the equations (2·76) are just those orthogonality conditions which must be satisfied for this to have a solution for W_p. In the particular case of isotropy,

$$\sum_{pq} L''_{pq} X_p Y_q = \sum_{pq} L''_{pq} Y_p Z_q = \sum_{pq} L''_{pq} Z_p X_q = 0 = \sum_p U_p X_p = \sum_p U_p Y_p,$$

whence
$$c_x = c_y = 0,$$
and
$$c_z = \epsilon^{-1} \sum_p U_p Z_p \Big/ \sum_{pq} L''_{pq} Z_p Z_q. \tag{2·77 a}$$

Also, W_p satisfies in this case the equation

$$\sum_q L'_{pq} W_q = \delta^{-1}\Big[U_p - \Big(\sum_p U_p Z_p \Big/ \sum_{pq} L''_{pq} Z_p Z_q\Big) \sum_q L''_{pq} Z_q\Big]. \tag{2·77 b}$$

We now proceed to consider the complementary function as given by equation (2·27) for the present situation. To deal with this, we shall use a perturbation technique, investigating how the eigenvalues and eigenvectors of $\delta M'_{pq} = \delta \sigma_p^{-1} L'_{pq}$ alter as a result of the applied perturbation $\epsilon M''_{pq} = \epsilon\sigma_p^{-1} L''_{pq}$. We shall see later that we are principally interested in the effect of this perturbation on the degenerate eigenvalue $\lambda = 0$, and it is only that eigenvalue which we shall consider now. Our general approach is that of standard first-order perturbation theory, as given, for instance, by Schiff (1955) and we shall be dealing with the well-known case of degeneracy, where several linearly independent eigenvectors exist for the given eigenvalue, and where it is necessary to find the correct combinations to be taken when the degeneracy is removed. A further complication is that of the existence of second-rank eigenvectors in our problem. These never occur in perturbation theory applied to quantum mechanics, since the operators appearing there are always Hermitian. In order to deal with this, we shall therefore derive our perturbation theory from first principles and, in the notation of §2·2, shall suppose that the matrix M'_{pq} possesses T first-rank eigenvectors $\mathscr{B}_p^{(t)}\ (1 \leqslant t \leqslant T)$ and S second-rank eigenvectors $\mathscr{D}_p^{(t)}\ (1 \leqslant t \leqslant S)$ corresponding to $\lambda = 0$. Then general first and second-rank eigenvectors, $\mathscr{T}_p$ and $\mathscr{F}_p$, respectively, will be given by

$$\mathscr{T}_p = \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)} \quad \text{and} \quad \mathscr{F}_p = \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)};$$

$\mathscr{D}_p^{(t)}$ satisfies $\sum_q M'_{pq} \mathscr{D}_q^{(t)} = \mathscr{C}_p^{(t)}$, where the $\mathscr{C}_p^{(t)}$ are discussed in §2·2. We shall suppose that the effect of the perturbation $\epsilon M''_{pq}$ is to cause the otherwise zero eigenvalue of M_{pq} to become λ, the corresponding eigenvector becoming $\mathscr{T}_p + \mathscr{U}_p$. Then our eigenvalue equation gives

$$\sum_q (\delta M'_{pq} + \epsilon M''_{pq})\,(\mathscr{T}_q + \mathscr{U}_q) = \lambda(\mathscr{T}_p + \mathscr{U}_p); \tag{2·78a}$$

that is,

$$\delta \sum_q M'_{pq} \mathscr{U}_q + \epsilon \sum_q M''_{pq} \mathscr{T}_q + \epsilon \sum_q M''_{pq} \mathscr{U}_q = \lambda \mathscr{T}_p + \lambda \mathscr{U}_p. \tag{2·78b}$$

We must now consider which terms in this equation may be neglected in first-order perturbation theory. It will transpire later that owing to the existence of second-rank eigenvectors, $\lambda \propto (\delta\epsilon)^{\frac{1}{2}}$ and $(\mathscr{U}_p/\mathscr{T}_p) \propto (\epsilon/\delta)^{\frac{1}{2}}$—in contradistinction to the usual case with no second-rank eigenvectors where $\lambda \propto \epsilon$ and $(\mathscr{U}_p/\mathscr{T}_p) \propto \epsilon/\delta$. Thus in our case, the terms in equation (2·78*b*) are respectively proportional to $(\epsilon\delta)^{\frac{1}{2}}$, ϵ, $\epsilon^{\frac{3}{2}}\delta^{-\frac{1}{2}}$, $(\epsilon\delta)^{\frac{1}{2}}$, ϵ reading from the left-hand side, and the only one that can be neglected is the third term. We may note in passing that when there are no second-rank eigenvectors these terms are respectively proportional to ϵ, ϵ, ϵ^2/δ, ϵ, ϵ^2/δ, and then both the third and last term may be neglected.

The vector $\mathscr{U}_p$ may now be expanded in terms of the eigenvectors of M'_{pq}. Here we must include both first- and second-rank eigenvectors, but since we deal only with first-order perturbation, we can omit the vectors $\mathscr{B}_p^{(t)}$. Thus we write

$$\mathscr{U}_p = \sum_{\substack{s \\ \lambda_s \neq 0}} \omega_s B_{ps} + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} = \mathscr{U}'_p + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)}, \tag{2·79}$$

where B_{ps} is an eigenvector of M'_{pq} with eigenvalue λ_s. Substituting this into equation (2·78*b*), and omitting the third term on the left-hand side yields

$$\delta \sum_{\substack{s \\ \lambda_s \neq 0}} \omega_s \lambda_s B_{ps} + \delta \sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)} + \epsilon \sum_{t=1}^{T} \sum_q \nu_t M''_{pq} \mathscr{B}_q^{(t)} = \lambda \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)} + \lambda \sum_{\substack{s \\ \lambda_s \neq 0}} \omega_s B_{ps} + \lambda \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)}. \tag{2·80}$$

