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# THE KINETIC THEORY OF AN IONIZED GAS

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Harwell, Berkshire.

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THE KINETIC THEORY OF AN IONIZED GAS

by

W. MARSHALL

ABSTRACT

This report is the first of three which discuss the kinetic theory of ionized gases. In this report only a simple gas is considered so that the notation and mathematical procedures used can be easily explained. In the second report, Part II of this study, the kinetic theory of an ionized gas with no magnetic fields present is described and in the third report, Part III, the complications introduced by the presence of a magnetic field are considered and the final results quoted.

A.E.R.E.,  
HARWELL.

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## INTRODUCTION

In §1 the Boltzmann equation for a simple gas is derived and its limitations discussed. In §2 the hydrodynamic equations are derived from the Boltzmann equation and the pressure tensor and heat flux vector are introduced. In §3 a discussion of collisions is given and the form in which they enter into the Boltzmann equation is written down. Some expressions are derived for the rate of change of any quantity due to collisions. The proof that, if left to itself, the gas will approach the equilibrium state described by the well known Maxwell distribution is given in §4. The properties of this equilibrium state are discussed. In §5 the physical significance of the various terms of the hydrodynamic equations is discussed. The simple "mean free time" theory is described in §6. The theory is formulated very carefully so as to make clear the approximations which are made. In §7 the formal procedure of Chapman and Cowling<sup>(1)</sup> for obtaining a solution of the Boltzmann equation is described. The very powerful variation method of Hirshfelder et al<sup>(2)</sup> for solving the integral equations which turn up in the theory is described and the results of applying this method to calculate the coefficients of viscosity and thermal conduction are given. These results are

$$\mu = 1.025 \frac{5}{4\sqrt{\pi}} \frac{\sqrt{m} (kT)^{\frac{5}{2}}}{e^4 \psi}$$

$$\lambda = 1.08 \frac{75}{16\sqrt{\pi}} \frac{k}{\sqrt{m}} \frac{(kT)^{\frac{5}{2}}}{e^4 \psi}$$

where

$$\psi = \log \left\{ 1 + \frac{4}{\pi} \frac{(kT)^3}{e^6 n} \right\},$$

$m$  is the mass of the particles,  $e$  their charge,  $T$  the temperature and  $k$  Boltzmann's constant. Tables of these quantities are given in the Appendix to Part II. In §9 it is pointed out that this variation method corresponds to asking for the maximum rate of entropy production.

One difficulty with this subject is that the notation, even when considering just the simple gas, becomes complicated. At the end of this report therefore is given a full list of all the symbols used together with their definitions.

## §1. THE BOLTZMANN EQUATION

The Boltzmann equation is the equation upon which all this work is based. It gives the rate of change of the distribution function  $F(\underline{v}, \underline{r}, t)$ , sometimes called "the density in phase space", where this function is defined so that

$$F(\underline{v}, \underline{r}, t) d\underline{v} d\underline{r}$$

is the number of particles in the velocity range  $\underline{v}$  to  $\underline{v} + d\underline{v}$ , ( $d\underline{v} = dv_x dv_y dv_z$ ), and at a position in space between  $\underline{r}$  and  $\underline{r} + d\underline{r}$ , ( $d\underline{r} = dx dy dz$ ), at time  $t$ . An exact knowledge of  $F(\underline{v}, \underline{r}, t)$  is not equivalent to a complete knowledge of the system but it does tell us as much as we need to know for most purposes. The Boltzmann equation is derived in the following way. Consider the particles which are within this phase volume  $d\underline{v} d\underline{r}$  centred on  $\underline{v}, \underline{r}$  at time  $t$ . If there were no collisions then each of these particles would move so that at an earlier time  $t-dt$  they would have been in the phase volume  $d\underline{v} d\underline{r}$  centred at  $\underline{v} - \underline{X} dt$ ,  $\underline{r} - \underline{v} dt$ . Here  $\underline{X}$  is the force per unit mass acting on a particle. Hence if there were no collisions we would have

$$F(\underline{v}, \underline{r}, t) d\underline{v} d\underline{r} = F(\underline{v} - \underline{X} dt, \underline{r} - \underline{v} dt, t-dt) d\underline{v} d\underline{r}.$$

But in addition to these particles which move smoothly into the range  $d\underline{v} d\underline{r}$  centred at  $\underline{v}, \underline{r}$  there are also particles which suffer a collision in the volume  $d\underline{r}$  so that their velocities get scattered into or out of the velocity range  $\underline{v}$  to  $\underline{v} + d\underline{v}$ . The nett number of particles scattered into the range will be proportional to  $d\underline{v} d\underline{r} dt$  and we write it as

$$\Delta F(\underline{v}, \underline{r}, t) d\underline{v} d\underline{r} dt.$$

Adding this term to the righthand side of the previous equation and making  $dt$  tend to zero gives

$$\left\{ \frac{\partial}{\partial t} + \underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial} \right\} F(\underline{v}, \underline{r}, t) = \Delta F(\underline{v}, \underline{r}, t) \quad (1.1)$$

where

$$\begin{aligned} \underline{\nabla} &= \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \\ \underline{\partial} &= \left( \frac{\partial}{\partial v_x}, \frac{\partial}{\partial v_y}, \frac{\partial}{\partial v_z} \right) \end{aligned} \quad (1.2)$$

This is Boltzmann's equation.

In deriving this equation we assumed we could define a "collision". This could certainly be done if the particles were hard spheres; we would then say that a collision takes place if the particles touch. But for particles with Coulomb interactions it is not obvious what should be called a collision because two particles interact no matter how far apart they are. Indeed in a formal way we could say that collisions just represent forces between particles and should therefore be included in the force term  $\underline{X}$  leaving zero on the right hand side of the equation. But this would not be convenient. We shall define a "collision" to take place when two particles approach nearer to one another than a certain distance. Fortunately it will turn out that our answers are not very sensitive to this distance. Chapman and Cowling take it to be half the mean interparticle separation. Nowadays it is generally considered better to take it to be the Debye cut-off distance  $d_0 = \{kT/4\pi e^2 n_1\}^{1/2}$  where  $k$  is Boltzmann's constant,  $T$  the temperature and  $n_1$  the electron number density. This is the distance we shall use.

It should be emphasised that the force  $\underline{X}$  therefore includes the forces due to particles separated by more than this distance as well as external forces. The contribution to  $\underline{X}$  coming from distant particles may be important, for example plasma oscillations might give rise to appreciable effects. Such questions will not be considered in this report.

Notice that the Boltzmann equation is only complete in itself if the right hand side, the collision term, can be expressed as a function of  $F$ . We shall see in §3, when we consider the collision term in detail, that this can be done so long as the gas is dilute enough so that correlations between the particles can be neglected, i.e. so long as the probability of finding one particle in a certain range  $d\underline{v} d\underline{r}$  while a second particle is in some other range is just the product of the individual probabilities. This is certainly not so in a liquid but it is probably always a good approximation in a plasma.

## §2. THE EQUATIONS OF HYDRODYNAMICS

In this section we shall deduce the hydrodynamic equations of motion from the Boltzmann equation. We start however, by writing down the definitions of fundamental quantities we want to know.

If  $\Psi$  is any property of the particles, depending in general on the velocity, position and on the time, then the mean value of  $\Psi$  at the position  $\underline{r}$  and at time  $t$  is

$$\bar{\Psi} = \frac{1}{n} \int d\underline{v} F \Psi \quad (2.1)$$

where  $n$  is the number density of particles, i.e.

$$n = \int d\underline{v} F \quad (2.2)$$

The density of the gas is

$$\rho = nm$$

where  $m$  is the mass of each particle.

The drift velocity is

$$\underline{u} = \bar{\underline{v}} = \frac{1}{n} \int d\underline{v} F \underline{v} \quad (2.3)$$

The random velocity of a particle,  $\underline{c}$ , is the difference between its actual velocity and  $\underline{u}$ . Thus

$$\underline{c} = \underline{v} - \underline{u} \quad (2.4)$$

Because of (2.3),  $\bar{\underline{c}}$  is zero.

The kinetic temperature  $T$  is defined by

$$\frac{3}{2} kT = \frac{1}{2} m \overline{\underline{c}^2} = \frac{1}{n} \int d\underline{v} F \frac{1}{2} m \underline{c}^2 \quad (2.5)$$

A quantity we shall want to know is the pressure tensor

$$p_{\alpha\beta} = nm \overline{c_\alpha c_\beta} = m \int d\underline{v} F c_\alpha c_\beta \quad (2.6)$$

Here  $\alpha$  and  $\beta$  stand for the three cartesian directions  $x, y, z$ . Thus  $c_\alpha$  is the  $\alpha$ -component of the vector  $\underline{c}$  where  $\alpha$  is  $x, y$ , or  $z$ . There are nine quantities  $p_{\alpha\beta}$  of which only six are independent since clearly

$$p_{\alpha\beta} = p_{\beta\alpha} \quad (2.7)$$

These six are

$$p_{xx}, p_{yy}, p_{zz}, p_{xy} = p_{yx}, p_{yz} = p_{zy} \text{ and } p_{zx} = p_{xz}$$

The heat flux vector is  $\underline{q}$  defined by

$$\underline{q}_\alpha = \frac{1}{2} n m \overline{c^2 c_\alpha} = \int d\underline{v} F \frac{1}{2} m c^2 c_\alpha \quad (2.8)$$

We shall see why  $p_{\alpha\beta}$  and  $\underline{q}$  are important presently.

The well known equations of hydrodynamics expressing continuity, conservation of momentum and conservation of energy can be derived from (1.1) without any detailed knowledge of the form of the collision term on the right hand side. The equation of continuity comes from integrating (1.1) over all velocities. This gives

$$\int d\underline{v} \frac{\partial F}{\partial t} + \int d\underline{v} \underline{v}_\alpha \nabla_\alpha F + \int d\underline{v} X_\alpha \partial_\alpha F = \int d\underline{v} \Delta F \quad (2.9)$$

In this equation we have written out the scalar products  $\underline{v} \cdot \underline{\nabla}$  and  $\underline{X} \cdot \underline{\partial}$  using the usual summation convention. With this convention whenever a subscript is repeated it is summed. Thus the scalar product of two vectors  $\underline{a}$  and  $\underline{b}$  is written in the form

$$\underline{a} \cdot \underline{b} = \sum_\alpha a_\alpha b_\alpha = a_\alpha b_\alpha \quad (2.10)$$

Consider the terms of (2.9) one by one. In the first term the differentiation with respect to time can be brought outside the integral to give

$$\frac{\partial}{\partial t} \int d\underline{v} F = \frac{\partial n}{\partial t}$$

In the second term the differentiation with respect to space can similarly

be brought outside the integral to give

$$\nabla_{\alpha} \int d\underline{v} F v_{\alpha} = \nabla_{\alpha} n u_{\alpha} = \underline{\nabla} \cdot (n \underline{u})$$

The third term can be integrated by parts to give

$$\sum_{\alpha} \int d\underline{v} \frac{dv_{\beta}}{v_{\gamma}} [X_{\alpha} F]_{v_{\alpha}=-\infty}^{v_{\alpha}=\infty} - \int d\underline{v} F \partial_{\alpha} X_{\alpha}$$

The first part of this expression vanishes because  $F$  must be zero for  $v_{\alpha} = \pm \infty$  and the second part vanishes if  $\partial_{\alpha} X_{\alpha}$  is zero. This is certainly so if  $\underline{X}$  is independent of velocity and it can still be true for some velocity dependent forces. For example it is true for magnetic forces because the force in any direction is independent of the velocity in that direction, i.e. the force  $X_x$  depends only on  $v_y$  and  $v_z$ . Assuming from now on that  $\underline{X}$  is such that  $\partial_{\alpha} X_{\alpha}$  vanishes, this third term is zero.

The term on the right hand side of (2.9) is the rate of increase of particles due to collisions and this must be zero if ionization is not taking place. Hence (2.9) becomes

$$\frac{\partial n}{\partial t} + \underline{\nabla} \cdot (n \underline{u}) = 0 \quad (2.11)$$

If we introduce the total time derivative

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \underline{u} \cdot \underline{\nabla} \quad (2.12)$$

which represents the total rate of change as seen by an element of fluid, (2.11) can be written in the form

$$\frac{Dn}{Dt} + n \underline{\nabla} \cdot \underline{u} = 0 \quad (2.13)$$

(2.11) and (2.13) are alternative forms of the continuity equation.

The equation of motion comes from multiplying (1.1) by  $mv_{\alpha}$  and then integrating over all velocities to get

$$\int d\underline{v} mv_{\alpha} \frac{\partial F}{\partial t} + \int d\underline{v} mv_{\alpha} v_{\beta} \nabla_{\beta} F + \int d\underline{v} mv_{\alpha} X_{\beta} \partial_{\beta} F = \int d\underline{v} mv_{\alpha} F \quad (2.14)$$

The first term becomes

$$\frac{\partial}{\partial t} \int d\underline{v} m v_{\alpha} F = \frac{\partial}{\partial t} (n m u_{\alpha})$$

The second term becomes

$$\begin{aligned} \nabla_{\beta} \int d\underline{v} m v_{\alpha} v_{\beta} F &= \nabla_{\beta} \int d\underline{v} m (u_{\alpha} + c_{\alpha})(u_{\beta} + c_{\beta}) F \\ &= \nabla_{\beta} (n m u_{\alpha} u_{\beta}) + \nabla_{\beta} (n m \overline{c_{\alpha} c_{\beta}}) \end{aligned}$$

since  $\overline{c}$  is zero. The sum of the first and second term is therefore, using the definition (2.3) and making use of (2.11),

$$\rho \frac{D}{Dt} u_{\alpha} + \nabla_{\beta} p_{\beta\alpha}$$

The third term of (2.14) can be integrated by parts to give

$$- \rho \overline{\dot{X}_{\alpha}}$$

The right hand side of (2.14) is the rate of change of momentum in the  $\alpha$  direction due to collisions and must be zero since momentum is conserved in collisions. Hence (2.14) becomes

$$\rho \frac{D}{Dt} u_{\alpha} = - \nabla_{\beta} p_{\beta\alpha} + \rho \overline{\dot{X}_{\alpha}} \quad (2.15)$$

which is the equation of motion. The interpretation of the terms in this equation is very simple. The left hand side is the mass times the acceleration in the  $\alpha$ -direction of a unit volume of the fluid; the right hand side is the force acting in this direction on this unit volume - and is made up of two terms, the force exerted by the surrounding fluid (pressure and viscous forces) and the force  $\overline{\dot{X}}$  which acts on all particles. If  $\dot{X}$  is velocity independent  $\overline{\dot{X}}$  is the same as  $\dot{X}$ . We shall discuss the physical interpretation of the pressure tensor terms in §5.

