

On the Velocity Distribution Function, and on the Stresses in a Non-Uniform Rarefied Monatomic Gas

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PHILOSOPHICAL TRANSACTIONS.

I. On the Velocity Distribution Function, and on the Stresses in a Non-Uniform Rarefied Monatomic Gas.

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CONTENTS.

	•			rage
§ 1.	Introduction			1
§ 2.	The fundamental integral equation			3
§ 3.	Consideration of the fundamental equation	•		5
§ 4.	The rate of change of molecular properties due to collisions			7
§ 5.	The form of F_1			10
§ 6.	Determination of the functions $P_1(C^2)$ and $P_2(C^2)$			11
§ 7.	The coefficient of viscosity and heat conduction			13
§ 8.	Consideration of the second-order derivatives in the velocity distribution function			14
§ 9.	The stresses in a rarefied gas			21
§ 10.	Evaluation of $\overline{\mathrm{C}^4\mathrm{Q}_1\left(\mathrm{C}^2\right)}$ and $\overline{\mathrm{C}^4\mathrm{Q}_2\left(\mathrm{C}^2\right)}$ for particular molecular models			22
§ 11.	Expressions for the stresses in a rarefied gas for particular molecular models	~		26
§ 12.	Discussion of the results	,		30

§ 1. Introduction.

THE application of the kinetic theory to the investigation of viscosity and other physical phenomena of a gas involves, in general, the determination of the distribution of the molecular velocities in the non-uniform state. This is unnecessary in the case of one special molecular model, successfully dealt with by MAXWELL,* but for more general models his treatment is inapplicable. It was shown by Boltzmann† that the function which expresses the law of distribution of the molecular velocities must satisfy a certain integral equation, but no solution of the equation was discovered nor any further progress made until Enskog, in 1911, applied to it the method of solution by

- * Maxwell, 'Scientific Papers,' vol. 2, p. 26.
- † Boltzmann, 'Vorlesungen über Gastheorie,' I, p. 114.
- ‡ Enskog, 'Physikalische Zeitschrift,' vol. 12, р. 58, 1911.

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series, and thereby obtained the form of the function. Later the same writer,* by a more elaborate treatment of the problem, succeeded in obtaining a solution applicable to the most general molecular model of a monatomic gas, and used it to calculate the numerical values of the coefficient of viscosity, heat conduction and of diffusion.

About two years before the appearance of Enskog's later work, a paper was published by Chapman, in which he obtained the form of the velocity distribution function, partly by using the fact that it must be an invariant. The complete solution of the function was found by applying MAXWELL'S equation of transfer to certain odd and even functions of the molecular velocity. The application of the solution to the evaluation of the coefficients of viscosity, heat conduction, and so on, yielded the same results as those afterwards obtained by Enskog.

Chapman and Enskog applied their methods chiefly to the case of a normal gas that is, one in which the mean free path of a molecule is small compared with the scale of length in which the properties of the gas, e.g. temperature, vary appreciably. such a gas it is sufficient to include in the distribution function only the first order derivatives of density, mean velocity, and temperature. In the present paper, the solution is extended to gases in which this condition no longer holds. The methods of Chapman and Enskog are applicable also in this case, but the procedure actually followed is somewhat different, and seems to lead more directly to the desired results. For purposes of illustration, and for the sake of completeness, the results obtained by the above writers for a normal gas are not assumed, as they might be, but are derived A new "equation of transfer," which is different in form from that of MAXWELL, forms the basis of the method, and seems to provide a simpler and more direct means of calculating the rate of change of molecular properties by collision than has been used This equation, together with Boltzmann's equation, readily provide a hitherto. solution of the distribution function to any desired degree of completeness.

The kinetic theory of rarefied gases was first considered by Maxwell,‡ who dealt as before only with his particular model. The mathematics was thus greatly simplified, and he was able (legitimately, though without proof) to assume a velocity distribution function containing terms of the first, second and third degrees only. By this means he showed that stresses are set up in a gas by non-uniformity of temperature: in a normal gas these stresses are negligible, but in a rarefied gas their magnitude becomes appreciable. § Maxwell suggested that this fact might provide a possible explanation of the phenomena of the radiometer.

^{*} Enskog, 'Kinetische Theorie der Vorgänge in mässig verdünnten Gasen,' Inaug. Dissertation, Upsala, 1917.

[†] Chapman, 'Phil. Trans.,' A, vol. 216, p. 279, 1915; cf. also 'Phil. Trans.,' A, vol. 217, p. 115, 1916.

[†] MAXWELL, 'Scientific Papers,' vol. 2, p. 681, 1879. A numerical mistake has crept into MAXWELL's results. This is pointed out in § 12 and the correct result given.

[§] May 25, 1922.—The degree of rarefaction required is of the order of one millionth of an atmosphere; see note on p. 33.

In the same year, Reynolds* published his paper, "On Certain Dimensional Properties of Matter in the Gaseous State," in which he also, by an entirely different method, discovered these temperature stresses. There is, however, a discrepancy between Maxwell's and Reynolds' results,† the magnitudes of their expressions for the stresses being in the ratio 3:1.