To obtain the possible values of λ, together with the corresponding ν_t and μ_t, we eliminate the terms in ω_s by multiplying this equation in turn by $\sigma_p \mathscr{B}_p^{(s)}\ (1 \leqslant s \leqslant T)$ and $\sigma_p \mathscr{D}_p^{(s)}\ (1 \leqslant s \leqslant S)$, and summing over p. Then since $\sum_p \sigma_p \mathscr{B}_p^{(s)} B_{pt} = \sum_p \sigma_p \mathscr{D}_p^{(s)} B_{pt} = 0$ for all s and t, as shown in appendix B, we obtain

$$\left.\begin{aligned} \sum_{t=1}^{T} (\epsilon E_{st} - \lambda K_{st})\, \nu_t + \sum_{t=1}^{S} (\delta N_{st} - \lambda P_{st})\, \mu_t = 0 \quad (1 \leqslant s \leqslant T), \\ \sum_{t=1}^{T} (\epsilon A_{st} - \lambda Q_{st})\, \nu_t + \sum_{t=1}^{S} (\delta H_{st} - \lambda V_{st})\, \mu_t = 0 \quad (1 \leqslant s \leqslant S), \end{aligned}\right\} \tag{2·81}$$

where $$E_{st} = \sum_{pq} L''_{pq} \mathscr{B}_p^{(s)} \mathscr{B}_q^{(t)}, \quad K_{st} = \sum_p \sigma_p \mathscr{B}_p^{(s)} \mathscr{B}_p^{(t)},$$

$$N_{st} = \sum_p \sigma_p \mathscr{B}_p^{(s)} \mathscr{C}_p^{(t)} = \sum_{pq} L'_{pq} \mathscr{B}_p^{(s)} \mathscr{D}_q^{(t)}, \quad P_{st} = \sum_p \sigma_p \mathscr{B}_p^{(s)} \mathscr{D}_p^{(t)}, \quad A_{st} = \sum_{pq} L''_{pq} \mathscr{D}_p^{(s)} \mathscr{B}_q^{(t)},$$

$$Q_{st} = P_{ts}, \quad H_{st} = \sum_p \sigma_p \mathscr{D}_p^{(s)} \mathscr{C}_p^{(t)} = \sum_{pq} L'_{pq} \mathscr{D}_p^{(s)} \mathscr{D}_q^{(t)}, \quad V_{st} = \sum_p \sigma_p \mathscr{D}_p^{(s)} \mathscr{D}_p^{(t)}.$$

Equations (2·81) constitute a set of $T+S$ homogeneous linear equations for the $T+S$ quantities ν_t, μ_t. In order that they should possess a solution, it is necessary that the determinant of the coefficients should vanish, and this condition will give rise to $T+S$ possible values of λ which may or may not be distinct. These values of λ will be the perturbed eigenvalues corresponding to the initially degenerate zero eigenvalue and the values of ν and μ corresponding to each of the possible values of λ will yield the relevant eigenvector. Since we shall presently see that $\mu_t/\nu_t \propto (\epsilon/\delta)^{\frac{1}{2}}$ and also that $\mathscr{U}'_p/\mathscr{T}_p \propto \epsilon/\delta$, it will follow that this approach yields our eigenvector accurate to terms in $(\epsilon/\delta)^{\frac{1}{2}}$, but neglects those in ϵ/δ.

In general, many of the coefficients appearing in equation (2·81) are zero, as may be shown by considering p and $\bar{p}$, and by making use of the conservation properties of L''_{pq}. It transpires from a detailed examination, that for all cases, except when the matrix L'_{pq} conserves energy and number while L''_{pq} conserves only energy, the matrix of coefficients in equation (2·81) may be partitioned in the following way

$$\begin{array}{c} \\ \mathscr{B}_{\bar{p}} = +\mathscr{B}_p \\ \mathscr{B}_{\bar{p}} = -\mathscr{B}_p \\ \mathscr{D}_{\bar{p}} = +\mathscr{D}_p \\ \mathscr{D}_{\bar{p}} = -\mathscr{D}_p \end{array} \begin{array}{c} \begin{array}{cccc} \mathscr{B}_{\bar{p}} = +\mathscr{B}_p & \mathscr{B}_{\bar{p}} = -\mathscr{B}_p & \mathscr{D}_{\bar{p}} = +\mathscr{D}_p & \mathscr{D}_{\bar{p}} = -\mathscr{D}_p \end{array} \\ \left(\begin{array}{cccc} 0 & -\lambda K & 0 & -\lambda P \\ -\lambda K & \epsilon E & -\lambda P & 0 \\ 0 & -\lambda Q & \delta H & -\lambda V \\ -\lambda Q & \epsilon A & -\lambda V & \delta H \end{array}\right), \end{array}$$

where the elements in any one submatrix are obtained from the eigenvectors satisfying the relations shown at the ends of the relevant row and column. On equating the determinant of this matrix to zero, it is readily seen that there remains a 2γ-fold degeneracy at $\lambda = 0$, where $\gamma = 1$ or 2 according to whether only energy, or energy and number remain conserved after the perturbation is applied. This result is, of course, expected from previous work, since energy and number each carry with them a single independent second-rank eigenvector. Further, it may be shown that non-zero solutions occur in pairs of $\pm\lambda$, as we would expect from results of appendix B. Also we may show that $\lambda \propto (\delta\epsilon)^{\frac{1}{2}}$.

Although the detailed form of equations (2·81) may be readily obtained for cases (3) and (4) of § 2·5, it was not considered necessary to give them here for general anisotropy, owing to their (algebraically) complicated nature. Rather, we shall confine ourselves to the isotropic situation, when, for case (3), the set of equations (2·81) becomes

$$\left.\begin{array}{lllllll} & \lambda f\nu_2 & & & & & =0\\ \lambda f\nu_1 & -\epsilon g\nu_2 & & & & & =0\\ & & \epsilon g\nu_3 & & -\lambda h\mu_1 & & =0\\ & & & \epsilon g\nu_4 & & -\lambda h\mu_2 & =0\\ & & -\lambda h\nu_3 & & +\delta h\mu_1 & & =0\\ & & & -\lambda h\nu_4 & & +\delta h\mu_2 & =0\end{array}\right\}, \tag{2·82}$$

where $f=\sum_p \sigma_p E_p X_p$, $g=\sum_{pq} L''_{pq} Y_p Y_q=\sum_{pq} L''_{pq} Z_p Z_q$, $h=\sum_p \sigma_p \mathscr{D}^{(1)}_p Y_p=\sum_p \sigma_p \mathscr{D}^{(2)}_p Z_p$. (2·83)