The energy equation comes from multiplying (1.1) by  $\frac{1}{2} m \underline{v}^2$  and integrating over all velocities to give

$$\int d\underline{v} \frac{1}{2} m \underline{v}_\alpha \underline{v}_\alpha \frac{\partial F}{\partial t} + \int d\underline{v} \frac{1}{2} m \underline{v}_\alpha \underline{v}_\alpha \underline{v}_\beta \nabla_\beta F + \int d\underline{v} \frac{1}{2} m \underline{v}_\alpha \underline{v}_\alpha X_\beta \partial_\beta F \quad (2.13)$$

$$= \int d\underline{v} \frac{1}{2} m \underline{v}^2 \Delta F$$

The first term is

$$\frac{\partial}{\partial t} \left( \frac{1}{2} n m \overline{\underline{v}_\alpha \underline{v}_\alpha} \right) =$$

$$= \frac{\partial}{\partial t} \left( \frac{1}{2} n m \underline{u}^2 \right) + \frac{\partial}{\partial t} \left( \frac{1}{2} n m \underline{c}^2 \right)$$

The second term is

$$\nabla_\beta \left( \frac{1}{2} n m \overline{\underline{v}_\alpha \underline{v}_\alpha \underline{v}_\beta} \right) = \nabla_\beta \left( \frac{1}{2} n m \underline{u}^2 \underline{u}_\beta \right) + \nabla_\beta \left( \frac{1}{2} n m \underline{u}_\beta \underline{c}^2 \right)$$

$$+ \nabla_\beta \left( n m \underline{u}_\alpha \overline{\underline{c}_\alpha \underline{c}_\beta} \right) + \nabla_\beta \left( \frac{1}{2} n m \overline{\underline{c}_\alpha \underline{c}_\alpha \underline{c}_\beta} \right)$$

and the third term is

$$- n m \overline{\underline{v}_\beta X_\beta} = - \rho \underline{u}_\beta \overline{X_\beta} - \rho \overline{\underline{c}_\beta X_\beta}$$

The right hand side of (2.13) is the rate of change of energy due to collisions and is zero because energy must be conserved in collisions. Collecting together these terms and making use of (2.11) and (2.15) we find this equation can be rearranged into the form

$$\frac{D}{Dt} \left( \frac{3}{2} n k T \right) = \frac{3}{2} k T \frac{Dn}{Dt} - \underline{V} \cdot \underline{q} - p_{\alpha\beta} \nabla_\beta \underline{u}_\alpha + \rho \overline{\underline{c}_\beta X_\beta} \quad (2.17)$$

or

$$\frac{3}{2} n k \frac{DT}{Dt} = - \underline{V} \cdot \underline{q} - p_{\alpha\beta} \nabla_\beta \underline{u}_\alpha + \rho \overline{\underline{c} \cdot \underline{X}} \quad (2.18)$$

which is the energy equation. The physical significance of each term is best seen from (2.17). The left hand side is the total rate of change of

the energy content of an element of the fluid per unit volume.

The terms on the right hand side are: the rate of change due to increase in the number density, each particle having an energy  $\frac{3}{2} kT$  on average; the heat flowing into the element due to thermal conduction; the work done in changing the shape and size of the element, and finally the work by the force  $\underline{X}$  in the random motions of the particles. This last term is certainly zero if  $\underline{X}$  is velocity independent for then it becomes  $\rho \underline{\bar{c}} \cdot \underline{X}$  and  $\underline{\bar{c}}$  is zero. We shall see later that it also vanishes for magnetic forces.

For most problems we would be quite content to obtain a solution to these equations of continuity, motion and energy without knowing the distribution function  $F(\underline{v}, \underline{r}, t)$  accurately. However in order to solve these equations for  $n$ ,  $\underline{u}$  and  $T$  it is necessary to know the pressure tensor  $p_{\alpha\beta}$  and the heat flux vector  $\underline{q}$  and these can only be obtained from a solution of Boltzmann's equation for the distribution function. Now to obtain a good solution of Boltzmann's equation is very difficult but later we shall show that we can formulate a procedure which, although giving only a poor solution to the Boltzmann equation, gives a good approximation to the coefficients of viscosity and thermal conduction which appear in the pressure tensor and heat flux vector respectively. Therefore, provided a solution of these macroscopic hydrodynamic equations is all we require we need not trouble to get a more accurate solution for the distribution function  $F(\underline{v}, \underline{r}, t)$  that this procedure gives us.

### §3. THE COLLISION TERM

So far all we have needed to know about the collision term is that in a collision the number of particles, the total momentum and the total energy must be conserved. To go further however we must examine the collision term more carefully. We shall do this now.

Consider the collision between a particle of velocity  $\underline{v}$  with a particle of velocity  $\underline{s}$ . Suppose that after the collision the velocities are  $\underline{v}'$  and  $\underline{s}'$  respectively. The velocity of the centre of gravity,  $\underline{G}$ , must remain constant so

$$\underline{G} = \frac{1}{2}(\underline{v} + \underline{s}) = \frac{1}{2}(\underline{v}' + \underline{s}') \quad (3.1)$$

We define the relative velocities before and after the collision to be

$$\underline{g} = \underline{s} - \underline{v} \quad \underline{g}' = \underline{s}' - \underline{v}' \quad (3.2)$$

Hence

$$\begin{aligned} \underline{s} &= \underline{G} + \frac{1}{2} \underline{g} & \underline{s}' &= \underline{G} + \frac{1}{2} \underline{g}' \\ \underline{v} &= \underline{G} - \frac{1}{2} \underline{g} & \underline{v}' &= \underline{G} - \frac{1}{2} \underline{g}' \end{aligned} \quad (3.3)$$

The total energy is conserved, i.e.

$$\frac{1}{2} m (\underline{v}^2 + \underline{s}^2) = \frac{1}{2} m (\underline{v}'^2 + \underline{s}'^2) \quad (3.4)$$

Substituting from (3.3) this gives

$$g = g' \quad (3.5)$$

where  $g$  is the magnitude of the vector  $\underline{g}$ .

To complete the specification of the collision we must give the geometry of the collision as well as the initial velocities  $\underline{v}$  and  $\underline{s}$ . We do this with reference to Figure I which shows the second particle moving relative to the first particle with velocity  $\underline{g}$  before the collision and with velocity  $\underline{g}'$  after the collision having been deflected through an angle  $\chi$ . If we specify the asymptotic distance of approach,  $b$ , then the angle  $\chi$  is determined by the law of interaction between the particles. Finally we must also fix the plane in which the collision takes place by specifying the angle  $\epsilon$  which this plane, that is the plane of the paper, makes with some fixed plane.

Now consider collisions which take place in a volume of space  $d\mathbf{r}$  in a time  $t$  to  $t + dt$  between particles with velocities in the range  $\mathbf{v}$  to  $\mathbf{v} + d\mathbf{v}$  and  $\mathbf{s}$  to  $\mathbf{s} + d\mathbf{s}$  respectively where the asymptotic distance of approach lies between  $b$  and  $b + db$  and the azimuthal angle of the plane of the collision is between  $\epsilon$  and  $\epsilon + d\epsilon$ . Provided we can neglect correlations the number of such collisions is proportional to the number of particles in the range  $d\mathbf{v} d\mathbf{r}$ , i.e. to  $F(\mathbf{v}, \mathbf{r}, t) d\mathbf{r} d\mathbf{v}$ , and to the number of particles in the velocity range  $d\mathbf{s}$  which are in a cylinder in space of length  $g dt$  and of base area  $b db d\epsilon$ . That is, the number of collisions of this type is

$$F(\mathbf{v}, \mathbf{r}, t) F(\mathbf{s}, \mathbf{r}, t) g b db d\epsilon d\mathbf{v} d\mathbf{s} d\mathbf{r} dt \quad (3.6)$$

In these collisions the final velocities lie between  $\mathbf{v}'$  and  $\mathbf{v}' + d\mathbf{v}'$  and between  $\mathbf{s}'$  and  $\mathbf{s}' + d\mathbf{s}'$  respectively where  $\mathbf{v}'$  and  $\mathbf{s}'$  depend upon  $\mathbf{v}$ ,  $\mathbf{s}$ ,  $b$ ,  $\epsilon$  and the law of interaction between the particles. It can be shown quite generally that

$$d\mathbf{v}' d\mathbf{s}' = d\mathbf{v} d\mathbf{s} . \quad (3.7)$$

Closely associated with collisions of this specified type are the inverse collisions shown in Figure 2 where the initial velocities are  $\mathbf{v}'$  and  $\mathbf{s}'$  and the other specifications  $b$  and  $\epsilon$  are the same. The final velocities in this case will be  $\mathbf{v}$  and  $\mathbf{s}$  by symmetry. The number of these inverse collisions is

$$F(\mathbf{v}', \mathbf{r}, t) F(\mathbf{s}', \mathbf{r}, t) g b db d\epsilon d\mathbf{v}' d\mathbf{s}' d\mathbf{r} dt \quad (3.8)$$

which by (3.5) and (3.7) is equal to

$$F(\mathbf{v}, \mathbf{r}, t) F(\mathbf{s}, \mathbf{r}, t) g b db d\epsilon d\mathbf{v} d\mathbf{s} d\mathbf{r} dt \quad (3.9)$$

The calculation of  $\mathbf{v}', \mathbf{s}'$  in terms of  $\mathbf{v}, \mathbf{s}, b$  and  $\epsilon$  for Coulomb interactions is given in Appendix A at the end of Part II. We need not consider it until later.

The collisions (3.6) scatter particles out of the range  $d\mathbf{v}$ , collisions (3.9) scatter particles into the range  $d\mathbf{v}$ , hence the nett number of particles scattered into  $d\mathbf{v}$  is

$$d\mathbf{v} d\mathbf{r} dt \int d\mathbf{s} \int_0^{2\pi} d\epsilon \int_0^d db b g [F(\mathbf{v}') F(\mathbf{s}') - F(\mathbf{v}) F(\mathbf{s})] \quad (3.10)$$

Hence  $d_0$  is the maximum value of  $b$  allowed by our definition of a

collision, is the Debye cut-off distance  $\{kT/4\pi e^2 n\}^{1/2}$ . Hence by the definition of  $\Delta F$  used in deriving the Boltzmann equation (1.1)

$$F(\underline{v}, \underline{r}, t) = \int d\underline{s} \int_0^{2\pi} d\epsilon \int_0^d db b g [F(\underline{v}')F(\underline{s}') - F(\underline{v})F(\underline{s})] \quad (3.11)$$

where  $\underline{v}'$  and  $\underline{s}'$  are function of  $\underline{v}, \underline{s}, b, \epsilon$  and the law of interaction between the particles. We shall make use of this expression frequently.

Now we shall prove some very important theorems about the rate of change of quantities due to collisions. If  $\Psi$  is any property of the particles, depending in general on the velocity, position and time then the mean value of  $\Psi$ , written as  $\bar{\Psi}$  is defined by (2.1) and the rate of change of this mean value due to collisions is

$$\begin{aligned} \Delta \bar{\Psi} &= \frac{1}{n} \int d\underline{v} \Psi \Delta F(\underline{v}) \\ &= \frac{1}{n} \int d\underline{v} d\underline{s} d\epsilon db b g \Psi(\underline{v}) [F(\underline{v}')F(\underline{s}') - F(\underline{v})F(\underline{s})] \end{aligned} \quad (3.12)$$

Alternatively we could derive an expression for  $\Delta \bar{\Psi}$  directly from (3.6). (3.6) is the number of collisions of a specified type in which  $\underline{v}$  changes to  $\underline{v}'$ . For each such collision  $\Psi$  changes by an amount  $\Psi(\underline{v}') - \Psi(\underline{v})$ . Hence the total rate of change of  $\bar{\Psi}$  due to collisions can also be written as

$$\Delta \bar{\Psi} = \frac{1}{n} \int d\underline{v} d\underline{s} d\epsilon db b g [\Psi(\underline{v}') - \Psi(\underline{v})] F(\underline{v})F(\underline{s}) \quad (3.13)$$

It can be verified that (3.12) and (3.13) are consistent as follows. The first term of (3.12) is

$$\frac{1}{n} \int d\underline{v} d\underline{s} d\epsilon db b g \Psi(\underline{v}') F(\underline{v}') F(\underline{s}') \quad (3.14)$$

In this expression we can change variables from  $\underline{v}$  and  $\underline{s}$  to  $\underline{v}'$  and  $\underline{s}'$  and by (3.7) the Jacobian is unity. By (3.5) we can replace  $g$  by  $g'$  and then this becomes

$$\frac{1}{n} \int d\underline{v}' d\underline{s}' d\epsilon b db g' \Psi(\underline{v}) F(\underline{v}') F(\underline{s}')$$

Now by symmetry  $\underline{v}$  is the same function of  $\underline{v}'$ ,  $\underline{s}'$ ,  $b$  and  $\epsilon$  as  $\underline{v}'$  is of  $\underline{v}$ ,  $\underline{s}$ ,  $b$  and  $\epsilon$ . Hence this last expression is the same as

$$\frac{1}{n} \int d\underline{v} d\underline{s} d\epsilon b db g \Psi(\underline{v}') F(\underline{v}) F(\underline{s}) \quad (3.15)$$

This together with the second term of (3.12) gives precisely (3.13).

Because all particles are equivalent (3.13) can also be written as

$$\Delta \bar{\Psi} = \frac{1}{2n} \int d\underline{v} d\underline{s} d\underline{\epsilon} b db g [\Psi(\underline{v}') + \Psi(\underline{s}') - \Psi(\underline{v}) - \Psi(\underline{s})] F(\underline{v}) F(\underline{s})$$

which, in the same way that (3.14) is equivalent to (3.15), can be shown to be

$$\Delta \bar{\Psi} = \frac{-1}{2n} \int d\underline{v} d\underline{s} d\underline{\epsilon} b db g [\Psi(\underline{v}') + \Psi(\underline{s}') - \Psi(\underline{v}) - \Psi(\underline{s})] F(\underline{v}') F(\underline{s}')$$

Adding (3.16) and (3.17) and dividing by 2 gives yet another formula

$$\Delta \bar{\Psi} = \frac{+1}{4n} \int d\underline{v} d\underline{s} d\underline{\epsilon} b db g [\Psi(\underline{v}') + \Psi(\underline{s}') - \Psi(\underline{v}) - \Psi(\underline{s})] [F(\underline{v}) F(\underline{s}) - F(\underline{v}') F(\underline{s}')] ]$$

It is convenient to collect together all these formulae for  $\Delta \bar{\Psi}$ . They are

$$\begin{aligned} \Delta \bar{\Psi} &= \frac{1}{n} \int d\underline{v} \Psi(\underline{v}) \Delta F(\underline{v}) \\ &= \frac{1}{n} \int d\underline{v} d\underline{s} d\underline{\epsilon} b db g \Psi(\underline{v}) [F(\underline{v}') F(\underline{s}') - F(\underline{v}) F(\underline{s})] \\ &= \frac{1}{n} \int d\underline{v} d\underline{s} d\underline{\epsilon} b db g [\Psi(\underline{v}') - \Psi(\underline{v})] F(\underline{v}) F(\underline{s}) \\ &= \frac{1}{2n} \int d\underline{v} d\underline{s} d\underline{\epsilon} b db g [\Psi(\underline{v}') + \Psi(\underline{s}') - \Psi(\underline{v}) - \Psi(\underline{s})] F(\underline{v}) F(\underline{s}) \\ &= \frac{-1}{4n} \int d\underline{v} d\underline{s} d\underline{\epsilon} b db g [\Psi(\underline{v}') + \Psi(\underline{s}') - \Psi(\underline{v}) - \Psi(\underline{s})] [F(\underline{v}') F(\underline{s}') - F(\underline{v}) F(\underline{s})] \\ &\dots (3.16) \end{aligned}$$

We shall frequently make use of the fact that these expressions for  $\Delta \bar{\Psi}$  are equivalent. All we have used in deriving them are certain symmetry properties of collisions. Clearly  $\Delta \bar{\Psi}$  is zero if  $\Psi$  is 1,  $m\underline{v}$  or  $\frac{1}{2} m\underline{v}^2$ . This just expresses conservation of particles, momentum and energy. Because these laws uniquely determine the final velocities of the particle in terms of the initial velocities and  $b$  and  $\epsilon$ , it follows that only for these choices of  $\Psi$  does  $\Delta \bar{\Psi}$  vanish. Conversely if  $\Delta \bar{\Psi}$  vanishes then  $\Psi$  must be a linear combination of "the collision invariants", 1,  $m\underline{v}$  and  $\frac{1}{2} m\underline{v}^2$ . We shall make use of this fact in the next section. Strictly speaking, because

electrons and many ions have spins, to complete the specification of a collision we should also describe the initial spin states. This requires two more parameters and gives two more collision invariants, the total spin and the z-component of total spin. But the spin dependent interaction between the particles arising from their magnetic moments is so much smaller than the Coulomb interaction that it can be neglected. In this case the spin specifications remain unchanged in a collision and so we can omit them altogether. It is also true that angular momentum is conserved in collisions, in our notation this means that for each collision the asymptotic distance between the particles after the collision is the same as it is initially, namely  $b$ . The angular momentum of a particle  $m \underline{r} \underline{v}$ , is an independent collision invariant because at a collision the centres of the molecules are at different points. But in our treatment of collisions we ignored this, for example in (3.6) both distribution functions are evaluated at the same point  $\underline{r}, t$ . Therefore because we have made this approximation the angular momentum must not be regarded as an independent collision invariant. Of course if we were considering molecules with some internal degrees of freedom so that angular momentum could be exchanged between the translational and internal modes of the particles then we would have to reconsider this question carefully.