On equating to zero the determinant of the matrix of coefficients of equation (2·82), we obtain doubly degenerate roots at

$$\lambda=\pm(g/h)^{\frac{1}{2}}\,(\delta\epsilon)^{\frac{1}{2}}, \tag{2·84}$$

apart from the expected doubly degenerate root at $\lambda=0$. Substituting from equation (2·84) into equation (2·82) yields

$$\nu_1=\nu_2=0,\quad \mu_1=\kappa\nu_3,\quad \mu_2=\kappa\nu_4,$$

where

$$\kappa=\pm(g/h)^{\frac{1}{2}}\,(\epsilon/\delta)^{\frac{1}{2}} \tag{2·85}$$

and ν_3, ν_4 are arbitrary; the ± sign in κ corresponds to that in λ. Thus we have

(*a*) $\lambda=+(g/h)^{\frac{1}{2}}\,(\delta\epsilon)^{\frac{1}{2}}$: two independent eigenvectors

$$Y_p+\kappa\mathscr{D}^{(1)}_p,\quad Z_p+\kappa\mathscr{D}^{(2)}_p; \tag{2·86a}$$

(*b*) $\lambda=-(g/h)^{\frac{1}{2}}\,(\delta\epsilon)^{\frac{1}{2}}$: two independent eigenvectors

$$Y_p-\kappa\mathscr{D}^{(1)}_p,\quad Z_p-\kappa\mathscr{D}^{(2)}_p. \tag{2·86b}$$

Results identical with (*a*) and (*b*) are obtained for the isotropic situation in case (4*b*) of §2·5. We note in passing that within the framework of a relaxation-time approximation, it can be shown that λ corresponds to a mean free path which is the geometrical mean of the mean free paths due to $\delta L'_{pq}$ and $\epsilon L''_{pq}$ acting separately.

We may now obtain formally in the isotropic case the remaining part of the perturbed eigenvector $\mathscr{U}'_p$ as given by equation (2·79). By means of equations (2·78*b*) and (2·80) it may be shown that $\mathscr{U}'_p$ satisfies the equation

$$\sum_q L'_{pq}\mathscr{U}'_q=(\epsilon/\delta)\,\nu[(g/h)\,\sigma_p\mathscr{D}_p-\sum_q L''_{pq}\mathscr{B}_q], \tag{2·87}$$

where $\mathscr{B}_p=Y_p$ or Z_p, and $\mathscr{D}_p$ and ν correspond. We notice that the right-hand side of equation (2·87) is orthogonal to Y_p and Z_p, as it must be for the equation to possess a solution; also that $\mathscr{U}'_p\propto\epsilon/\delta$ and that $\mathscr{U}'_{\bar{p}}=-\mathscr{U}'_p$.

We now proceed to investigate the form of the general solution (2·42) in the isotropic situation; our conclusions, suitably modified, will apply also to the case of anisotropy. It follows from equations (2·74), (2·77), (2·86), and the discussion in §2·5 that this general solution now takes the form

$$\begin{aligned}\Phi_p(x)={}&\sum_s l_s(B_{ps}\,\mathrm{e}^{-\lambda_s x}-B_{\bar{p}s}\,\mathrm{e}^{+\lambda_s x})+m'\{[Y_p+(\epsilon/\delta)\,\mathscr{V}^{(1)}_p]\,(\mathrm{e}^{-\lambda x}+\mathrm{e}^{+\lambda x})\\&+\kappa\mathscr{D}^{(1)}_p(\mathrm{e}^{-\lambda x}-\mathrm{e}^{+\lambda x})\}+m''\{[Z_p+(\epsilon/\delta)\,\mathscr{V}^{(2)}_p]\,(\mathrm{e}^{-\lambda x}+\mathrm{e}^{+\lambda x})\\&+\kappa\mathscr{D}^{(2)}_p(\mathrm{e}^{-\lambda x}-\mathrm{e}^{+\lambda x})\}+\epsilon^{-1}(\sum_p U_p Z_p/\sum_{pq} L''_{pq} Z_p Z_q)\,Z_p+\delta^{-1}\mathscr{W}_p.\end{aligned} \tag{2·88}$$

Here, the first summation is over all s, excepting $\lambda_s = 0$ or λ. m' and m'' are arbitrary constants, while $\mathscr{V}_p = (\delta/\epsilon)\,\mathscr{U}'_p$ and $\mathscr{W}_p = \delta\, W_p$. It follows from equation (2·43) that the boundary conditions now take the form

$$\begin{aligned}\sum_s l_s({}^*B_{ps}\,\mathrm{e}^{+\lambda_s a} - {}^*B_{\bar{p}s}\,\mathrm{e}^{-\lambda_s a}) &+ m'\{[{}^*Y_p + (\epsilon/\delta)\,{}^*\mathscr{V}^{(1)}_p]\,(\mathrm{e}^{+\lambda a} + \mathrm{e}^{-\lambda a}) \\ &+ \kappa\,{}^*\mathscr{D}^{(1)}_p(\mathrm{e}^{+\lambda a} - \mathrm{e}^{-\lambda a})\} + m''\{[{}^*Z_p + (\epsilon/\delta)\,{}^*\mathscr{V}^{(2)}_p]\,(\mathrm{e}^{+\lambda a} + \mathrm{e}^{-\lambda a}) + \kappa\,{}^*\mathscr{D}^{(2)}_p(\mathrm{e}^{+\lambda a} - \mathrm{e}^{-\lambda a})\} \\ &= -\epsilon^{-1}\Big(\sum_p U_p Z_p \Big/ \sum_{pq} L''_{pq} Z_p Z_q\Big)\,{}^*Z_p - \delta^{-1}\,{}^*\mathscr{W}_p, \qquad (2{\cdot}89)\end{aligned}$$

which equations are to be solved for l_s, m' amd m''. Now, since $\delta \gg \epsilon$, the first term on the right-hand side containing ${}^*Z_p$ is much greater than the second term, and thus the value of m'', being the coefficient of ${}^*Z_p$ on the left-hand side, is much greater than the other arbitrary constants. Hence we may put $m'' = m + l'$, where

$$m = -\Big[\Big(\sum_p U_p Z_p\Big)\Big/\epsilon\Big(\sum_{pq} L''_{pq} Z_p Z_q\Big)\,(\mathrm{e}^{+\lambda a} + \mathrm{e}^{-\lambda a})\Big], \qquad (2{\cdot}90)$$

and where l' is of the order of magnitude of the other arbitrary constants. With the use of equations (2·83) and (2·85), this therefore allows equation (2·88) to be written

$$\begin{aligned}\Phi_p(x) = \sum_s l_s(B_{ps}\,\mathrm{e}^{-\lambda_s x} - B_{\bar{p}s}\,\mathrm{e}^{+\lambda_s x}) &+ \epsilon^{-1}\Big(\sum_p U_p Z_p \Big/ \sum_{pq} L''_{pq} Z_p Z_q\Big)\,(1 - \cosh\lambda x\,\mathrm{sech}\,\lambda a)\,Z_p \\ &+ (\delta\epsilon)^{-\frac{1}{2}}\Big[\Big(\sum_p U_p Z_p\Big)\Big/\Big(\sum_{pq} L''_{pq} Z_p Z_q\Big)^{\frac{1}{2}}\Big(\sum_p \sigma_p Z_p \mathscr{D}^{(2)}_p\Big)^{\frac{1}{2}}\Big]\,(\sinh\lambda x\,\mathrm{sech}\,\lambda a)\,\mathscr{D}^{(2)}_p \\ &+ \delta^{-1}\Big\{\mathscr{W}_p - \Big(\sum_p U_p Z_p \Big/ \sum_{pq} L''_{pq} Z_p Z_q\Big)\,(\cosh\lambda x\,\mathrm{sech}\,\lambda a)\,\mathscr{V}^{(2)}_p\Big\}, \qquad (2{\cdot}91)\end{aligned}$$

where the first summation now includes $\lambda_s = \lambda$ and where the l_s are now all of the same order of magnitude; the corresponding boundary conditions may be immediately written down.

In order to consider the general properties of the solution (2·91) we introduce the mean free paths for (*a*) $\delta L'$ acting alone, (*b*) $\epsilon L''$ acting alone, and (*c*) $\delta L'$ and $\epsilon L''$ acting together. We shall call these $\mathscr{L}'$, $\mathscr{L}''$ and $\mathscr{L}$, respectively, where

$$\mathscr{L}'(\sim \lambda_s^{-1}) \ll \mathscr{L}'' \quad \text{and} \quad \mathscr{L} = (\mathscr{L}'\mathscr{L}'')^{\frac{1}{2}} \sim \lambda^{-1}$$

as mentioned earlier. The general nature of the solution (2·91) will depend on the ratio of a to these three mean free paths. Let us consider first the situation when $a < \mathscr{L}$, that is $\lambda a < 1$. Then we can expand all exponential terms in equation (2·91) (other than in the first summation) as a power series in λ and, retaining only the first two non-zero terms, we obtain

$$\begin{aligned}\Phi_p(x) = \sum_s l_s(B_{ps}\,\mathrm{e}^{-\lambda_s x} - B_{\bar{p}s}\,\mathrm{e}^{+\lambda_s x}) &+ \tfrac{1}{2}\delta\Big(\sum_p U_p Z_p \Big/ \sum_p \sigma_p \mathscr{D}^{(2)}_p Z_p\Big)\,(a^2 - x^2)\,[1 - (\lambda^2/12)\,(5a^2 - x^2) \\ &+ \dots]\,Z_p + \Big(\sum_p U_p Z_p \Big/ \sum_p \sigma_p \mathscr{D}^{(2)}_p Z_p\Big)\,x[1 - (\lambda^2/6)\,(3a^2 - x^2) + \dots]\,\mathscr{D}^{(2)}_p \\ &+ \delta^{-1}\Big\{\mathscr{Y}_p + \tfrac{1}{2}\Big(\sum_p U_p Z_p \Big/ \sum_{pq} L''_{pq} Z_p Z_q\Big)\,\lambda^2(a^2 - x^2)\,\mathscr{V}^{(2)}_p + \dots\Big\}. \qquad (2{\cdot}92)\end{aligned}$$

Here we have substituted for λ from equations (2·83) and (2·84) in the first term of the expansions, and have introduced the vector $\mathscr{Y}_p$ which we see from equations (2·77) and (2·87) satisfies

$$\sum_q L'_{pq}\mathscr{Y}_q = U_p - \Big(\sum_p U_p Z_p \Big/ \sum_p \sigma_p \mathscr{D}^{(2)}_p Z_p\Big)\,\sigma_p \mathscr{D}^{(2)}_p. \qquad (2{\cdot}93)$$

If we now let $\epsilon \to 0$, $\lambda \to 0$ and it is readily seen that equation (2·92) becomes the result obtained in § 2·4 and § 2·5 for the situation when only N-processes occur. The equation (2·92) gives the first-order corrections to be applied to this result when $\lambda a \ll 1$, but is non-zero. This may have relevance to the effect of helium-3 impurities in decreasing the phonon heat flow in helium-4; it is hoped to follow up this point in later work.

We now consider the situation when $a \gg \mathscr{L}'$. Then it may be shown, as in the discussion at the end of § 2·5, that when sufficiently distant from the boundaries, the first, third and fourth terms in equation (2·91) may be neglected as compared with the term in Z_p. From equation (2·52) we see that the total particle flow along the z direction in this case is given by

$$\Delta_z(N) = (1/4\pi^3)\,\epsilon^{-1}\Big(\sum_p U_p Z_p\Big)\Big(\sum_p \sigma_p^{(z)} Z_p\Big)\Big(\sum_{pq} L''_{pq} Z_p Z_q\Big)^{-1} a[1-(\lambda a)^{-1}\tanh \lambda a]. \qquad (2{\cdot}94)$$

Thus as far as variation with respect to a is concerned, $\Delta_z \propto a[1-(\lambda a)^{-1}\tanh\lambda a]$, and we would hope to observe this effect by experiments on the flow with $0{\cdot}1 \leqslant \lambda a \leqslant 10$. Such work could give a direct experimental value for λ; we might think of trying it with impurities in liquid helium, or with impurities and Umklapp processes in dielectrics at low temperatures. Of course, as $\lambda \to 0$, the result (2·94) tends to the usual result for 'viscous' flow, with $\Delta_z \propto a^3$.

We now consider the situation when $a \gg \mathscr{L}$ and therefore $\lambda a \gg 1$. Then from the previous discussion and equation (2·91) we see that when sufficiently distant from either boundary

$$\Phi_p(x) = \epsilon^{-1}\,\Big(\sum_p U_p Z_p \Big/ \sum_{pq} L''_{pq} Z_p Z_q\Big)\,(1-\mathrm{e}^{-\lambda x'})\,Z_p, \qquad (2{\cdot}95)$$

where x' is the distance from the boundary. Thus when we are well away from the boundaries, $\Phi_p(x)$ is constant at the value it would have in an infinite medium, while when approaching the boundaries its decrease to zero is accurately characterized (at more than a few $\mathscr{L}'$) by the relaxation length λ^{-1}. We note from the result (2·94) that Δ_z is now proportional to $(a-\lambda^{-1})$.