#### §4. THE EQUILIBRIUM STATE

In this section we shall prove that the system, if left to itself, will approach an equilibrium state in which the distribution function is of the familiar Maxwell form. We shall then go on to prove some properties of this equilibrium state, namely that the temperature is uniform and that the drift velocity can only vary in a certain restricted way.

Consider the quantity

$$S(t) = -k \int d\underline{r} \int d\underline{v} F(\underline{v}, \underline{r}, t) \log F(\underline{v}, \underline{r}, t) \quad (4.1)$$

In equilibrium we shall show that  $S$  becomes the entropy of the system apart from an additive constant. Differentiating gives

$$\frac{dS}{dt} = -k \int d\underline{r} \int d\underline{v} \{1 + \log F\} \frac{\partial F}{\partial t} \quad (4.2)$$

Now substituting for  $\frac{\partial F}{\partial t}$  from (1.1) gives

$$\begin{aligned} \frac{1}{k} \frac{dS}{dt} &= \int d\underline{r} \int d\underline{v} \{1 + \log F\} v_{\alpha} \nabla_{\alpha} F \\ &+ \int d\underline{r} \int d\underline{v} \{1 + \log F\} X_{\alpha} \partial_{\alpha} F \\ &- \int d\underline{r} \int d\underline{v} \{1 + \log F\} \Delta F \end{aligned} \quad (4.3)$$

Consider the terms on the right hand side of this equation one by one. The first term can be rewritten

$$\int d\underline{r} \nabla_{\alpha} \int d\underline{v} v_{\alpha} F \log F$$

which can be transformed to an integral over the surface of the container of the system

$$\int dA \int d\underline{v} v_n F \log F \quad (4.4)$$

Here  $dA$  is an element of area of the container and  $v_n$  is the component of velocity perpendicular to this area. Now provided the wall of the container is smooth and every particle which hits the wall bounces back elastically then  $F$  is an even function of  $v_n$  and (4.4) an odd

function of  $v_n$  and so the integral in (4.4) vanishes. We shall now go on to show that provided (4.4) does vanish then the system must tend to the equilibrium state given by Maxwells distribution. Thus the system will not reach the Maxwell equilibrium state if the conditions for the vanishing of (4.4) are violated, i.e. if the wall is rough or the particles lose energy to the walls on hitting them or if particles are being absorbed or emitted from the wall. This is reasonable physically, for example if the walls continually absorb particles we cannot possibly get an equilibrium state.

Assuming (4.4) to vanish then we are left with the second and third terms on the right hand side of (4.3). The second term can be written as

$$\int d\underline{r} \int d\underline{v} X_\alpha \partial_\alpha F \log F$$

which can be integrated by parts since  $\partial_\alpha X_\alpha$  is zero, to give

$$\sum_\alpha \int d\underline{r} \int d\underline{v}_R d\underline{v}_Y [X_\alpha F \log F]_{v_\alpha = -\infty}^{v_\alpha = +\infty}$$

which certainly vanishes because  $F$  must tend to zero more rapidly than  $\log F$  goes to infinity as  $v_\alpha \rightarrow \infty$ .

The last term of (4.3) is

$$- \int d\underline{r} n \nabla \{1 + \log F\}$$

Hence using (3.16)

$$\begin{aligned} \frac{dS}{dt} = \frac{k}{4} \int d\underline{r} \int d\underline{v} d\underline{s} d\underline{s}' d\underline{e} d\underline{b} d\underline{b}' g [\log F(\underline{v}') + \log F(\underline{s}') - \log F(\underline{v}) - \log F(\underline{s})] \\ \times [F(\underline{v}') F(\underline{s}') - F(\underline{v}) F(\underline{s})] \end{aligned}$$

which can be rewritten as

$$\frac{dS}{dt} = \frac{k}{4} \int d\underline{r} \int d\underline{v} d\underline{s} d\underline{s}' d\underline{e} d\underline{b} d\underline{b}' g F(\underline{v}) F(\underline{s}) \left\{ \frac{F(\underline{v}') F(\underline{s}')}{F(\underline{v}) F(\underline{s})} - 1 \right\} \log \frac{F(\underline{v}') F(\underline{s}')}{F(\underline{v}) F(\underline{s})} \quad (4.5)$$

Now the two factors of this expression,  $\left\{ \frac{F(\underline{v}') F(\underline{s}')}{F(\underline{v}) F(\underline{s})} - 1 \right\}$  and  $\log \frac{F(\underline{v}') F(\underline{s}')}{F(\underline{v}) F(\underline{s})}$ ,

are either both positive or both negative according as  $F(\underline{v}')F(\underline{s}')$  is greater or less than  $F(\underline{v})F(\underline{s})$ . Thus the product of these two factors is always positive or zero and therefore the integral in (4.5) is either positive or zero, i.e.

$$\frac{dS}{dt} \geq 0. \quad (4.6)$$

Hence as the distribution function changes it does so in such a way that the entropy increases. Indeed we shall show later that it changes in such a way that the rate of entropy production is the maximum possible subject to certain restraints. The entropy cannot increase indefinitely for it can be shown that this would require the energy content of the gas to increase indefinitely, so eventually a state is reached where  $S$  no longer increases and the equality sign holds in (4.6). This state is the equilibrium state. In the equilibrium state

$$F(\underline{v}')F(\underline{s}') = F(\underline{v})F(\underline{s}) \quad (4.7)$$

for all collisions, i.e. for all collisions

$$\log F(\underline{v}') + \log F(\underline{s}') - \log F(\underline{v}) - \log F(\underline{s}) = 0 \quad (4.8)$$

Hence in the equilibrium state  $\log F(\underline{v})$  must be a linear combination of the collision invariants, i.e.

$$\log F(\underline{v}) = a_1 + m \underline{a}_2 \underline{v} - \frac{1}{2} m a_3 \underline{v}^2 \quad (4.9)$$

where  $a_1$ ,  $\underline{a}_2$  and  $a_3$  are quantities independent of  $\underline{v}$ . From (4.9)

$$F(\underline{v}) = a_0 e^{-\frac{1}{2} m a_3 (\underline{v} - \underline{a}_4)^2} \quad (4.10)$$

where  $a_0$  and  $\underline{a}_4$  are new quantities independent of  $\underline{v}$  which are simply related to the constants  $a_1$ ,  $\underline{a}_2$  and  $a_3$  appearing in (4.9). The physical significance of  $a_0$ ,  $a_3$  and  $\underline{a}_4$  is found as follows. The number density of the gas is given by (2.2). Substituting for  $F(\underline{v})$  from (4.10) and performing the integral gives the relation

$$n = a_0 \left( \frac{2\pi}{m a_3} \right)^{\frac{3}{2}} \quad (4.11)$$

The drift velocity is defined by (2.3) and this gives

$$\underline{u} = \underline{a}_4 \quad (4.12)$$

The temperature is defined by (2.5) and this gives

$$kT = \frac{1}{a_3} \quad (4.13)$$

Hence in the equilibrium state the distribution function is given by

$$F(\underline{v}) = f(\underline{v}) \quad (4.14)$$

where throughout this report  $f(\underline{v})$  stands for the Maxwell distribution

$$f(\underline{v}) = n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(\underline{v}-\underline{u})^2} \quad (4.15)$$

So far we have said nothing about the spatial dependence of  $n, \underline{u}$  and  $T$  in this equilibrium state. We can examine what possibilities are allowed by substituting (4.15) into the Boltzmann equation (1.1). The right hand side is then zero, and assuming there is no dependence on time, we have

$$\{\underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial}\} f(\underline{v}) = 0$$

$$\text{i.e.} \quad \{\underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial}\} \log f(\underline{v}) = 0.$$

Substituting from (1.31) this is, in terms of the random velocity  $\underline{c}$ ,

$$\begin{aligned} \{c_\alpha + u_\alpha\} \left\{ \frac{1}{n} \nabla_\alpha n - \frac{3}{2T} \nabla_\alpha T + \frac{mc_\alpha^2}{2kT^2} \nabla_\alpha T + \frac{m}{kT} c_\beta \nabla_\alpha u_\beta \right\} \\ - \frac{m}{kT} \underline{X} \cdot \underline{c} = 0. \end{aligned} \quad (4.16)$$

Now (4.16) must hold over all space and for all velocities  $\underline{c}$ . Hence the coefficient of each power of  $\underline{c}$  must vanish. For simplicity we shall assume throughout the rest of this section that  $\underline{X}$  is independent of velocity. The only term of order  $c^3$  is

$$c_\alpha \frac{mc_\alpha^2}{2kT^2} \nabla_\alpha T.$$

Hence

$$\nabla_\alpha T = 0 \quad (4.17)$$

i.e. the temperature is uniform in the equilibrium state. It should be remembered that this result and those to be derived presently are only true if (4.4) is zero, i.e. if collisions with the walls are elastic. The term of order  $c^2$  is

$$\frac{n}{kT} c_\alpha c_\beta \nabla_\alpha u_\beta.$$

Hence

$$\nabla_\alpha u_\beta + \nabla_\beta u_\alpha = 0 \quad (4.18)$$

for all  $\alpha, \beta$ . The most general solution of (4.18) is

$$\underline{u} = \underline{u}_0 + \underline{\omega} \times \underline{r} \quad (4.19)$$

where  $\underline{u}_0$  and  $\underline{\omega}$  are constants. The flow (4.19) is a superposition of a uniform drift  $\underline{u}_0$  upon a rotation with constant angular velocity  $\underline{\omega}$ . This is the only flow pattern allowed in the equilibrium state. [Of course  $\underline{u}_0$  and  $\underline{\omega}$  could both be zero, i.e. the gas could be stationary.] The term of order  $c$  is

$$c_\alpha \left\{ \nabla_\alpha \log n + \frac{m}{kT} u_\beta \nabla_\beta u_\alpha - \frac{m}{kT} X_\alpha \right\}$$

Hence

$$X_\alpha = \frac{kT}{m} \nabla_\alpha \left\{ \log n - \frac{m}{2kT} \underline{u}^2 \right\}. \quad (4.20)$$

It follows that the curl of  $X_\alpha$  is zero, i.e.  $X_\alpha$  must be the gradient of a scalar potential  $V$ , i.e.

$$X_\alpha = - \nabla_\alpha V \quad (4.21)$$

Such a force is known as a conservative force. From (4.20) and (4.21)

$$n = n_0 e^{-\frac{1}{kT} mV - \frac{m}{2kT} \underline{u}^2} \quad (4.22)$$

There is not an error of sign in this equation; the term in  $\underline{u}^2$  is the centrifugal potential and we see that in centrifugal motion the density is greatest where the velocity is greatest, i.e. at the outside of the rotating system.

The term in (4.16) independent of  $\underline{c}$  is

$$u_\alpha \nabla_\alpha \log n.$$

Hence

$$u_{\alpha} \nabla_{\alpha} \left\{ V - \frac{1}{2} \underline{u}^2 \right\} = 0 . \quad (4.23)$$

But

$$u_{\alpha} \nabla_{\alpha} \underline{u}^2 = 2 u_{\alpha} u_{\beta} \nabla_{\alpha} u_{\beta} = 0$$

by (4.18). Hence (4.23) is

$$u_{\alpha} \nabla_{\alpha} V = 0 \quad (4.24)$$

which tells us that in the equilibrium state the flow must be along equipotentials.

Knowing the distribution function we can easily calculate the pressure tensor and the heat flux vector from their definitions (2.6) and (2.9).

We find that in this equilibrium state

$$p_{\alpha\beta} = p \delta_{\alpha\beta} = n kT \delta_{\alpha\beta} \quad (4.25)$$

$$q = 0 \quad (4.26)$$

(4.25) shows that in the equilibrium state only simple hydrostatic pressure forces appear in the pressure tensor and (4.26) shows that no heat flow takes place.

In the equilibrium state the quantity  $S$  of (4.1) becomes

$$S = -k \int d\underline{r} n \left[ \log n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} - \frac{3}{2} \right] \quad (4.27)$$

which apart from an additive constant is the entropy of the gas.

## §5. THE PHYSICAL SIGNIFICANCE OF THE EQUATIONS

In §2 we defined the pressure tensor and the heat flux vector and deduced the equations of hydrodynamics from the Boltzmann equation in a formal mathematical way. In this section we shall discuss the pressure tensor and the heat flux vector in a way which brings out their physical significance clearly and then we shall rederive the equations of hydrodynamics in a physical way so as to get a clear idea of the meaning of each term in the equations.

Imagine a small element of area  $dS$  moving with the local drift velocity  $\underline{u}$  so that relative to the gas it appears stationary. The orientation and size of this area we can indicate by a vector  $\underline{dS}$  erected at the centre of the area so that it is normal to it and of magnitude  $dS$ . This is shown in Figure III.

Now consider the particles crossing this element of area in the positive sense, i.e. from left to right in the Figure, with relative velocities  $\underline{c}$  to  $\underline{c} + d\underline{c}$  in time  $t$  to  $t + dt$ . These particles are those which have relative velocities  $\underline{c}$  to  $\underline{c} + d\underline{c}$  which are in a small cylinder in space erected on  $dS$  as base with axis parallel to  $\underline{c}$  and of length  $c dt$ . The volume of this cylinder is

$$\underline{dS} \cdot \underline{c} dt \quad (5.1)$$

The number of such particles is therefore, by definition of the distribution function

$$\underline{dS} \cdot \underline{c} dt d\underline{c} F(\underline{v}, \underline{r}, t) \quad (5.2)$$

where  $\underline{r}$  is the position of the element at time  $t$ .

Each of these particles carries a random energy of  $\frac{1}{2} m \underline{c}^2$  (as distinct from a total energy  $\frac{1}{2} m \underline{v}^2$  which is partly ordered) across  $dS$ . Hence the total amount of random energy, i.e. heat, carried across  $dS$  in the positive sense is

$$\int d\underline{v} \frac{1}{2} m \underline{c}^2 \underline{dS} \cdot \underline{c} dt F(\underline{v}, \underline{r}, t)$$

In this expression those particles crossing  $dS$  in the opposite sense have a negative value for  $\underline{dS} \cdot \underline{c}$  and hence contribute a negative amount as they should do. The rate of heat transfer across  $dS$  is therefore

$$d\mathbf{S} \cdot \int d\mathbf{v} \frac{1}{2} m \mathbf{c}^2 \mathbf{F}(\mathbf{v}, \mathbf{r}, t) = d\mathbf{S} \cdot \mathbf{q} \quad (5.3)$$

by definition of  $\mathbf{q}$ .

Hence the physical interpretation of  $\mathbf{q}$  is that it is the rate of heat flow, i.e. the heat flux. We shall show later that for the simple gas  $\mathbf{q}$  is given by

$$\mathbf{q} = -\lambda \nabla T. \quad (5.4)$$

where  $\lambda$  is the coefficient of thermal conductivity.

Each of the particles (5.2) also carries a momentum  $m\mathbf{v}$  and so the rate of transfer of momentum across  $d\mathbf{S}$  in the positive sense is

$$\int d\mathbf{v} m\mathbf{v} d\mathbf{S} \cdot \mathbf{c} F(\mathbf{v}, \mathbf{r}, t) \quad (5.5)$$

But the rate of transfer of momentum across  $d\mathbf{S}$  in the positive sense is equal to the force exerted across the surface  $d\mathbf{S}$  by fluid to the negative on fluid to the positive side. Hence (5.5) is this force. It is of course a vector quantity and written in component form is

$$\begin{aligned} \int d\mathbf{v} m(u_x + c_x, u_y + c_y, u_z + c_z) d\mathbf{S} \cdot \mathbf{c} F(\mathbf{v}, \mathbf{r}, t) \\ \int d\mathbf{v} m(c_x, c_y, c_z) d\mathbf{S} \cdot \mathbf{c} F(\mathbf{v}, \mathbf{r}, t) \end{aligned} \quad (5.6)$$

which by (2.6) is

$$d\mathbf{S} \cdot (p_{\alpha x}, p_{\alpha y}, p_{\alpha z}) \quad (5.7)$$

where of course a summation over components  $\alpha$  is implied.