Finally, we compare these results with those existing in the absence of N-processes. In the latter case we shall have $L_{pq} = \epsilon L''_{pq}$ (see equation (2·73)), and our general solution $\Phi'_p(x)$ will be given by

$$\Phi'_p(x) = \sum_s l'_s(B'_{ps}\,\mathrm{e}^{-\lambda'_s x} - B'_{\bar{p}s}\,\mathrm{e}^{+\lambda'_s x}) + \epsilon^{-1}\,\Theta'_p, \qquad (2{\cdot}96)$$

where dashed quantities refer to $\epsilon L''_{pq}$, and Θ'_p satisfies $\sum_q L''_{pq}\,\Theta'_q = U_p$. Now, it may be shown by the usual variational principle for an infinite medium (Kohler 1949 *b*) that $\Theta'_p > \Theta_p$, where Θ_p $[=(\sum_p U_p Z_p / \sum_{pq} L''_{pq} Z_p Z_q)\,Z_p]$ is the corresponding solution for an infinite medium when $L_{pq} = \delta L'_{pq} + \epsilon L''_{pq}$. Also, as we leave the boundary, the increase to the value Θ'_p is characterized by a relaxation length $\sim (1/\lambda'_s) \gg (1/\lambda)$. Thus in general terms, we may conclude that $\Phi'_p > \Phi_p$ when we are at a distance from the boundary greater than a few $\mathscr{L}'$, but that as we leave the boundary the value of Φ_p increases to its maximum value much quicker than does that of Φ'_p. Hence, if we introduce N-processes into a bounded medium previously possessing only a few U-processes, the effect of the former will be, first, to decrease the flow due to the decrease in Θ_p, and secondly, to increase it due to the increase in λ. As the number of N-processes increases, the value of Θ_p will tend to a definite lower limit, while λ becomes continually larger, being proportional to $\delta^{\frac{1}{2}}$. Whether or not the limiting total flow will have increased or decreased as compared with the initial total flow will depend on the ratio of a to $\mathscr{L}''$.

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APPENDIX A

Suppose we are dealing with collisions, represented by a collision term $L[\Phi]$ in the Boltzmann equation (1·5), in which some physical property Γ of the particles is conserved; for the situations we are considering Γ could be the number, energy or the three independent components of the wave number of the particle. Then if $\delta(x)$ is the Dirac δ-function, we have

$$L = Q\delta([\Gamma]), \tag{A 1}$$

where Q is an integral operator, since this expression for L is zero if Γ is not conserved in collisions. It follows that

$$L[\Gamma] = Q\delta([\Gamma])\,[\Gamma] = 0, \tag{A 2}$$

since the δ-function is non-zero only when $[\Gamma]$ is zero. Hence we see that Γ is a solution of the homogeneous equation $L[\Phi] = 0$; alternatively we may say that Γ is an eigenfunction of the operator L, corresponding to an eigenvalue of zero.

Since Γ is conserved in collisions, we would expect the total rate of change of Γ due to collisions to be zero. We can readily see this to be so from the above analysis, since the total rate of change of Γ is proportional to $\int \Gamma L[\Phi]\,\mathrm{d}\mathbf{k}$, and hence from the remarks at the end of § 1·1 is proportional to $\int [\Gamma]\, L[\Phi]\,\mathrm{d}\mathbf{k}$ for any displacement Φ from the equilibrium distribution. We have

$$\int [\Gamma]\, L[\Phi]\,\mathrm{d}\mathbf{k} = \int Q[\Phi]\,\delta([\Gamma])[\Gamma]\,\mathrm{d}\mathbf{k} = 0 \tag{A 3}$$

from equation (A 1), as required. We may note that this important physical result is not given by a relaxation-time approximation, since for it to be true we would require that $\int w\Phi\tau^{-1}\Gamma\,\mathrm{d}\mathbf{k} = 0$, which certainly cannot be satisfied by a fixed τ for arbitrary Φ.

APPENDIX B

We prove here the following properties concerning the eigenvalues and eigenvectors of the matrix M_{pq} defined in equation (2·8).

(1) The eigenvalues λ are all real.

(2) (*a*) If $\lambda \neq 0$, no eigenvectors of rank greater than unity exist.

(*b*) If $\lambda = 0$, no eigenvectors of rank greater than two exist.

(3) Eigenvectors χ_p and ψ_p corresponding to different eigenvalues are orthogonal in the sense that

$$\sum_p \sigma_p \chi_p \psi_p = 0. \tag{B 1}$$

(4) (*a*) Corresponding to any non-zero eigenvalue λ with an eigenvector χ_p, there always exists an eigenvalue $-\lambda$ with eigenvector $\psi_p = \chi_{\bar{p}}$.

(*b*) If $\lambda = 0$, then all eigenvectors χ_p of both first and second rank may be chosen to satisfy either $\chi_{\bar{p}} = +\chi_p$ or $\chi_{\bar{p}} = -\chi_p$.

(5) If $L_{pq} = L_{p\bar{q}}$ $(p \neq q)$, then for any eigenvalue λ and corresponding eigenvector χ_p,

$$\chi_p(M_{pp}-\lambda) = \chi_{\bar{p}}(M_{pp}+\lambda). \tag{B 2}$$

Proof of (1). Since the matrix M_{pq} is not Hermitian (although L_{pq} is), we cannot invoke any general principle concerning the reality of the eigenvalues, but must prove the result from first principles. If χ_p is the eigenvector corresponding to eigenvalue λ, we have

$$\sum_q L_{pq}\chi_q = \lambda\sigma_p\chi_p,$$

whence
$$\lambda\sum_p \sigma_p\chi_p\chi_p^* = \sum_{pq} L_{pq}\chi_q\chi_p^*, \tag{B 3}$$

where χ_p^* is the complex conjugate of χ_p. Now, since σ_p and $\chi_p\chi_p^*$ are real, $\sum_p \sigma_p\chi_p\chi_p^*$ is also real, while the discussion at the end of § 1·1 shows that $\sum_{pq} L_{pq}\chi_q\chi_p^*$ is real, and less than or equal to zero. If it is less than zero, we can then deduce from equation (B 3) that λ is real. This cannot be done if $\sum_{pq} L_{pq}\chi_q\chi_p^* = 0$, but the discussion in § 1·1 shows this to be possible only if $\sum_q L_{pq}\chi_q = 0$, and this, of course, means that $\lambda = 0$. Thus λ is always real, and so, of course, are the eigenvectors χ_p.