Thus for example if  $d\mathbf{S}$  is parallel to the  $x$  axis, i.e. the area  $d\mathbf{S}$  lies in the  $y$ - $z$  plane, this force is

$$d\mathbf{S} \cdot (p_{xx}, p_{xy}, p_{xz}) \quad (5.8)$$

Hence  $p_{\alpha\beta}$  is the force exerted in the  $\beta$  direction across a surface

facing the  $\alpha$  direction. Later we shall show that  $p_{\alpha\beta}$  is given by

$$p_{\alpha\beta} = \left\{ p + \frac{2}{3} \mu \nabla \cdot \underline{u} \right\} \delta_{\alpha\beta} - \mu (\nabla_{\alpha} u_{\beta} + \nabla_{\beta} u_{\alpha}) \quad (5.9)$$

i.e.

$$\begin{aligned} p_{xx} &= p + \frac{2}{3} \mu \nabla \cdot \underline{u} - 2\mu \nabla_x u_x \\ p_{yy} &= \text{etc} \\ p_{xy} &= -\mu (\nabla_x u_y + \nabla_y u_x) = p_{yx} \\ p_{zx} &= \text{etc.} \end{aligned} \quad (5.10)$$

Here  $p$  is the hydrostatic pressure  $nkT$  and  $\mu$  the coefficient of viscosity.

Now we have discussed  $q$  and  $p_{\alpha\beta}$  let us rederive the hydrodynamic equations (2.11), (2.15) and (2.17) using physical arguments instead of the purely mathematical derivation we gave in §2 which started from the Boltzmann equation. To do this consider a small rectangular element of volume  $dx dy dz$  centred on the point  $\underline{r}$  as shown in Figure IV. In this figure the two faces normal to the  $x$  direction, with area  $dy dz$ , we shall call the  $x$ -faces. The first  $x$ -face is the one passing through  $\underline{r} - \frac{1}{2} \underline{dx}$ , the second  $x$ -face passes through  $\underline{r} + \frac{1}{2} \underline{dx}$ . We use a similar nomenclature for the other faces. We suppose that each part of the element moves with the local drift velocity so that, unless the drift velocity is uniform the element will not retain the same volume or shape.

We can calculate the rate of volume change as follows. The volume at time  $t$  is

$$dx dy dz,$$

Consider the element at a later time  $t + dt$ . The point  $\underline{r} - \frac{1}{2} \underline{dx}$  will now have moved to the point

$$\underline{r} - \frac{1}{2} \underline{dx} + dt \underline{u}(\underline{r} - \frac{1}{2} \underline{dx})$$

and the point  $\underline{r} + \frac{1}{2} \underline{dx}$  will have moved to

$$\underline{r} + \frac{1}{2} \underline{dx} + dt \underline{u}(\underline{r} + \frac{1}{2} \underline{dx})$$

The x component of the distance between them is therefore

$$\begin{aligned} dx + dt \{ u_x (x + \frac{1}{2} dx) - u_x (x - \frac{1}{2} dx) \} \\ = dx \{ 1 + dt \frac{d u_x}{dx} \} \end{aligned}$$

Similarly the dimension in the y direction changes from dy to

$$dy \{ 1 + dt \frac{d u_y}{dy} \}$$

and in the z direction to

$$dz \{ 1 + dt \frac{d u_z}{dz} \}$$

To first order in dt therefore the volume changes from dx dy dz to

$$dx dy dz \{ 1 + dt \nabla \cdot \underline{u} \}$$

$$\text{so} \quad \frac{D}{Dt} \{ dx dy dz \} = dx dy dz \nabla \cdot \underline{u} \quad (5.11)$$

Now let us derive the equation of continuity. The total number of particles in the element is  $n dx dy dz$ . The rate of change of this number is

$$\frac{D}{Dt} \{ n dx dy dz \} \quad (5.12)$$

This must be equated to the rate that particles flow into the element across the surfaces. But this is zero because it is given by the integral of an expression like (5.2). For example the rate particles cross the first x-face is

$$dy dz \int d\epsilon c_x F = dy dz n \overline{c_x} = 0$$

Hence (5.12) is zero, i.e.

$$dx dy dz \frac{Dn}{Dt} + n \frac{D}{Dt} (dx dy dz) = 0$$

If we now use (5.11) and then divide by  $dx dy dz$  we get the continuity equation in the form (2.13).

Now let us derive the momentum equation. The total rate of change of the  $\alpha$ -component of the momentum of the element is

$$\frac{D}{Dt} (\rho u_{\alpha} dx dy dz) \quad (5.13)$$

This must be equated to the force acting on the element. The force  $\underline{X}$  produces a force in the  $\alpha$  direction

$$\rho \bar{X}_{\alpha} dx dy dz \quad (5.14)$$

In addition to this there are forces acting on the element across the surfaces. By (5.8) the force acting across the first  $x$  face in the  $\alpha$  direction is

$$dy dz p_{x\alpha} \left( r - \frac{1}{2} dx \right)$$

The force acting across the second  $x$ -face, on the element, in the  $\alpha$  direction is

$$- dy dz p_{x\alpha} \left( r + \frac{1}{2} dx \right)$$

Hence the total force acting across the  $x$  faces is

$$\begin{aligned} & - dy dz [p_{x\alpha} \left( r + \frac{1}{2} dx \right) - p_{x\alpha} \left( r - \frac{1}{2} dx \right)] \\ & = - dx dy dz \frac{d}{dx} p_{x\alpha} \end{aligned}$$

Adding contributions from the  $y$  and  $z$  faces gives a total surface force

$$- dx dy dz \nabla_{\beta} p_{\beta\alpha} \quad (5.15)$$

Adding (5.14) and (5.15) to equate to (5.13) gives

$$\frac{D}{Dt} \{ \rho u_{\alpha} dx dy dz \} = \rho \bar{X}_{\alpha} dx dy dz - dx dy dz \nabla_{\beta} p_{\beta\alpha}$$

Since (5.12) is zero this is, dividing by  $dx dy dz$

$$\rho \frac{Du_\alpha}{Dt} = -\nabla_\gamma p_{\alpha\gamma} + \rho \tau_\alpha \quad (5.16)$$

which is the equation of motion.

Finally let us derive the energy equation. The total energy in the element is

$$\frac{1}{2} \rho \overline{v^2} dx dy dz = \frac{1}{2} \rho \overline{u^2} dx dy dz + \frac{3}{2} n kT dx dy dz \quad (5.17)$$

The rate of change of this must be equated to the rate that heat flows into the element plus the work done by the forces. By (5.3) the rate that heat flows across the first x-face into the element is

$$dy dz q_x \left( x - \frac{1}{2} dx \right)$$

The rate heat flows across the second x-face out of the element is

$$dy dz q_x \left( x + \frac{1}{2} dx \right)$$

The nett rate of heat flow into the element across the x-faces is therefore

$$- dx dy dz \frac{d}{dx} q_x$$

Adding similar contributions due to flow across the y and z faces gives as the total rate heat flows into the element

$$- dx dy dz \nabla \cdot \underline{q} \quad (5.18)$$

The rate the force  $\underline{X}$  does work is

$$\rho \overline{\underline{X} \cdot \underline{v}} dx dy dz = \rho (\overline{\underline{X} \cdot \underline{u}} + \overline{\underline{X} \cdot \underline{c}}) dx dy dz \quad (5.19)$$

The rate the surface force across the first x face does work on the element is

$$dy dz p_{x\alpha} \left( x + \frac{1}{2} dx \right) u_\alpha \left( x + \frac{1}{2} dx \right)$$

2<sup>a</sup>.

The nett rate the surface forces acting across the x-faces do work is therefore

$$- dx dy dz \frac{d}{dx} (p_{x\alpha} u_{\alpha})$$

and the total rate all the surface forces do work is

$$- dx dy dz \nabla_{\beta} (p_{\beta\alpha} u_{\alpha}) \quad (5.20)$$

Equating the rate of change of (5.17) to the sum of (5.18), (5.19) and (5.20) gives

$$\begin{aligned} & \frac{D}{Dt} \left( \frac{1}{2} \rho u^2 dx dy dz \right) + \frac{D}{Dt} \left( \frac{3}{2} nkT dx dy dz \right) \\ = & - dx dy dz \nabla \cdot \underline{q} + \rho (\overline{\underline{X} \cdot \underline{u}} + \overline{\underline{X} \cdot \underline{c}}) dx dy dz \\ & - dx dy dz \nabla_{\beta} (p_{\beta\alpha} u_{\alpha}) \end{aligned} \quad (5.21)$$

The left hand side, remembering (5.12) is zero, can be rewritten

$$\frac{1}{2} \rho dx dy dz \frac{D}{Dt} u^2 + n dx dy dz \frac{D}{Dt} \left( \frac{3}{2} kT \right)$$

hence, dividing by  $dx dy dz$ , (5.21) becomes

$$\begin{aligned} \rho u_{\alpha} \frac{D u_{\alpha}}{Dt} + n \frac{D}{Dt} \left( \frac{3}{2} kT \right) = & - \nabla \cdot \underline{q} + \rho \overline{\underline{X} \cdot \underline{u}} + \rho \overline{\underline{X} \cdot \underline{c}} \\ & - \nabla_{\beta} (p_{\beta\alpha} u_{\alpha}) \end{aligned} \quad (5.22)$$

Now multiplying (5.16) by  $u_{\alpha}$  gives an expression for the first term on the left hand side of (5.22). Substituting this expression we find that (5.22) can be rewritten as

$$n \frac{D}{Dt} \left( \frac{3}{2} kT \right) = - \nabla \cdot \underline{q} + \rho \overline{\underline{X} \cdot \underline{c}} - p_{\beta\alpha} \nabla_{\beta} u_{\alpha} \quad (5.23)$$

which is the energy equation in the form (2.18).

## §6. THE MEAN FREE TIME THEORY

In this section we shall describe the mean free path theory of kinetic processes, i.e. of viscosity and thermal conduction. This theory gives a useful insight into the physics of the effects but it is not precise and suffers from internal inconsistencies. Qualitatively however for the simple gas it gives the same results as the more complete analysis to be described in the next section. Usually the theory is based on the concept of a "mean free path" but we shall formulate it in terms of a "mean free time" as it is this formulation which can be easily extended to consider the same problems in the presence of a magnetic field. As usually described it is not clear just what approximations are made in this theory and this is one possible reason why there has been no successful attempt to improve the mean free path theory until it is quantitatively as well as qualitatively correct. We shall therefore formulate the theory exactly before going over to the customary theory and this will enable us to see the approximations which must be made.

The idea of all mean free path or mean free time theories is to follow the motion of each particle back to when it suffered its last collision and so relate the distribution function at any given time to the distribution function at the earlier time of the collision. The theory is therefore essentially an attempt to solve the Boltzmann equation.

The motion of a particle between collisions is particularly simple if  $\underline{X}$  is velocity independent and constant. In this case the equation of motion

$$\frac{d^2}{dt^2} \underline{r} = \underline{X}$$

is easily integrated to give

$$\frac{d}{dt} \underline{r} = \underline{v} = \underline{v}_0 + (t - t_0) \underline{X} \quad (6.1)$$

$$\underline{r} = \underline{r}_0 + (t - t_0) \underline{v}_0 + \frac{1}{2} (t - t_0)^2 \underline{X} \quad (6.2)$$

where  $\underline{v}_0$  and  $\underline{r}_0$  are the velocity and position of the particle at a given time  $t_0$ .

Let  $\tau(\underline{v}, \underline{r}, t)$  be the mean time between collisions for a particle of velocity  $\underline{v}$  at the point  $\underline{r}$  and at time  $t$ . Of course the

dependence on  $\underline{r}$  and  $t$  is only implicit through the dependence on number density and temperature. Then the number of collisions in a volume  $d\underline{r}$  about  $\underline{r}$  in time  $t$  to  $t + dt$  by particles with velocities  $\underline{v}$  to  $\underline{v} + d\underline{v}$  is

$$d\underline{v} d\underline{r} dt \frac{F(\underline{v}, \underline{r}, t)}{\tau(\underline{v}, \underline{r}, t)}. \quad (6.3)$$

Comparing this with the formula we derived earlier (3.6) we see that

$$\frac{1}{\tau(\underline{v}, \underline{r}, t)} = \int d\underline{s} d\underline{e} b db g F(\underline{s}, \underline{r}, t). \quad (6.4)$$

Define  $p(t)$  to be the probability that a particle survives making collisions up to time  $t$  given that it made a collision at time zero. To calculate  $p(t)$  consider this probability at a later time  $t + dt$ . The probability the particle survives up to time  $t + dt$  is the probability it survives up to time  $t$  minus the probability it suffers its first collision in time  $t$  to  $t + dt$ . The latter is the probability that it survives up to time  $t$  times the probability it suffers a collision in a time interval  $dt$ . Hence

$$p(t + dt) = p(t) - p(t) \frac{dt}{\tau} \quad (6.5)$$

which, if  $\tau$  were constant would have the solution

$$p(t) = e^{-t/\tau}. \quad (6.6)$$

But actually in (6.5)  $\tau$  is the collision time for a particle with velocity  $\underline{v}$  at position  $\underline{r}$ , time  $t$ , where  $\underline{r}$  and  $\underline{v}$  are given in terms of the position and velocity at time zero by equations like (6.3) and (6.4). A more precise solution taking this into account is

$$p(t) = e^{-\int_0^t \frac{dt'}{\tau(t')}}. \quad (6.7)$$

Now we have seen in §5. that in order to calculate  $\underline{q}$  and  $\underline{p}$ , i.e. the coefficients of thermal conductivity and viscosity, it is necessary to evaluate (5.2) which is the number of particles crossing an element of area in time  $dt$  with velocities in a certain range. Usually the theory is formulated to give this directly but since this number is simply related to  $F$  we may alternatively regard the theory as an attempt to calculate  $F$ , i.e. to solve Boltzmann's equation. We shall now describe the theory.