Proof of (2*a*). We suppose that corresponding to a non-zero eigenvalue λ there exists a set of T linearly independent first-rank eigenvectors $B_p^{(t)}$ $(1 \leqslant t \leqslant T)$. Then the general first-rank eigenvector corresponding to this eigenvalue is $\sum_{t=1}^{T} \nu_t B_p^{(t)}$, where the ν_t are arbitrary constants. From the discussion in § 2·2 we see that the existence of a second-rank eigenvector depends on the existence of a solution F_p to the equation

$$\sum_q J_{pq}F_q = \sum_{t=1}^{T} \nu_t B_p^{(t)} \tag{B 4}$$

with ν_t not all zero. Such a solution will exist if

$$\sum_p \sum_{t=1}^{T} \nu_t B_p^{(t)}\eta_p = 0 \tag{B 5}$$

for *all* η_p, where η_p is a solution of the homogeneous equation, adjoint to (B 4):

$$\sum_q J_{qp}\eta_q = \sum_q \sigma_q^{-1}L_{pq}\eta_q - \lambda\eta_p = 0 \tag{B 6}$$

since $L_{pq} = L_{qp}$. Now, equation (B 6) may be written

$$\sum_q M_{pq}(\sigma_q^{-1}\eta_q) = \lambda\sigma_p^{-1}\eta_p, \tag{B 7}$$

which shows that $\sigma_p^{-1}\eta_p$ is an eigenvector of M_{pq}, and may thus equal any of the $B_p^{(t)}$; that is, $\eta_p^{(t)} = \sigma_p B_p^{(t)}$. The fulfilment of the condition (B 5) may therefore be seen to depend on the existence of non-zero solutions for ν_t in the set of T linear equations

$$\sum_{t=1}^{T} K_{st}\nu_t = 0, \tag{B 8}$$

where
$$K_{st} = \sum_p \sigma_p B_p^{(s)} B_p^{(t)}. \tag{B 9}$$

A necessary and sufficient condition for this to be the case is that $|K_{st}| = 0$, and we now proceed to investigate the possibility of this being satisfied.

From equation (B 9) we have

$$\lambda K_{st} = \lambda\sum_p \sigma_p B_p^{(s)} B_p^{(t)} = \sum_{pq} \sigma_p M_{pq} B_q^{(s)} B_p^{(t)} = \sum_{pq} L_{pq} B_q^{(s)} B_p^{(t)}. \tag{B 10}$$

Also, making use of the fact shown above, that the B_p are real, we have from the negative definite character of L_{pq} that since $\lambda \neq 0$,

$$\sum_{pq} L_{pq} (\sum_s \rho_s B_q^{(s)}) \, (\sum_t \rho_t B_p^{(t)}) < 0 \tag{B 11}$$

for any real ρ_t. Thus, from equation (B 10),

$$\lambda \sum_{st} K_{st} \rho_s \rho_t < 0. \tag{B 12}$$

But a necessary condition for the inequality (B 12) to hold for all ρ_s is that $\lambda \, |K_{st}| < 0$ (Ferrar 1951), which shows that $|K_{st}| \neq 0$, and hence that no eigenvectors of rank greater than unity exist.

Proof of (2*b*). An integral part of the reasoning in the above proof was that $\lambda \neq 0$. If $\lambda = 0$, second-rank eigenvectors *may* exist, but we now proceed to show that eigenvectors of rank greater than two cannot exist. Suppose that corresponding to eigenvalue zero there exists a set of T linearly independent first-rank eigenvectors $\mathscr{B}_p^{(t)}$ $(1 \leqslant t \leqslant T)$ and a set of S linearly independent second-rank eigenvectors $\mathscr{D}_p^{(s)}$ $(1 \leqslant s \leqslant S)$ which satisfy the equation

$$\sum_q L_{pq} \mathscr{D}_q^{(s)} = \sigma_p \sum_{t=1}^{T} \nu_t^{(s)} \mathscr{B}_p^{(t)}. \tag{B 13}$$

This equation will be soluble for S independent sets of $\nu_t^{(s)}$ $(1 \leqslant s \leqslant S)$ obtained from equation (B 8), and giving rise to our S independent $\mathscr{D}_p$'s. It follows that a general second-rank eigenvector $\mathscr{F}_p$ is given by

$$\mathscr{F}_p = \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)}$$

for arbitrary μ_t and ν_t, and the existence of a third-rank eigenvector $\mathscr{A}_p$ depends on the existence of a solution to the equation

$$\sum_q M_{pq} \mathscr{A}_q = \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} + \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)} \tag{B 14}$$

with non-zero μ_t. It follows from the discussion of orthogonality conditions given in the proof of (2*a*) that the existence of such a solution to equation (B 14) depends on the existence of solutions for ν_t in the set of T linear equations

$$\sum_{t=1}^{T} K_{st} \nu_t = - \sum_{t=1}^{S} \mu_t [\sum_p \sigma_p \mathscr{D}_p^{(t)} \mathscr{B}_p^{(s)}] \tag{B 15}$$

(where K_{st} is defined in equation (B 9)), with μ_t not being identically zero. Now in order that equation (B 15) should possess solutions for ν_t it is necessary that the right-hand side should be orthogonal to all solutions of the adjoint homogeneous equation, which now takes the form (B 8) since $K_{st} = K_{ts}$. This latter equation is soluble for the S sets of ν_t mentioned earlier, and thus the fulfilment of this orthogonality condition reduces to the existence of solutions for μ_t in the set of S linear equations

$$\sum_{t=1}^{S} H_{rt} \mu_t = 0, \tag{B 16}$$

where

$$H_{rt} = \sum_p \mathscr{D}_p^{(t)} \sigma_p \left[\sum_{s=1}^{T} \nu_s^{(r)} \mathscr{B}_p^{(s)} \right] = \sum_p \mathscr{D}_p^{(t)} \sigma_p \mathscr{C}_p^{(r)} = \sum_{pq} L_{pq} \mathscr{D}_p^{(t)} \mathscr{D}_q^{(r)}, \tag{B 17}$$

from equation (B 13). It now follows from the negative definite character of L_{pq}, together with $\sum_q L_{pq}\mathscr{D}_q^{(r)} \neq 0$, that $\sum_{rt} H_{rt}\rho_r\rho_t < 0$ for all ρ_r (see the latter part of the proof of (2*a*)), and hence that $|H_{rt}| \neq 0$. Thus no solutions for μ_t exist to equation (B 16) and so there are no third-rank eigenvectors.

Proof of (3). We first prove equation (B 1) for the case where χ_p and ψ_p are both first-rank eigenvectors. We then have

$$\sum_q M_{pq}\chi_q = \mu\chi_p \quad \text{and} \quad \sum_q M_{pq}\psi_q = \lambda\psi_p, \tag{B 18}$$

where μ and λ are the corresponding eigenvalues. Since $L_{pq} = \sigma_p M_{pq}$, these equations yield

$$\mu\sum_p \sigma_p\chi_p\psi_p = \sum_{pq} L_{pq}\chi_q\psi_p \tag{B 19a}$$

and

$$\lambda\sum_p \sigma_p\chi_p\psi_p = \sum_{pq} L_{pq}\psi_q\chi_p = \sum_{pq} L_{pq}\chi_q\psi_p, \tag{B 19b}$$

use being made of $L_{pq} = L_{qp}$. Subtraction of the equations (B 19) then gives

$$(\mu-\lambda)\sum_p \sigma_p\chi_p\psi_p = 0, \tag{B 20}$$

whence we obtain equation (B 1) since $\mu \neq \lambda$.

If ψ_p is a second-rank eigenvector corresponding to eigenvalue zero, it may be shown by a proof similar to that given above, that the orthogonality relation (B 1) still holds.

Proof of (4*a*). Since χ_p is an eigenvector corresponding to an eigenvalue λ, we have

$$\sum_q M_{pq}\chi_q = \lambda\chi_p. \tag{B 21}$$

Thus

$$\sum_q M_{\bar{p}\bar{q}}\chi_{\bar{q}} = \lambda\chi_{\bar{p}}. \tag{B 22}$$

But

$$M_{\bar{p}\bar{q}} = \sigma_{\bar{p}}^{-1}L_{\bar{p}\bar{q}} = -\sigma_p^{-1}L_{pq} = -M_{pq}, \tag{B 23}$$

whence, from equation (B 22),

$$\sum_q M_{pq}\chi_{\bar{q}} = -\lambda\chi_{\bar{p}}. \tag{B 24}$$

Hence $\psi_p = \chi_{\bar{p}}$ is an eigenvector with eigenvalue $-\lambda$.

Proof of (4*b*). If χ_p is a first-rank eigenvector with eigenvalue zero we have

$$\sum_q L_{pq}\chi_q = 0. \tag{B 25}$$

Now, since L_{pq} is invariant to the inversion group, where this consists of replacing p by $\bar{p}$, it follows from the eigenvalue equation (B 25) that χ_p can be chosen to transform as some representation of this group; that is $\chi_{\bar{p}} = +\chi_p$ or $\chi_{\bar{p}} = -\chi_p$.

In the case of second-rank eigenvectors corresponding to eigenvalue zero, it may be shown by a detailed consideration of the possible solutions of equation (B 8) that the solutions of equation (B 13) can be chosen to satisfy either $\mathscr{D}_{\bar{p}} = +\mathscr{D}_p$ or $\mathscr{D}_{\bar{p}} = -\mathscr{D}_p$.

Proof of (5). Since χ_p is an eigenvector with eigenvalue λ we have

$$M_{pp}\chi_p + \sum_{q\neq p} M_{pq}\chi_q = \lambda\chi_p. \tag{B 26}$$

Thus

$$M_{\bar{p}\bar{p}}\chi_{\bar{p}} + \sum_{q\neq p} M_{\bar{p}q}\chi_q = \lambda\chi_{\bar{p}}. \tag{B 27}$$

But since

$$L_{\bar{p}q} = L_{pq} \quad (q \neq p),$$

$$M_{\bar{p}q} = \sigma_{\bar{p}}^{-1}L_{\bar{p}q} = -\sigma_p^{-1}L_{pq} = -M_{pq} \quad (q \neq p), \tag{B 28}$$

and from equation (B 23), $M_{\bar{p}\bar{p}} = -M_{pp}$. Hence, equation (B 27) becomes

$$-M_{pp}\chi_{\bar{p}} - \sum_{q \neq p} M_{pq}\chi_q = \lambda\chi_{\bar{p}}. \tag{B 29}$$

Adding this to equation (B 26) gives

$$M_{pp}(\chi_p - \chi_{\bar{p}}) = \lambda(\chi_p + \chi_{\bar{p}}), \tag{B 30}$$

from which equation (B 2) follows. We may note that if $\lambda = 0$, $\chi_{\bar{p}} = +\chi_p$.

Appendix C

We prove here that the set of equations (2·11) (excepting $n = 0$) and (2·30) (*a*) have no solution if $Q = 1$ and (*b*) always have a solution if $Q = 2$.

(*a*) If $Q = 1$, we are concerned with finding solutions to

$$\sum_q M_{pq} A_q^{(1)} = 0, \tag{C 1a}$$

$$\sum_q M_{pq} A_q^{(0)} = \sigma_p^{-1} U_p - A_p^{(1)}. \tag{C 1b}$$

Equation (C 1 *a*) has the solution $A_p^{(1)} = \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)}$ (see equation (2·12)), where the S independent sets of $\nu_t^{(r)}$ $(1 \leqslant r \leqslant S)$, considered in equation (B 13), are obtained from the solution of equation (B 8). We know from equation (B 7) and previous discussions that equation (C 1 *b*) will only be soluble if the orthogonality condition

$$\sum_p \sigma_p \mathscr{B}_p^{(s)} [\sigma_p^{-1} U_p - A_p^{(1)}] = 0 \tag{C 2a}$$

is satisfied. Making use of equation (B 9) we readily see that the condition (C 2 *a*) becomes

$$\sum_{t=1}^{T} K_{st} \nu_t = G_s, \tag{C 2b}$$

where

$$G_s = \sum_p U_p \mathscr{B}_p^{(s)}. \tag{C 3}$$

Thus our equations (C 1) will only possess a solution if equation (C 2 *b*) possesses a solution for ν_t. Such a solution will exist if G_s is orthogonal to all solutions of the homogeneous equation (B 8) (since $K_{ts} = K_{st}$); that is, if the S equations

$$\sum_{s=1}^{T} \nu_s^{(r)} G_s = \sum_p U_p \left[\sum_{s=1}^{T} \nu_s^{(r)} \mathscr{B}_p^{(s)} \right] = \sum_p U_p \mathscr{C}_p^{(r)} = 0 \tag{C 4}$$

are satisfied ,where $\mathscr{C}_p^{(r)}$ is defined in equation (2·19). Now, it can be shown that the $\mathscr{C}_p^{(r)}$ may be chosen to satisfy either $\mathscr{C}_{\bar{p}}^{(r)} = +\mathscr{C}_p^{(r)}$ or $\mathscr{C}_{\bar{p}}^{(r)} = -\mathscr{C}_p^{(r)}$. For the former, equation (C 4) is automatically satisfied, but for the latter, which will necessarily exist when L_{pq} is an N-matrix, equation (C 4) will not be satisfied, and hence no solutions of equations (C 1) exist.