The number of particles in a given volume  $\underline{r}_0$  to  $\underline{r}_0 + d\underline{r}_0$  with velocities  $\underline{v}_0$  to  $\underline{v}_0 + d\underline{v}_0$  at time  $t_0$  is, by definition

$$d\underline{v}_0 d\underline{r}_0 F(\underline{v}_0, \underline{r}_0, t_0). \quad (6.8)$$

Now consider those particles of this set which suffered their last collision at time  $t$  to  $t + dt$ , [ $t < t_0$ ]. These are those particles which suffer a collision in time  $t$  to  $t + dt$  at  $\underline{r}$  to  $\underline{r} + d\underline{r}$  so that their final velocities after the collision lie in  $\underline{v}$  to  $\underline{v} + d\underline{v}$  where  $\underline{r}$  and  $\underline{v}$  are given in terms of  $\underline{r}_0, \underline{v}_0$  by (6.2) and (6.1) and

$$d\underline{r} = d\underline{r}_0, \quad d\underline{v} = d\underline{v}_0. \quad (6.9)$$

The number of such particles is given by integrating (3.9) over  $\underline{s}$ ,  $b$  and  $\epsilon$  to give

$$d\underline{v} d\underline{r} dt \int d\underline{s} d\epsilon b db g F(\underline{v}', \underline{r}, t) F(\underline{s}', \underline{r}, t) \quad (6.10)$$

which using (3.11) in Boltzmann's equation can be written in the alternative form

$$d\underline{v} d\underline{r} dt \left\{ \frac{F(\underline{v}, \underline{r}, t)}{\tau(\underline{v}, \underline{r}, t)} + \left[ \frac{\partial}{\partial t} + \underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial} \right] F(\underline{v}, \underline{r}, t) \right\}. \quad (6.11)$$

Not all of these particles make a contribution to the set (6.9), however, because they may suffer a second collision in the time interval  $t_0 - t$ . The probability they survive is

$$e^{-\int_t^{t_0} \frac{dt_1}{\tau(\underline{v}_1, \underline{r}_1, t_1)}} \quad (6.12)$$

where

$$\begin{aligned} \underline{v}_1 &= \underline{v}_0 + (t_1 - t_0) \underline{X} \\ \underline{r}_1 &= \underline{r}_0 + (t_1 - t_0) \underline{v}_0 + \frac{1}{2} (t_1 - t_0)^2 \underline{X}. \end{aligned} \quad (6.13)$$

Multiplying (3.11) by (6.12), integrating over all  $t$  and equating to (3.8) gives

$$F(\underline{v}_0, \underline{r}_0, t_0) = \int_{-\infty}^{t_0} dt e^{-\int_t^{t_0} \frac{dt_1}{\tau(\underline{v}_1, \underline{r}_1, t_1)}} \left\{ \frac{F(\underline{v}, \underline{r}, t)}{\tau(\underline{v}, \underline{r}, t)} + \left[ \frac{\partial}{\partial t} + \underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial} \right] F(\underline{v}, \underline{r}, t) \right\} \quad (6.14)$$

This is a formula which relates the distribution function at time  $t_0$  to the distribution function at earlier times  $t$ . We have made no approximations so far and (6.14) is exact. To prove this we notice that the first term of (6.14) can be rewritten as

$$\int_{-\infty}^{t_0} dt F(\underline{v}, \underline{r}, t) \frac{d}{dt} \left\{ e^{-\int_t^{t_0} \frac{dt_1}{\tau(\underline{v}_1, \underline{r}_1, t_1)}} \right\}$$

which can be integrated by parts to give

$$\left[ F(\underline{v}, \underline{r}, t) e^{-\int_t^{t_0} \frac{dt_1}{\tau(\underline{v}_1, \underline{r}_1, t_1)}} \right]_{-\infty}^{t_0} - \int_{-\infty}^{t_0} e^{-\int_t^{t_0} \frac{dt_1}{\tau(\underline{v}_1, \underline{r}_1, t_1)}} \frac{d}{dt} F(\underline{v}, \underline{r}, t)$$

The first term of this expression evaluated at  $t_0$  is  $F(\underline{v}_0, \underline{r}_0, t_0)$ , evaluated at  $-\infty$  is zero; in the second term we note that

$$\frac{d}{dt} F(\underline{v}, \underline{r}, t) = \left[ \frac{\partial}{\partial t} + \underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial} \right] F(\underline{v}, \underline{r}, t)$$

so this second term exactly cancels off with the second term of (6.14). Thus the right hand side of (6.14) reduces to  $F(\underline{v}_0, \underline{r}_0, t_0)$  as it should.

In the mean free time theory we now use an iteration procedure on the formula equivalent to (6.14)

$$F(\underline{v}_0, \underline{r}_0, t_0) = \int_{-\infty}^{t_0} dt e^{-\int_t^{t_0} \frac{dt_1}{\tau(\underline{v}_1, \underline{r}_1, t_1)}} \int d\underline{s} d\underline{s}' d\underline{b} d\underline{b}' g F(\underline{v}, \underline{r}, t) F(\underline{s}', \underline{r}', t) \quad (6.15)$$

obtained by using (6.10) in place of (6.11). [We cannot use an iteration procedure on (6.14) itself because the discussion just given shows that any distribution function would satisfy the equation.] The iteration procedure consists of inserting an approximate expression for  $F$  in the right hand side and performing the integrations to get a better approximation for  $F(\underline{v}_0, \underline{r}_0, t_0)$ .

The simplest approximation is to replace  $F$  on the right hand side of (6.15) by a local Maxwellian distribution. This is a good approximation

if the collision time is short compared with any macroscopic relaxation time of the gas. Then remembering that

$$f(\underline{v}', \underline{r}, t) f(\underline{s}', \underline{r}, t) = f(\underline{v}, \underline{r}, t) f(\underline{s}, \underline{r}, t) \quad (6.16)$$

where  $f(\underline{v}, \underline{r}, t)$  stands for a Maxwellian distribution at  $\underline{r}$  and  $t$ . Ignoring the variation of the collision time over the path of the particle, (6.15) becomes

$$F(\underline{v}_0, \underline{r}_0, t_0) = \int_{-\infty}^{t_0} dt \, e^{-\frac{(t-t_0)}{\tau(\underline{v}_0, \underline{r}_0, t_0)}} \int d\underline{s} \, d\underline{s}' \, d\underline{b} \, d\underline{b}' \, g f(\underline{v}, \underline{r}, t) f(\underline{s}, \underline{r}, t)$$

(6.17)

$$= \int_{-\infty}^{t_0} dt \, e^{-\frac{(t-t_0)}{\tau_0}} \frac{f(\underline{v}, \underline{r}, t)}{\tau_0} \quad (6.18)$$

where  $\tau_0$  is shorthand for  $\tau(\underline{v}_0, \underline{r}_0, t_0)$ .

We now expand  $f(\underline{v}, \underline{r}, t)$  in powers of  $(t-t_0)$  to give

$$f(\underline{v}, \underline{r}, t) = f(\underline{v}_0, \underline{r}_0, t_0) + (t-t_0) \left[ \frac{\partial}{\partial t_0} + \underline{v}_0 \cdot \underline{\nabla}_0 + \underline{X} \cdot \underline{\partial}_0 \right] f(\underline{v}_0, \underline{r}_0, t_0) + \approx (t-t_0)^2 \quad (6.19)$$

where  $\underline{\nabla}_0 = \left( \frac{\partial}{\partial x_0}, \frac{\partial}{\partial y_0}, \frac{\partial}{\partial z_0} \right)$ ,  $\underline{\partial}_0 = \left( \frac{\partial}{\partial v_{0x}}, \frac{\partial}{\partial v_{0y}}, \frac{\partial}{\partial v_{0z}} \right)$ .

Ignoring the terms of order  $(t-t_0)^2$  which give contributions  $(\tau^2)$  and performing the integrations over  $t$  gives, dropping the subscript  $0$ ,

$$F(\underline{v}, \underline{r}, t) = f(\underline{v}, \underline{r}, t) - \tau \left[ \frac{\partial}{\partial t} + \underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial} \right] f(\underline{v}, \underline{r}, t) \quad (6.20)$$

At this stage, without any real justification the normal mean free time theory replaces (6.20) by

$$\begin{aligned} F(\underline{v}, \underline{r}, t) &= f(\underline{v}, \underline{r}, t) - \tau n \underline{c} \cdot \underline{\nabla} \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT} (\underline{v}-\underline{u})^2} \\ &= f(\underline{v}, \underline{r}, t) - \tau n [c_\alpha(\underline{v}T) \frac{\partial}{\partial T} + c_\alpha(\underline{v}T) \frac{\partial}{\partial u_\beta}] \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT} (\underline{v}-\underline{u})^2} \\ &= f(\underline{v}, \underline{r}, t) \left\{ 1 + \tau \left( \frac{\beta}{2} - \frac{mc^2}{2kT} \right) \frac{1}{T} \underline{c} \cdot \underline{\nabla} T - \frac{\tau m}{kT} c_\alpha c_\beta \nabla_\alpha u_\beta \right\} \quad (6.21) \end{aligned}$$

??.

At first sight it looks as though to get this result the terms

$$- \tau \left[ \frac{\partial}{\partial t} + \underline{u} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial} \right] f(\underline{v}, \underline{r}, t) \quad (6.22)$$

in (6.20) have been ignored and furthermore that it has been assumed that the gas has uniform density so that  $\underline{\nabla} n = 0$ . In fact, however, a careful examination of these terms shows that, to the order we are working, (6.21) is qualitatively correct and can be made quantitative merely by modifying the terms so that it reads

$$F(\underline{v}, \underline{r}, t) = f(\underline{v}, \underline{r}, t) \left\{ 1 + \tau \left( \frac{5}{2} - \frac{mc^2}{2kT} \right) \frac{1}{T} \underline{u} \cdot \underline{\nabla} T - \frac{\tau m}{kT} \left( c_\alpha c_\beta - \frac{1}{3} c^2 \delta_{\alpha\beta} \right) \nabla_\alpha u_\beta \right\} \quad (6.23)$$

The details of this careful examination are given in the beginning of the next section. The idea involved is that the term  $\frac{\partial f}{\partial t}$  of (6.22) involves  $\frac{\partial n}{\partial t}$ ,  $\frac{\partial \underline{u}}{\partial t}$  and  $\frac{\partial T}{\partial t}$  and these three quantities are related to the spatial derivatives  $\underline{\nabla} n$ ,  $\nabla_\alpha u_\beta$  and  $\underline{\nabla} T$  by the equations of motion. When these relations are used to eliminate the time derivatives in (6.20) it is found that many terms cancel and (6.23) is the final result.

Quite apart from the fact that the normal theory gives no kind of justification for this last step it is unsatisfactory for two reasons. Firstly the non-Maxwellian parts of  $F$  if inserted on the right hand side of (6.15) would lead to terms comparable to the non-Maxwellian terms in (6.23). Secondly in going from (6.17) to (6.18) it is inconsistent to take account of the difference of  $f(\underline{v}, \underline{r}, t)$  from  $f(\underline{v}_0, \underline{r}_0, t_0)$  but ignore the variation of  $\tau$  over the path of the particle. For these reasons we cannot expect (6.23) to be more than qualitatively correct.

It is clear that a better procedure than that which we have described would be to assume a small departure from Maxwellian and solve for this self consistently. Assuming

$$F(\underline{v}, \underline{r}, t) = f(\underline{v}, \underline{r}, t) \{1 + \varphi(\underline{v}, \underline{r}, t)\} \quad (6.24)$$

where  $\varphi$  is small, (6.15) gives to first order in  $\varphi$

$$\begin{aligned} f(\underline{v}_0, \underline{r}_0, t_0) \{1 + \varphi(\underline{v}_0, \underline{r}_0, t_0)\} = & \int_{-\infty}^{t_0} dt e^{\frac{(t-t_0)}{\tau}} \int d\underline{s} d\underline{e} d\underline{b} d\underline{b}' g f(\underline{v}, \underline{r}, t) f(\underline{s}, \underline{r}, t) \\ & + \tau \int d\underline{s} d\underline{e} d\underline{b} d\underline{b}' g f(\underline{v}_0, \underline{r}_0, t_0) f(\underline{s}_0, \underline{r}_0, t_0) \{\varphi(\underline{v}_0') + \varphi(\underline{s}_0')\} \end{aligned} \quad (6.25)$$

Making use of the expansion (3.19) and the argument leading to (6.23) this gives dropping the subscript  $\alpha$ ,

$$\begin{aligned} f(\underline{c}) \varpi(\underline{c}) = & \tau f(\underline{c}) \left( \frac{5}{2} - \frac{mc^2}{2kT} \right) \frac{1}{T} \underline{c} \cdot \underline{\nabla} T - \tau f(\underline{c}) \frac{m}{kT} c_\alpha c_\beta \nabla_\alpha u_\beta \\ & + \tau^2 \int d\underline{s} \, d\underline{e} \, b \, db \, g f(\underline{c}) f(\underline{s}) \left[ \left( \frac{5}{2} - \frac{ms^2}{2kT} \right) \frac{1}{T} \underline{s} \cdot \underline{\nabla} T - \frac{m}{kT} s_\alpha s_\beta \nabla_\alpha u_\beta \right] \\ & + \tau \int d\underline{s} \, d\underline{e} \, b \, db \, g f(\underline{c}) f(\underline{s}) \{ \varpi(\underline{c}') + \varpi(\underline{s}') \} . \end{aligned} \quad (6.26)$$

But this is a more difficult equation to solve for  $\varpi$  than the equation obtained by substituting (6.24) directly into the Boltzmann equation and we shall see in the next section that this is essentially what is done by Chapman and Cowling.

Qualitatively, however, (6.23) is correct and substituting it into the definition of the pressure tensor (2.6) we get the formula (5.9) [for the details of this calculation see equations (7.34) to (7.41)] where

$$\mu = n kT \tau . \quad (6.27)$$

Similarly if we substitute (6.23) into the definition of the heat flux vector (2.8) we get

$$\underline{q} = -\lambda \underline{\nabla} T \quad (6.28)$$

where

$$\lambda = \frac{5k}{2m} n kT \tau \quad (6.29)$$

[for details see the similar calculation (7.33) to (7.32).]

## §7. THE FORMAL THEORY OF KINETIC PROCESSES

In this section we shall describe the Chapman-Cowling method for solving the Boltzmann equation by successive approximations. We shall see that we obtain only a very crude idea of the complete distribution function but that we obtain quite accurate expressions for the pressure tensor and the heat flux vector, that is for the coefficients of viscosity and thermal conduction. This is usually as much as we need.

It is assumed that collisions are most important in determining the distribution function and that to a first approximation we have a Maxwellian distribution at each point in space. Then we calculate the corrections to this. Mathematically we can indicate this process by rewriting (1.1) as

$$\left\{ \frac{\partial}{\partial t} + \underline{v} \cdot \underline{\nabla} + \underline{X} \cdot \underline{\partial} \right\} F = \frac{1}{\eta} \Delta F$$

$$= \frac{1}{\eta} \int d\underline{s} d\underline{\varepsilon} b db g \{ F(\underline{v}') F(\underline{s}') - F(\underline{v}) F(\underline{s}) \} \quad (7.1)$$

Of course we set  $\eta$  equal to unity eventually but we write the equation in this way to indicate the way the terms will be grouped. We now write

$$F = F^{(0)} \{ 1 + \eta \varphi + \eta^2 \psi + \dots \} \quad (7.2)$$

where by taking more and more terms we get successive approximations.

Substituting (7.2) into (7.1) and setting the coefficients of each power of  $\eta$  equal to zero gives a set of equations which, in principle, gives a complete solution of (7.1). In practice it is only the first two coefficients which are considered because the work rapidly becomes too difficult.

The only term of order  $\frac{1}{\eta}$  is

$$\frac{1}{\eta} \int d\underline{s} d\underline{\varepsilon} db b g \{ F^{(0)}(\underline{v}') F^{(0)}(\underline{s}') - F^{(0)}(\underline{v}) F^{(0)}(\underline{s}) \} \quad (7.3)$$

which has solution

$$F^{(0)}(\underline{v}, \underline{r}, t) = f = n \left\{ \frac{m}{2\pi kT} \right\}^{\frac{3}{2}} e^{-\frac{m}{2kT} (\underline{v}-\underline{u})^2} \quad (7.4)$$

i.e. the Maxwell distribution.