(*b*) If $Q = 2$, we are concerned with finding solutions to

$$\sum_q M_{pq} A_q^{(2)} = 0, \tag{C 5a}$$

$$\sum_q M_{pq} A_q^{(1)} = -2A_p^{(2)}, \tag{C 5b}$$

$$\sum_q M_{pq} A_q^{(0)} = \sigma_p^{-1} U_p - A_p^{(1)}. \tag{C 5c}$$

Equation (C 5a) has the solution

$$A_p^{(2)} = \sum_{t=1}^{S} \mu_t \mathscr{C}_p^{(t)}, \tag{C 6}$$

while, from equation (C 5b), we see that $A_p^{(1)}$ is a general second-rank eigenvector, being given by

$$A_p^{(1)} = \sum_{t=1}^{T} \nu_t \mathscr{B}_p^{(t)} + \sum_{t=1}^{S} \mu_t \mathscr{D}_p^{(t)} \tag{C 7}$$

(see equation (2·21)). Equation (C 5c) will only be soluble if the orthogonality condition (C 2a) is satisfied, and this now becomes

$$\sum_{t=1}^{T} K_{st} \nu_t = G_s - \sum_{t=1}^{S} \mu_t [\sum_p \sigma_p \mathscr{D}_p^{(t)} \mathscr{B}_p^{(s)}]. \tag{C 8}$$

For this to possess a solution for ν_t, we require the right-hand side to be orthogonal to all the $\nu_t^{(r)}$ satisfying equation (B 8). This condition may be written

$$\sum_{t=1}^{S} H_{rt} \mu_t = \sum_{s=1}^{T} G_s \nu_s^{(r)} = \sum_p U_p \mathscr{C}_p^{(r)}, \tag{C 9}$$

where H_{rt} is defined in equation (B 17). It is proved there that $|H_{rt}| \neq 0$, and hence equation (C 9) always possesses a unique solution for μ_t, which combined with the ν_t, then obtainable from equation (C 8), yields a solution of equations (C 5) giving our required particular integral. The solution of equation (C 8) will be arbitrary to the extent of $\nu_t^{(r)}$ satisfying equation (B 8). This, however, will just duplicate part of the complementary function, as also will the arbitrary $\mathscr{B}_p^{(t)}$ arising in the solution of equation (C 5c) for $A_p^{(0)}$.

APPENDIX D

We prove here that in the usual formulation of the Boltzmann equation, it is valid to use velocity as the 'motion' variable for gas molecules, but that for electrons, wave number must be employed instead of velocity, unless the energy is a quadratic function of the former. To show this, let us consider a particle state to be specified by a position variable **q** and a 'motion' variable **r**; we shall consider presently precisely what physical quantity **r** can be. Then if we represent **q** and **r** by a single six-dimensional vector **s** in **q**–**r** space, we give the number of particles in a volume d**s** as $(1/8\pi^3) f(\mathbf{s})\, \mathrm{d}\mathbf{s}$. We now obtain the Boltzmann equation via the physical requirement that the rate of change of the number of particles inside any volume V of phase space due to collisions, should equal the rate of flow of particles out of V. If dA is an element of the surface of V, this yields

$$\int_V (\partial f/\partial t)_c \,\mathrm{d}\mathbf{s} = \int_V f \dot{\mathbf{s}} \,.\, \mathrm{d}A = \int_V \mathrm{div}_{\mathbf{s}} (f \dot{\mathbf{s}})\, \mathrm{d}\mathbf{s}, \tag{D 1}$$

where $(\partial f/\partial t)_c$ is the rate of change of f due to collisions, and the dot notation implies differentiation with respect to time. Thus we obtain the Boltzmann equation in the form

$$(\partial f/\partial t)_c = \mathrm{div}_{\mathbf{s}} (f \dot{\mathbf{s}}) = \dot{\mathbf{q}} \,.\, \mathrm{grad}_{\mathbf{q}} f + \dot{\mathbf{r}} \,.\, \mathrm{grad}_{\mathbf{r}} f + f[\mathrm{div}_{\mathbf{q}} \dot{\mathbf{q}} + \mathrm{div}_{\mathbf{r}} \dot{\mathbf{r}}], \tag{D 2}$$

where we now specify **q** and **r** separately. Owing to an inadequate analysis of the situation, many derivations of the Boltzmann equation do not yield the final term T in square brackets of equation (D 2). However, it may be readily shown that for classical particles obeying Hamilton's equations, for example gas molecules, this term T is zero if **r** is either the momentum **p** or the velocity **v**.

Considering now the case of quantum particles, for example, electrons, **r** may represent either the wave number $\mathbf{k}$ or the velocity $\mathbf{v}$ ($=\hbar^{-1}\,\mathrm{grad}_{\mathbf{k}}\,E$, where E is the particle energy). If $\mathbf{r}=\mathbf{k}$, it follows immediately that T is zero, since the number of particle states in a volume $\mathrm{d}\mathbf{s}$ ($=\mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{k}$) of $\mathbf{q}-\mathbf{r}$ space is proportional to $\mathrm{d}\mathbf{s}$, and is independent of the time. If $\mathbf{r}=\mathbf{v}$, on the other hand, $T=(\partial\dot{v}_i/\partial v_i)_{qi}$, and this may now be transformed to yield

$$T=\mathbf{k}_i\frac{\partial\ln|\partial^2E/\partial\mathbf{k}_p\,\partial\mathbf{k}_q|}{\partial\mathbf{k}_i}, \tag{D 3}$$

where $|M_{pq}|$ is the determinant of the matrix M_{pq}. Hence we see that for this case T will be non-zero, unless E is a quadratic function of $\mathbf{k}$. Thus the usual formulation of the Boltzmann equation, omitting the term T, will in general be incorrect for electrons in a periodic potential if $\mathbf{v}$ is the 'motion' variable.

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