The terms independent of  $\eta$  on the right hand side of (7.1) are

$$\int d\underline{s} d\underline{e} b db g[f(\underline{v}')f(\underline{s}')\{\varphi(\underline{v}')+\varpi(\underline{s}')\} - f(\underline{v})f(\underline{s})\{\varphi(\underline{v})+\varpi(\underline{s})\}] \quad (7.5)$$

and since

$$f(\underline{v}')f(\underline{s}') = f(\underline{v})f(\underline{s}) \quad (7.6)$$

this can be rewritten

$$\int d\underline{s} d\underline{e} b db g f(\underline{v}) f(\underline{s})[\varphi(\underline{v}') + \varpi(\underline{s}') - \varphi(\underline{v}) - \varpi(\underline{s})] \quad (7.7)$$

The terms independent of  $\eta$  coming from the last two terms on the left hand side of (7.1) are

$$\{\underline{v} \cdot \nabla + \underline{X} \cdot \partial\} f = - \frac{m}{kT} f \underline{X} \cdot \underline{c} + \frac{\partial f}{\partial n} \underline{v} \cdot \underline{\nabla} n + \frac{\partial f}{\partial u_\alpha} v_\beta \nabla_\beta u_\alpha + \frac{\partial f}{\partial T} \underline{v} \cdot \underline{\nabla} T \quad (7.8)$$

where clearly

$$\begin{aligned} \frac{\partial f}{\partial n} &= \frac{f}{n} \\ \frac{\partial f}{\partial u_\alpha} &= f \frac{m}{kT} c_\alpha \\ \frac{\partial f}{\partial T} &= - f \left\{ \frac{\partial}{\partial T} - \frac{m}{2kT^2} \underline{c}^2 \right\} \end{aligned} \quad (7.9)$$

The terms independent of  $\eta$  coming from the first term of (7.1) need a little care to derive. They must be contained in the term

$$\frac{\partial f}{\partial t} = \frac{\partial n}{\partial t} \frac{\partial f}{\partial n} + \frac{\partial u_\alpha}{\partial t} \frac{\partial f}{\partial u_\alpha} + \frac{\partial T}{\partial t} \frac{\partial f}{\partial T} \quad (7.10)$$

and now we can substitute for  $\frac{\partial n}{\partial t}$ ,  $\frac{\partial u_\alpha}{\partial t}$  and  $\frac{\partial T}{\partial t}$  from (2.11), (2.15)

and (2.13). When we do so, however, we must remember that in the spirit of this approach some terms of these equations are of higher order in  $\eta$ . Thus the pressure tensor in (2.15) and (2.18) and the heat flux vector in (2.18) are given to zero order in  $\eta$  by (4.25)

and (4.26). Thus to determine  $\frac{\partial n}{\partial t}$ ,  $\frac{\partial u_\alpha}{\partial t}$  and  $\frac{\partial T}{\partial t}$  to zero order

in  $\eta$  we use

$$\frac{\partial n}{\partial t} + \nabla \cdot (n \underline{u}) = 0$$

$$\frac{\partial u_\alpha}{\partial t} + (\underline{u} \cdot \nabla) u_\alpha = -\frac{1}{\rho} \nabla_\alpha p + X_\alpha \quad (7.11)$$

$$\frac{3}{2} n k \frac{\partial T}{\partial t} + \frac{3}{2} n k \underline{u} \cdot \nabla T = -p \nabla \cdot \underline{u}$$

Substituting into (7.10) using (7.9) and adding to (7.8) it is found that many terms cancel and after some tedious algebra we obtain as an equation for  $\varphi$

$$\begin{aligned} f(\underline{v}) \{ 2[w_\alpha w_\beta - \frac{1}{3} \underline{w}^2 \delta_{\alpha\beta}] \nabla_\alpha u_\beta - (\frac{5}{2} - \underline{w}^2) \underline{c} \cdot \nabla \log T \} \\ = \int d\underline{s} \, d\underline{e} \, b \, d\underline{b} \, g \, f(\underline{v}) \, f(\underline{s}) \, [\varphi(\underline{v}') + \varphi(\underline{s}') - \varphi(\underline{v}) - \varphi(\underline{s})] \end{aligned} \quad (7.12)$$

Here  $\underline{w}$  is the random velocity expressed in dimensionless form by

$$\underline{w} = \underline{c} \sqrt{\frac{m}{2kT}} \quad (7.13)$$

Similarly by considering the terms of order  $\eta$  in (7.1) we could derive an equation for the next correction term to the distribution function. But this would be extremely tedious so we shall not do it. These higher terms have been considered by Burnett and are also discussed by Chapman and Cowling. They give contributions to the distribution function proportional to the second differentials of the temperature or the drift velocity and to products of the first differentials. Hence provided all gradients are small it is reasonable to neglect these higher terms. Effects corresponding to these higher terms should be observable in the structure of strong shocks but experiments have so far failed to detect them.

Now let us discuss the solution of (7.12). First of all it is convenient to introduce a notation to stand for the tensor which appears on the left hand side of (7.12). Let

$$(\underline{w}^O w)_{\alpha\beta} = w_\alpha w_\beta - \frac{1}{3} \underline{w}^2 \delta_{\alpha\beta} \quad (7.14)$$

Because (7.12) is linear in  $\varphi$  it follows that the solution is of the form

$$\varphi(\underline{v}) = -B_{\alpha\beta} \nabla_\alpha u_\beta - A_\alpha \nabla_\alpha \log T. \quad (7.15)$$

Where the tensor  $\underline{\underline{B}}$  satisfies the equation

$$-2 f(\underline{v}) \underline{w^0 w} = \int d\underline{s} d\underline{a} b d\underline{b} g f(\underline{v}) f(\underline{s}) [\underline{B}(\underline{v}') + \underline{B}(\underline{s}') - \underline{B}(\underline{v}) - \underline{B}(\underline{s})] \quad (7.16)$$

and the vector  $\underline{A}$  satisfies

$$f(\underline{v}) \left( \frac{5}{2} - \underline{w}^2 \right) \underline{c} = \int d\underline{s} d\underline{a} b d\underline{b} g f(\underline{v}) f(\underline{s}) [\underline{A}(\underline{v}') + \underline{A}(\underline{s}') - \underline{A}(\underline{v}) - \underline{A}(\underline{s})] \quad (7.17)$$

From the form of these equations it is clear that the tensor  $\underline{\underline{B}}$  is of the form

$$\underline{\underline{B}} = \underline{w^0 w} \beta(\underline{w}^2) \quad (7.18)$$

where  $\beta(\underline{w}^2)$  is some scalar function of the magnitude  $\underline{w}^2$ . Similarly it is clear that

$$\underline{A} = \underline{w} \mathfrak{A}(\underline{w}^2) \quad (7.19)$$

where  $\mathfrak{A}(\underline{w}^2)$  is a scalar function of the magnitude  $\underline{w}^2$ .

The problem has now reduced to solving for these scalar quantities  $\beta$  and  $\mathfrak{A}$ . Besides being solutions of (7.16) and (7.17)  $\underline{A}$  and  $\underline{\underline{B}}$  must be such that

$$\underline{\underline{c}} = 0$$

i.e. that

$$\frac{1}{n} \int d\underline{v} f(\underline{v}) \{1 + \varphi(\underline{v})\} \underline{c} = 0. \quad (7.20)$$

Substituting for  $\varphi(\underline{v})$  from (7.15) and for  $\underline{A}$  and  $\underline{\underline{B}}$  from (7.19) and (7.18) this becomes

$$\frac{1}{\pi^2} \int d\underline{w} e^{-\underline{w}^2} \underline{w}^2 \mathfrak{A}(\underline{w}^2) = 0, \quad (7.21)$$

i.e. there is no condition imposed on  $\beta(\underline{w}^2)$ .

We now have an exact solution for  $\varphi(\underline{v})$  if we can find  $\mathfrak{A}$  and  $\beta$  exactly. One reasonable method of proceeding would be to take power series in  $\underline{w}^2$  with undetermined coefficients for  $\mathfrak{A}$  and  $\beta$ , i.e. to take

$$\mathfrak{A} = c_0 + c_1 \underline{w}^2 + c_2 \underline{w}^4 + \dots$$

However, it turns out to be much more convenient to rearrange the terms of this expansion and redefine coefficients so that we can write,

38.

$$\begin{aligned} \beta &= a_0 + a_1 \left( \frac{5}{2} - w^2 \right) + a_2 \left( \frac{35}{8} - \frac{7}{2} w^2 + \frac{1}{2} w^4 \right) + \dots \\ &= \sum_{m=0}^{\infty} a_m S_{\frac{5}{2}}^m(w^2) \end{aligned} \quad (7.22)$$

where  $S_n^m(w^2)$  is called a Sonine polynomial defined by

$$S_n^m(w^2) = \sum_j \frac{(-1)^j (m+n)!}{(n+j)! (m-j)! j!} w^{2j} \quad (7.23)$$

Here if  $n$  is a half integer

$$n! = n(n-1)(n-2) \dots \frac{5}{2} \frac{3}{2} \frac{\sqrt{\pi}}{2}. \quad (7.24)$$

We have written out the first three terms of (7.22) and we see that this expansion is essentially like a power series expression but it is in an extremely convenient form because it can be shown that Sonine polynomials satisfy the orthogonality formula

$$\int_0^{\infty} dy y^{2n+1} e^{-y^2} S_n^m(y^2) S_n^m(y^2) = \frac{1}{2} \frac{(n+m)!}{m!} \delta_{m,m'} \quad (7.25)$$

and this orthogonality property simplifies the calculations enormously. In (7.22) we made the special choice of  $n = \frac{5}{2}$  for this will turn out to be most convenient. For  $\beta$  it turns out to be more convenient to choose  $n = \frac{5}{2}$  so we write

$$\begin{aligned} \beta &= b_0 + b_1 \left( \frac{7}{2} - w^2 \right) + \dots \\ &= \sum_{m=0}^{\infty} b_m S_{\frac{7}{2}}^m(w^2) \end{aligned} \quad (7.26)$$

To obtain a complete solution to the problem we need to know all the coefficients  $a_m$  and  $b_m$ . But before we describe how to determine these coefficients let us see how the pressure tensor and the heat flux vector are related to them and what the condition (7.2) is.

Substituting (7.22) into (7.21) gives

$$\sum_m a_m \frac{1}{\pi^2} \int dw e^{-w^2} w^2 S_{\frac{5}{2}}^m(w^2) = 0.$$

Performing the integrations over angles and remembering that  $S_{\frac{3}{2}}^0 = 1$  this becomes

$$\sum_m a^m \frac{4\pi}{\pi^{\frac{3}{2}}} \int_0^\infty dw w^4 e^{-w^2} S_{\frac{3}{2}}^0(w^2) S_{\frac{3}{2}}^m(w^2) = 0.$$

But this integral is of precisely the form (7.25) and hence this condition becomes

$$a^{(0)} = 0, \quad (7.27)$$

which is a very simple condition. It is simple because we are using these Sonine polynomials with their useful orthogonality properties.

The heat flux vector is defined by (2.8). Substituting for  $F$  from (7.2), for  $\varphi$  from (7.15) and for  $\underline{A}$  and  $\underline{B}$  from (7.19) and (7.18) this becomes

$$q_Y = \int d\underline{v} f \{1 - \nabla_\alpha u_\beta \frac{w_\alpha w_\beta}{w^2} \beta(w^2) - \frac{1}{T} \nabla_\alpha T w_\alpha \beta(w^2)\} \frac{1}{2} mc^2 c_Y. \quad (7.28)$$

The term in  $\beta$  certainly vanishes because it is odd in the random velocity  $\underline{c}$ . Substituting for  $\beta$  from (7.22) using (7.13) and remembering (7.27), the other term becomes

$$q_Y = -\frac{1}{T} \nabla_\alpha T \cdot n k T \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \sum_{m=1}^\infty a^m \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} e^{-w^2} w^2 w_\alpha w_Y S_{\frac{3}{2}}^m(w^2) \quad (7.29)$$

The integral is zero unless  $\alpha = Y$  and we may replace  $w_Y^2$  by  $\frac{1}{3} w^2$  to give

$$q_Y = -\nabla_Y T n k \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \sum_{m=1}^\infty a^m \frac{4\pi}{3\pi^{\frac{3}{2}}} \int_0^\infty dw w^6 e^{-w^2} S_{\frac{3}{2}}^m(w^2). \quad (7.30)$$

Since

$$\frac{5}{2} S_{\frac{3}{2}}^0(w^2) - S_{\frac{3}{2}}^1(w^2) = w^2$$

the final integral can be rewritten as

$$\begin{aligned} & \int_0^\infty dw w^4 \left[ \frac{5}{2} S_{\frac{3}{2}}^0(w^2) - S_{\frac{3}{2}}^1(w^2) \right] S_{\frac{3}{2}}^m(w^2) e^{-w^2} \\ &= \frac{15\sqrt{\pi}}{16} \{\delta_{m,0} - \delta_{m,1}\}. \end{aligned}$$

Hence (7.30) becomes

$$q_Y = \frac{5}{4} n k \left(\frac{2kT}{m}\right)^{\frac{1}{2}} a^1 \nabla_Y T. \quad (7.31)$$

If we define the coefficient of thermal conduction,  $\lambda$ , by

$$\underline{q} = - \lambda \underline{\nabla} T \quad (7.32)$$

then

$$\lambda = - \frac{5}{4} nk \left( \frac{2kT}{m} \right)^{\frac{1}{2}} a^1. \quad (7.33)$$

The important point to notice about these equations (7.31) and (7.33) is that they involve only the coefficient  $a^1$ . Thus although we need all the coefficients  $a^m$ ,  $b^m$  to give the distribution function we only need the coefficient  $a^1$  to give the thermal conductivity.

Now consider the pressure tensor defined by (2.6). Substituting for  $F$  from (7.2), for  $\phi$  from (7.15) and for  $\underline{B}$  and  $\underline{A}$  from (7.18) and (7.19) we find

$$p_{\alpha\beta} = m \int d\underline{v} c_\alpha c_\beta f \{ 1 - \nabla_\gamma u_\epsilon \frac{w_\alpha w_\beta}{\gamma \epsilon} \beta(w^2) - \frac{1}{T} \nabla_\gamma T w_\gamma \beta(w^2) \} \quad (7.34)$$

The term involving  $\underline{A}$  vanishes because it is odd in the random velocities. The first term is zero unless  $\alpha = \beta$  and is

$$\begin{aligned} \delta_{\alpha\beta} n m \left( \frac{2kT}{m} \right) \frac{1}{3} \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} w^2 e^{-w^2} \\ = \delta_{\alpha\beta} n kT = \alpha\beta p. \end{aligned} \quad (7.35)$$

The second term is

$$- n m \left( \frac{2kT}{m} \right) \nabla_\gamma u_\epsilon \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} e^{-w^2} w_\alpha w_\beta \{ w_\gamma w_\epsilon - \frac{1}{3} w^2 S_{\gamma\epsilon} \} \beta(w^2) \quad (7.36)$$

which has to be considered rather carefully. If  $\alpha \neq \beta$  then the second term in the bracket contributes nothing and the first term contributes only if  $\gamma = \alpha$  and  $\epsilon = \beta$  or if  $\gamma = \beta$  and  $\epsilon = \alpha$ . If  $\alpha \neq \beta$  therefore (7.36) is

$$\begin{aligned} - n 2 kT (\nabla_\alpha u_\beta + \nabla_\beta u_\alpha) \int d\underline{w} e^{-w^2} w_\alpha^2 w_\beta^2 \beta(w^2) \\ = - \frac{1}{2} n kT (\nabla_\alpha u_\beta + \nabla_\beta u_\alpha) b^0. \end{aligned} \quad (7.37)$$

If  $\alpha = \beta$  then the second term in the bracket of (7.36) gives

$$\begin{aligned} 2 n kT (\nabla \cdot \underline{u}) \frac{1}{9} \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} e^{-w^2} w^4 \beta(\underline{w}^2) \\ = \frac{5}{6} n kT (\nabla \cdot \underline{u}) b^0 \end{aligned} \quad (7.38)$$

while the first term in the bracket gives

$$\begin{aligned} - 2 n kT \nabla_{\alpha} u_{\alpha} \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} e^{-w^2} w_{\alpha}^4 \beta(\underline{w}^2) \\ - 2 n kT \sum_{(\gamma \neq \alpha)} (\nabla_{\gamma} u_{\gamma}) \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} e^{-w^2} w_{\alpha}^2 w_{\gamma}^2 \beta(\underline{w}^2) \\ = - \frac{3}{2} n kT b^0 \nabla_{\alpha} u_{\alpha} - \frac{1}{2} n kT b^0 \sum_{(\gamma \neq \alpha)} \nabla_{\gamma} u_{\gamma} \\ = - \frac{1}{2} n kT b^0 \nabla \cdot \underline{u} - n kT b^0 \nabla_{\alpha} u_{\alpha}. \end{aligned} \quad (7.39)$$

Collecting together all these results we find that if

$$\text{if } \alpha \neq \beta, \quad p_{\alpha\beta} = - \frac{1}{2} n kT b^0 (\nabla_{\alpha} u_{\beta} + \nabla_{\beta} u_{\alpha}) \quad (7.40)$$

$$\text{if } \alpha = \beta, \quad p_{\alpha\alpha} = n kT + \frac{1}{3} n kT b^0 (\nabla \cdot \underline{u}) - n kT b^0 \nabla_{\alpha} u_{\alpha}$$

i.e. in general

$$p_{\alpha\beta} = \left\{ p + \frac{2}{3} \mu (\nabla \cdot \underline{u}) \right\} \delta_{\alpha\beta} - \mu (\nabla_{\alpha} u_{\beta} + \nabla_{\beta} u_{\alpha}) \quad (7.41)$$

where

$$\mu = \frac{1}{2} n kT b^0 \quad (7.42)$$

is the coefficient of viscosity. Notice that we need only the coefficient  $b^0$  to calculate the coefficient of viscosity. So we see that really we are only interested in calculating the two coefficients  $a^1$  and  $b^0$ .

Finally, to complete this section, we shall describe the formal variation procedure used by Hirschfelder et al which in principle could give all the coefficients  $a^m$ ,  $b^m$  and which in practise gives excellent approximations to  $b^0$  and  $a^1$  the only coefficients we really want.

If  $G$  and  $H$  are any properties of the particles define

$$G : H = \sum_{\alpha} G_{\alpha} H_{\alpha} = \underline{G} \cdot \underline{H} \quad \text{if } \underline{G} \text{ and } \underline{H} \text{ are both vectors} \quad (7.43)$$

$$\sum_{\alpha, \beta} G_{\alpha\beta} H_{\beta\alpha} = G_{\alpha\beta} H_{\beta\alpha} \quad \text{if } \underline{G} \text{ and } \underline{H} \text{ are both tensors.}$$

Now define what we shall call "collision integrals" as

$$[G, H] = - \frac{1}{n^2} \int d\underline{v} d\underline{s} d\epsilon b db g f(\underline{v}) f(\underline{s}) G(\underline{v}) : [H(\underline{v}') + H(\underline{s}') - H(\underline{v}) - H(\underline{s})] \quad (7.44)$$

By symmetry this is also

$$[G, H] = - \frac{1}{2n^2} \int d\underline{v} d\underline{s} d\epsilon b db g f(\underline{v}) f(\underline{s}) [G(\underline{v}) + G(\underline{s})] : [H(\underline{v}') + H(\underline{s}') - H(\underline{v}) - H(\underline{s})] \quad (7.45)$$

or

$$[G, H] = \frac{1}{4n^2} \int d\underline{v} d\underline{s} d\epsilon b db g f(\underline{v}) f(\underline{s}) [G(\underline{v}') + G(\underline{s}') - G(\underline{v}) - G(\underline{s})] : [H(\underline{v}') + H(\underline{s}') - H(\underline{v}) - H(\underline{s})] \quad (7.46)$$

Notice from this last form that

$$[G, G] \geq 0. \quad (7.47)$$

Now the equations we have to solve, (7.16) and (7.17) are of the form

$$R(\underline{v}) = \int d\underline{s} d\epsilon b db g f(\underline{v}) f(\underline{s}) [T(\underline{v}') + T(\underline{s}') - T(\underline{v}) - T(\underline{s})] \quad (7.48)$$

where  $R$  and  $T$  are either vectors or tensors,  $R$  is known and  $T$  is to be found. Let  $t(\underline{v})$  be any trial solution of this equation subject only to the condition that

$$\int d\underline{v} t(\underline{v}) : R(\underline{v}) = \int d\underline{s} d\underline{v} d\epsilon b db g f(\underline{v}) f(\underline{s}) t(\underline{v}) : [t(\underline{v}') + t(\underline{s}') - t(\underline{v}) - t(\underline{s})] \\ = - n^2 [t, t]. \quad (7.49)$$

But from (7.48)

$$\int d\underline{v} t(\underline{v}) : R(\underline{v}) = - n^2 [t, T]. \quad (7.50)$$

so provided  $t$  is chosen to satisfy (7.49)

$$[t, t] = [t, T]. \quad (7.51)$$

Now consider

$$[t-T, t-T] = [t, t] - 2[t, T] + [T, T]. \quad (7.52)$$

By (7.47) this is positive or zero, hence using (7.51)

$$[t, t] < [T, T] \quad (7.53)$$

or using (7.49)

$$-\frac{1}{n^2} \int d\underline{y} \, t(\underline{y}): R(\underline{y}) = [t, t] < [T, T]. \quad (7.54)$$

This is the relation upon which the variation procedure is based. We first choose a trial function with as many undetermined parameters as is convenient. In our case we take the trial functions to be

$$\underline{A} = \underline{w} \, \mathcal{A}(w^2) = \underline{w} \sum_{m=1}^{\infty} a^m S_{\frac{9}{2}}^m(w^2) \quad (7.55)$$

or

$$\underline{B} = \underline{w^0 w} \, \mathcal{B}(w^2) = \underline{w^0 w} \sum_{m=0} b^m S_{\frac{5}{2}}^m(w^2) \quad (7.56)$$

depending upon whether we are considering (7.17) or (7.16) respectively. We then take all but a few of the coefficients  $a^m, b^m$  to be zero. For example in (7.55) the first trial function is obtained by putting all the coefficients  $a^m$  equal to zero except  $a^1$ . A second trial function giving a better result is obtained by putting all except  $a^1$  and  $a^2$  equal to zero. The third trial function takes  $a^1, a^2$  and  $a^3$  to be non-zero etc. Having picked our trial function we then ensure that the coefficients are such that the equation in (7.54) is satisfied and then we maximise either the left or right hand side of this equation. Those values of the coefficients which give the maximum value give the best approximation to the correct answer. As we shall see in the next section when we apply this variation method, this procedure gives excellent values for  $a^1$  and  $b^0$  very rapidly.

## 8. RESULTS

In this section we shall apply the variation method to the equations and finally obtain the coefficients of viscosity and thermal conduction.

Considering (7.13) first we see, comparing this equation to the general form (7.48), that in this case

$$R(\underline{y}) = -2 f(\underline{y}) \frac{w^0}{w} \quad (8.1)$$

Hence using (7.50) for  $t(\underline{y})$  we get the left hand side of (7.54) to be

$$\begin{aligned} -\frac{1}{n^2} \int d\underline{y} \, t(\underline{y}) : R(\underline{y}) &= \frac{2}{n^2} \sum_{m=0}^{\infty} b^m \int d\underline{y} \, f(\underline{y}) \frac{w^0}{w} : \frac{w^0}{w} S_{\frac{5}{2}}^m(w^2) \\ &= \frac{2}{n} \sum_m b^m \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} \left\{ w_{\alpha\beta} w_{\beta} - \frac{1}{3} w^2 \delta_{\alpha\beta} \right\} \left\{ w_{\alpha\beta} w_{\beta} - \frac{1}{3} w^2 \delta_{\alpha\beta} \right\} S_{\frac{5}{2}}^m(w^2) \\ &= \frac{4}{3n} \sum_m b^m \frac{1}{\pi^{\frac{3}{2}}} \int d\underline{w} \, w^4 S_{\frac{5}{2}}^m(w^2) \\ &= \frac{5b^0}{n} \end{aligned} \quad (8.2)$$

Hence (7.54) is

$$\frac{5b^0}{n} \sum_{mm'} b^m b^{m'} \left[ \frac{w^0}{w} S_{\frac{3}{2}}^m(w^2), \frac{w^0}{w} S_{\frac{3}{2}}^{m'}(w^2) \right] < [T, T] \quad (8.3)$$

The variational problem is now easy because of the very simple form of the left hand side of (8.3). We must simply look for the largest value of  $b^0$  which the equation (8.3) will allow. The simple form of the left hand side of (8.3) is another consequence of the use of Sonine polynomials. From the general theory of variational methods we can expect to get good values for  $b^0$  with quite poor trial functions, i.e. with only a few non-zero coefficients. But we see from (7.42) that  $u$  is directly related to  $b^0$  so we can expect to get very good values for  $u$  very rapidly. We shall give a numerical illustrations of this presently.

By taking more and more non-zero coefficients we can get successive approximations to  $b^0$  which we shall write as

$$[b^0]_1, [b^0]_2, [b^0]_3 \dots \text{etc.}$$

the corresponding successive approximations to  $u$  we write as

$$[u]_1, [u]_2, [u]_3 \dots \text{etc.}$$

Each time we improve the trial function we will get a bigger value for  $b_0$  hence

$$[b^0]_1 < [b^0]_2 < [b^0]_3 < \dots \text{etc.}$$

and correspondingly

$$[u]_1 < [u]_2 < [u]_3 < \dots \text{etc.} \quad (8.4)$$

The first trial function is obtained by setting all the coefficients except  $b^0$  equal to zero. (8.3) then becomes

$$\frac{5b^0}{n} = (b^0)^2 [\underline{w^0 w}, \underline{w^0 w}] < [T.T] \quad (8.5)$$

This is particularly easy to maximise for it only has two solutions

$$b^0 = 0 \text{ or } b^0 = \frac{5}{n} [\underline{w^0 w}, \underline{w^0 w}]^{-1} \quad (8.6)$$

The second solution is positive by (7.47) and therefore is the one which maximises (8.5). From (7.42) the corresponding value of  $u$  is

$$[u]_1 = \frac{5}{2} kT [\underline{w^0 w}, \underline{w^0 w}]^{-1} \quad (8.7)$$

The evaluation of collision integrals like that appearing in (8.7) is discussed in the Appendix to PART II. There is shown that

$$[\underline{w^0 w}, \underline{w^0 w}] = \frac{2 \sqrt{\pi} e^4 \psi}{\sqrt{m} (kT)^{\frac{3}{2}}} \quad (8.8)$$

where  $m$  is the mass of the particle,  $e$  the charge and  $\psi$  is given by

$$\psi = \log \left[ 1 + \left\{ \frac{4kTd}{e^2} \right\}^2 \right] \quad (8.9)$$

and  $d$  is the Debye cut-off distance mentioned in §1,

$$d = \left\{ \frac{kT}{4\pi e^2 n} \right\}^{\frac{1}{2}} \quad (8.10)$$

Because  $d$  only enters through this logarithmic factor (8.9) is insensitive to the precise value of  $d$  and so there is only a few per cent possible uncertainty about the value of these collision integrals.

From (8.8) and (8.7) we find

$$[\mu]_1 = \frac{5}{4\sqrt{\pi}} \frac{\sqrt{m} (kT)^{\frac{5}{2}}}{e^2 \psi} \quad (8.11)$$

[There is an error of a factor of 2 in the formula quoted by Chapman and Cowling].

The numerical value of this is given for a gas of positive ions by the table at the end of PART II. We see that (8.11) has the same qualitative form as was given by the mean free path theory.

Now let us consider the next approximation to  $\mu$  so that we can get an idea of how accurate we may expect (8.11) to be. The second approximation is obtained by setting all the coefficients except  $b^0$  and  $b^1$  equal to zero in the trial function. Then (8.3) becomes

$$\begin{aligned} \frac{5b^0}{n} = & (b^0)^2 \left[ \underline{\underline{w^0 w}}, \underline{\underline{w^0 w}} \right] + 2b^0 b^1 \left[ \underline{\underline{w^0 w}}, \underline{\underline{w^0 w}} S_{\frac{5}{2}}^1(w^2) \right] \\ & + (b^1)^2 \left[ \underline{\underline{w^0 w}} S_{\frac{5}{2}}^1(w^2), \underline{\underline{w^0 w}} S_{\frac{5}{2}}^1(w^2) \right] \end{aligned} \quad (8.12)$$

and the maximum value of  $b^0$  allowed is that for which (8.12) still has a real solution for  $b^1$ . This maximum value of  $b^0$  is therefore obtained by setting the discriminant of (8.12) regarded as an equation for  $b^1$  equal to

zero. This gives

$$[b^0]_2 = \frac{\varepsilon}{n} [\underline{w}^0, \underline{w}^0]^{-1} \left\{ 1 - \frac{[\underline{w}^0, \underline{w}^0] S_{\frac{5}{2}}^1]^2}{[\underline{w}^0, \underline{w}^0] [\underline{w}^0, \underline{w}^0] S_{\frac{5}{2}}^1, \underline{w}^0 S_{\frac{5}{2}}^1} \right\}^{-1} \quad (8.13)$$

Evaluating the collision integrals from the Appendix this becomes

$$[b^0]_2 = [b^0]_1 \cdot 1.025 \quad (8.14)$$

Hence

$$[\mu]_2 = [\mu]_1 \cdot 1.025 \quad (8.15)$$

So this second approximation only gives a 2.5% correction to the first approximation. We may therefore be confident that the true value of  $\mu$  differs from (8.15) by at most a few per cent. But this is of the same order of magnitude as the uncertainty in the values of the collision integrals due to the uncertainty in the precise value to be used for the cut-off distance  $d$  so there is no point in improving this value for  $\mu$  further by taking higher approximations.

Now consider the thermal conductivity equation (7.17). Comparing to the general form (7.48) we see that in this case

$$R(\underline{v}) = \left(\frac{5}{2} - \underline{v}^2\right) \underline{c} = S_{\frac{3}{2}}^1(\underline{v}^2) \underline{c} \quad (8.16)$$

Using (7.55) as  $t$  we find

$$\begin{aligned} \frac{-1}{n^2} \int d\underline{v} \, t : R &= \frac{-1}{n^2} \sum_{m=1}^{\infty} a^m \int d\underline{v} \, f(\underline{v}) S_{\frac{3}{2}}^1(\underline{v}^2) \underline{c} \cdot \underline{w} S_{\frac{3}{2}}^m(\underline{v}^2) \\ &= \frac{-15}{4n} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} a^1 \end{aligned} \quad (8.17)$$

so (7.54) becomes

$$\frac{-15}{4n} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} a^1 = \sum_{m, m'} a^m a^{m'} [\underline{w} S_{\frac{3}{2}}^m, \underline{w} S_{\frac{3}{2}}^{m'}] < [T, T] \quad (8.18)$$

Once again we see that the variation method is very simple and consists of looking for the most negative value of  $a^1$  possible. We can expect to get good values for this coefficient with quite poor trial functions and from (7.33) this corresponds to getting excellent values for the coefficient of thermal conduction  $\lambda$ . A relation similar to (8.4) holds for  $\lambda$  too, namely

$$[\lambda]_1 < [\lambda]_2 < [\lambda]_3 < \dots \quad (8.19)$$

The first trial function is obtained by setting all the coefficients except  $a^1$  equal to zero. (8.18) then becomes

$$\frac{-15}{4n} \left( \frac{2kT}{m} \right)^{\frac{1}{2}} a^1 = \{a^1\}^2 \left[ \underline{w} S_{\frac{3}{2}}^1, \underline{w} S_{\frac{3}{2}}^1 \right] \quad (8.20)$$

which has only two solutions

$$a^1 = 0 \quad \text{or} \quad a^1 = \frac{-15}{4n} \left( \frac{2kT}{m} \right)^{\frac{1}{2}} \left[ \underline{w} S_{\frac{3}{2}}^1, \underline{w} S_{\frac{3}{2}}^1 \right]^{-1} \quad (8.21)$$

It is the second solution which maximises (8.20). The corresponding value of the thermal conductivity is

$$[\lambda]_1 = \frac{75k}{16} \frac{2kT}{m} \left[ \underline{w} S_{\frac{3}{2}}^1, \underline{w} S_{\frac{3}{2}}^1 \right]^{-1} \quad (8.22)$$

The collision integral, evaluated in the Appendix to PART II, is precisely the same as (8.8). Hence

$$[\lambda]_1 = \frac{75}{16\sqrt{\pi}} \frac{k (kT)^{\frac{5}{2}}}{\sqrt{m} \psi e^4} \quad (8.23)$$

The second approximation is obtained by setting all the coefficients except  $a^1$  and  $a^2$  equal to zero. Then (8.18) becomes

$$\frac{-15}{4n} \left( \frac{2kT}{m} \right)^{\frac{1}{2}} a^1 = \{a^1\}^2 \left[ \underline{w} S_{\frac{3}{2}}^1, \underline{w} S_{\frac{3}{2}}^1 \right] + 2 a^1 a^2 \left[ \underline{w} S_{\frac{3}{2}}^1, \underline{w} S_{\frac{3}{2}}^2 \right] \quad (8.24)$$

$$+ \{a^2\}^2 \left[ \underline{w} S_{\frac{3}{2}}^2, \underline{w} S_{\frac{3}{2}}^2 \right]$$

which by analogy to (8.12) is maximised by

$$[a^1]_2 = [a^1]_1 \left\{ 1 - \frac{[\underline{w} S_{\frac{3}{2}}^1, \underline{w} S_{\frac{3}{2}}^2]^2}{[\underline{w} S_{\frac{3}{2}}^1, \underline{w} S_{\frac{3}{2}}^1] [\underline{w} S_{\frac{3}{2}}^2, \underline{w} S_{\frac{3}{2}}^2]} \right\} \quad (8.25)$$

Evaluating the collision integrals from the Appendix this is

$$[a^1]_2 = [a^1]_1 \cdot 1.08 \quad (8.26)$$

and so

$$[\lambda]_2 = [\lambda]_1 \cdot 1.08 \quad (8.27)$$

Hence the second approximation gives an 8% correction this time whereas for the viscosity it gave only a 2.5% correction. Nevertheless the correction is so small that there is no need to go to further approximations and we may be confident that (8.27) is correct to a few per cent error at most.

Notice that

$$\frac{[\lambda]_1}{[u]_1} = \frac{15k}{4m} \quad (8.28)$$

This is a well known result. It is only correct in the first approximation, however.

There is an error of a factor of 2 in Chapman and Cowling's formulae  $[u]_1$  and  $[\lambda]_1$  for this case. This error has been reproduced in a previous report (Marshall. The Structure of Magnetohydrodynamic Shocks)(3).

## 89. THE PHYSICAL SIGNIFICANCE OF THE VARIATION PROCEDURE

It has been pointed out by Zimon<sup>(4)</sup> that the variation procedure which we have just described, has the simple physical interpretation that it corresponds to maximising the rate of production of entropy for given temperature and velocity gradients. This may be seen as follows.

If  $\delta W$  and  $\delta E = c_v dT$  are increments of heat added to the gas and of internal energy respectively then

$$\delta W = \delta E + p \delta \left( \frac{1}{\rho} \right) \quad (9.1)$$

$$\text{i.e.} \quad \frac{DW}{Dt} = c_v \frac{DT}{Dt} - \frac{p}{\rho^2} \frac{D\rho}{Dt} \quad (9.2)$$

This is the rate of heat added per unit mass. The rate of entropy production per unit volume is

$$\frac{DS}{Dt} = \frac{\rho}{T} \frac{DW}{Dt} = \frac{3k}{2m} \frac{\rho}{T} \frac{DT}{Dt} - \frac{p}{\rho T} \frac{D\rho}{Dt} \quad (9.3)$$

Substituting from (2.13) and (2.18) we find, assuming  $\overline{\underline{c} \cdot \underline{X}}$  to be zero,

$$\frac{DS}{Dt} = -\frac{1}{T} \underline{\nabla} \cdot \underline{q} - \frac{1}{T} p_{\alpha\beta} \nabla_{\alpha} u_{\beta} + \frac{p}{T} \underline{\nabla} \cdot \underline{u} \quad (9.4)$$

Using (7.32) for  $\underline{q}$  and (7.41) for  $p_{\alpha\beta}$  gives

$$\begin{aligned} \frac{DS}{Dt} &= \frac{1}{T} \underline{\nabla} \cdot \lambda \underline{\nabla} T - \frac{2}{3} \frac{\underline{u}}{T} (\underline{\nabla} \cdot \underline{u})^2 + \frac{\underline{u}}{2T} (\nabla_{\alpha} u_{\beta} + \nabla_{\beta} u_{\alpha}) (\nabla_{\alpha} u_{\beta} + \nabla_{\beta} u_{\alpha}) \\ &= \underline{\nabla} \cdot \frac{\lambda}{T} \underline{\nabla} T + \frac{\lambda}{T^2} (\underline{\nabla} T)^2 + \frac{4}{3} \frac{\underline{u}}{T} (\underline{\nabla} \cdot \underline{u})^2 \\ &\quad + \frac{\underline{u}}{T} \sum_{\alpha < \beta} (\nabla_{\alpha} u_{\beta} + \nabla_{\beta} u_{\alpha})^2 \end{aligned} \quad (9.5)$$

The first term of (9.5) gives zero when integrated over space. The other terms are all positive definite and proportional to  $\lambda$  or  $\underline{u}$ .

Now in §8 we saw that the variation principle essentially maximised  $\lambda$  and  $u$ . Hence it corresponds exactly to maximising the rate of production of entropy for given temperature and velocity gradients. Alternatively we can say the method corresponds to minimising the entropy for given heat flux and pressure tensor. This result is closely connected with a theorem of Prigogine's.

#### REFERENCES

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- (2) J. O. Hirshfelder, C. F. Curtiss and R. B. Bird  
"The Molecular Theory of Gases and Liquids" Chapters VII and VIII, John Wiley and Sons: Chapman and Hall Ltd., London.
- (3) W. Marshall, "The Structure of Magnetohydrodynamic Shocks"  
A.E.R.E. T/R 1718.
- (4) J. M. Zimon. The General Variational Principle of Transport Theory. Canadian Journal of Physics 34, 1256, 1264, 1956.

## NOTATION

### Mathematical

Vectors are indicated by an underlining, thus  $\underline{r}$  is a vector of magnitude  $r$ .

Tensors are indicated by a double underlining, thus  $\underline{\underline{p}}$ .

The components of vectors and tensors are indicated by Greek subscript  $\alpha, \beta, \gamma, \epsilon, \varphi \dots$ , thus  $r_\alpha$  stands for  $x, y$  or  $z$ ;  $v_\alpha$  for  $v_x, v_y$  or  $v_z$ .

When a subscript is repeated a summation is implied. Thus a scalar product is written

$$\underline{a} \cdot \underline{b} = a_\alpha b_\alpha = a_x b_x + a_y b_y + a_z b_z$$

An element of volume in space is written as

$$d\underline{r} = dx \, dy \, dz$$

An element of volume in velocity space is

$$d\underline{v} = dv_x \, dv_y \, dv_z$$

A differentiation with respect to position is described by  $\underline{\nabla}$  where

$$\underline{\nabla} = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

A differentiation with respect to velocity is described by  $\underline{\hat{\nabla}}$  where

$$\underline{\hat{\nabla}} = \left( \frac{\partial}{\partial v_x}, \frac{\partial}{\partial v_y}, \frac{\partial}{\partial v_z} \right)$$

$\frac{D}{Dt}$  is shorthand for  $\frac{\partial}{\partial t} + \underline{u} \cdot \underline{\nabla}$

$\delta_{\alpha\beta} = 1$  if  $\alpha = \beta$   
 $= 0$  if  $\alpha \neq \beta$  is the Kroencher- $\delta$  symbol

## Symbols

$\mathbf{r}$  position in space

$\mathbf{v}$  velocity of a particle

$t$  the time

$F(\mathbf{v}, \mathbf{r}, t)$  the distribution function

$\mathbf{X}$  the force per unit mass acting on the particles

$\Delta$  denotes rate of change due to collisions

$\Psi$  stands for any property of the particles depending in general on their velocity, position and time.

$n$  the number density of particles

$m$  the mass of each particle

$\rho = n m$ , the density

$\bar{\Psi} = \frac{1}{n} \int d\mathbf{v} \Psi F$  denotes the mean value of  $\Psi$  at the point  $\mathbf{r}$  and time  $t$

$\mathbf{u} = \bar{\mathbf{v}}$  the drift velocity

$\mathbf{c} = \mathbf{v} - \mathbf{u}$  the random velocity of a particle with actual velocity  $\mathbf{v}$

$T = \frac{m}{3k} \overline{c^2}$ , the temperature

$k$  Boltzmann's constant

$p_{\alpha\beta} = \rho \overline{c_\alpha c_\beta}$  the pressure tensor

$p = nkT$  the static pressure

$\mathbf{q} = \frac{1}{2} n m \overline{c^2 \mathbf{c}}$  the heat flux vector

$\mathbf{s}$  always used to stand for the velocity of the "other particle" in a collision.

$\mathbf{v}'$  and  $\mathbf{s}'$ , the velocities of the particles after the collision

$\mathbf{c} = \frac{1}{2} (\mathbf{v} + \mathbf{s})$  the centre of gravity velocity in a collision

$\mathbf{g} = \mathbf{s} - \mathbf{v}$  the relative velocity of the particles in a collision

$b$  the asymptotic distance of approach in a collision

$\chi$  the scattering angle in a collision  
 $\epsilon$  the angle the plane of the collision makes with some fixed plane  
 $d$  the Debye cut-off distance.  $d = \left\{ \frac{kT}{4\pi e^2 n} \right\}^{\frac{1}{2}}$   
 $e$  the charge on the particles  
 $S$  the entropy of the gas  
 $V$  the potential from which  $\underline{X}$  is derived,  $\underline{X} = \underline{\nabla} V$   
 $ds$  a unit of area whose orientation is described by the vector  $\underline{ds}$  drawn normal to it  
 $\tau$  a collision time  
 $p(t)$  the probability that a particle survives making collisions for a time greater than  $t$  after making a collision  
 $\eta$  an expansion parameter in the formal theory.  $\eta = 1$   
 $f$  stands for the Maxwell distribution  
 $\underline{w} = \underline{c} \sqrt{\frac{m}{2kT}}$  a dimensionless random velocity  
 $\frac{w^0_{\alpha\beta}}{w_{\alpha\beta}} = w_{\alpha\beta} - \frac{1}{3} \underline{w}^2 \delta_{\alpha\beta}$   
 $a^m$  coefficients in the expansion of 3. Equation (7.22)  
 $b^m$  coefficients in the expansion of 6. Equation (7.23)  
 $S_n^m$  a Sonine polynomial  
 $\mu$  the coefficient of viscosity  
 $\lambda$  the coefficient of thermal conductivity  
 $G$  and  $H$  any properties of the particles  
 $[G, H]$  a "collision integral" defined by (7.44)  
 $[u]_1, [u]_2, [u]_3 \dots$  etc. denote successive approximations to  $u$ .  
 $\psi$  the logarithmic cut-off term defined by (8.9)

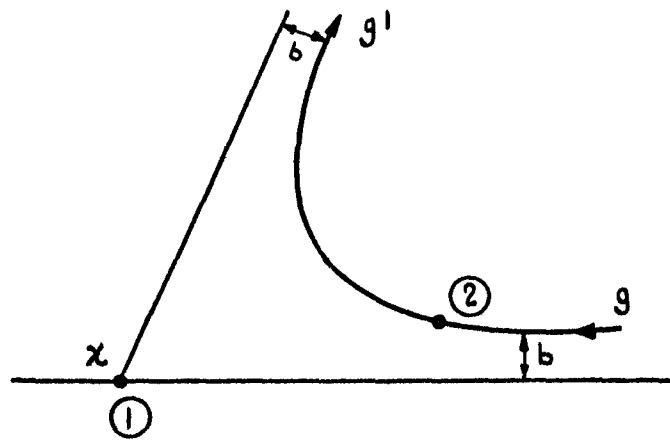


FIG. 1. THE GEOMETRY OF A COLLISION.

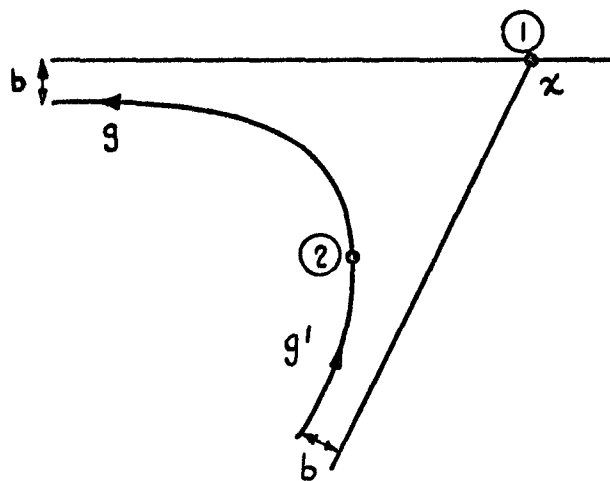


FIG. 2. THE GEOMETRY OF AN INVERSE COLLISION.

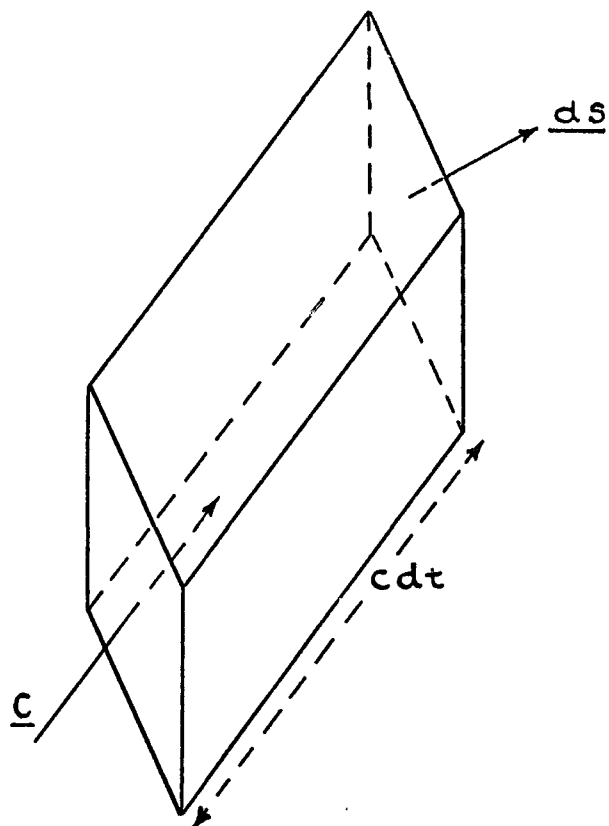


FIG. 3. THE CYLINDER CONTAINING THOSE PARTICLES WHICH CROSS  $ds$  WITH VELOCITY  $\underline{c}$  IN TIME  $dt$ .

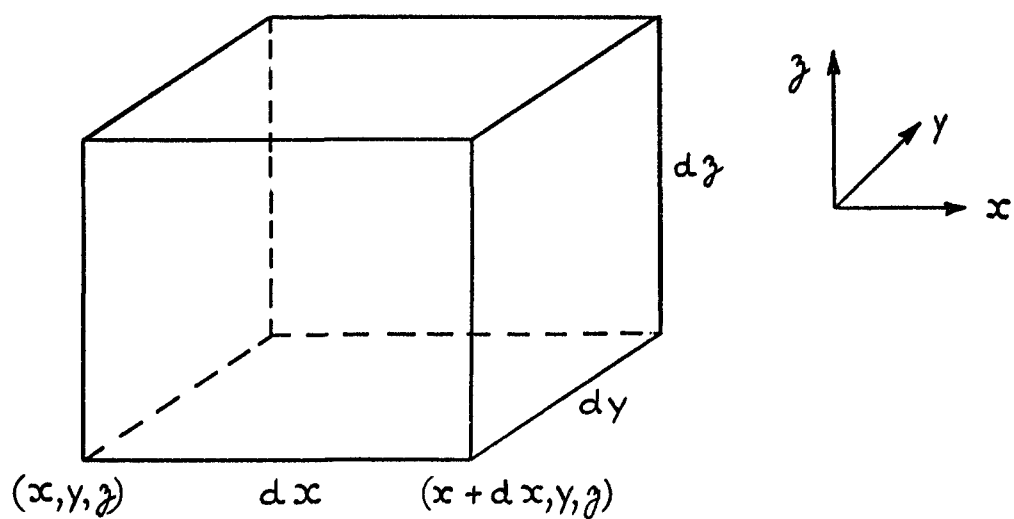


FIG. 4. A RECTANGULAR ELEMENT OF FLUID.