A general demonstration of the existence of temperature stresses was afterwards given by Brillouin, but without any attempt to estimate their magnitude. More recently Enskog investigated the problem in the case of a stationary gas without assuming the molecules to be Maxwellian: he carried his calculations only to a first approximation, and found that to this order all molecular models give the same result.

The investigation is here dealt with afresh by the special methods of this paper and general formulæ obtained for the stresses. The various special molecular models discussed include centres of force varying inversely as the n^{th} power of the distance and rigid elastic spherical molecules. In the former case, Maxwell's result for n=5is confirmed, while in the latter case the calculations are carried to the third approximation, and the numerical coefficient obtained differs by about 20 per cent. from that of the Maxwellian gas. A detailed comparison of the results with those of previous writers is given in the concluding paragraph.

§ 2. THE FUNDAMENTAL INTEGRAL EQUATION.

The present investigation will be confined to a simple monatomic gas. By "simple" we imply that the molecules of the gas are similar in every respect, and by "monatomic" we mean that the molecules are spherically symmetrical. We shall also suppose that the gas is "nearly perfect"—that is, that the mean free path of a molecule is large compared with its radius of action.

(a) The Notation.

We denote the pressure, density and temperature of the gas by p, ρ and T. number of molecules per unit volume we shall denote by ν and the mass of each by m. When the molecules are acted on by external forces, we shall denote by X, Y, Z their components per unit mass with respect to any convenient rectangular co-ordinate The symbols u, v, w will be used for the components of velocity of a molecule relative to the same axes, u_0 , v_0 , w_0 for the components of the mean velocity of the gas, while the peculiar velocities, $u-u_0$, etc., will be represented by U, V, W. In considering the collision of two molecules, it is convenient to use the suffixes 1 and 2 to distinguish their velocities, both actual and "peculiar"; an accent serves to indicate

- * REYNOLDS, 'Phil. Trans.,' Part II, 1879; 'Papers,' vol. 1, p. 367.
- † The writer wishes to acknowledge his indebtedness and to express his best thanks to Prof. S. Chapman, who pointed out to him the different results, and encouraged an inquiry into the causes of the disagreement.
 - ‡ Brillouin, 'Annales de Chimie et de Physique,' 7 série, t. XX., août 1900.
 - § Enskog, 1917, loc. cit., Chapter VI.

the corresponding velocities after impact, as, for example, u_1 , u'_2 , U_1 and U'_2 . The fraction of the molecules in an element of volume dx dy dz about a point (x, y, z) at time t, which possess velocities lying between u, v, w and u + du, v + dv, w + dw will be represented by f(u, v, w, x, y, z, t) du dv dw dx dy dz, so that the number of such molecules in the volume considered will be

$$\nu f(u, v, w, x, y, z, t) du dv dw dx dy dz.$$

As indicated, f will be a function of u, v, w, x, y, z and t. A knowledge of the nature of f will give the required law of velocity distribution. The number ν will be a function of x, y, z and t alone, but it may sometimes be convenient to consider νf as one function of u, v, w, x, y, z and t.

(b) The Fundamental Equation.

By considering the change in the number of those molecules in a given element of volume, whose velocities lay within the limits u, v, w, and u + du, v + dv, w + dw, Boltzmann* showed that the function f must satisfy the equation,

$$\left\{ \frac{\partial}{\partial t} + X \frac{\partial}{\partial u_1} + Y \frac{\partial}{\partial v_1} + Z \frac{\partial}{\partial w_1} + u_1 \frac{\partial}{\partial x} + v_1 \frac{\partial}{\partial y} + w_1 \frac{\partial}{\partial z} \right\} (\nu f) = \left[\frac{\partial}{\partial t} (\nu f) \right]_{\text{coll.}}^{\bullet} . \quad (2.01)$$

where the term on the right represents the rate of increase by collisions.

In the case of molecules attracting or repelling with a force which is proportional to some power of the distance between them, we can write†

$$\left[\frac{\partial}{\partial t}(\nu f)\right]_{\text{coll.}} = \iiint \nu^2 (f^{(1)'} f^{(2)'} - f^{(1)} f^{(2)}) \, V \, du_2 \, dv_2 \, dw_2 p \, dp \, d\epsilon, \, . \quad (2.02)$$

where u_2 , v_2 , w_2 refer to the velocities of a molecule before colliding with one of those considered above, *i.e.* velocities u_1 , v_1 , w_1 ; V denotes their relative velocity before an encounter, p the perpendicular from one molecule on to the line of relative velocity of the other, ϵ the angular co-ordinate of p in a plane perpendicular to V. The symbol $f^{(1)}$ is an abbreviation for $f(u_1, v_1, w_1, x, y, z, t)$. Similarly, $f^{(1)'}$, $f^{(2)'}$ signify the form of f, when u'_1 , v'_1 , w'_1 and u'_2 , v'_2 , w'_2 are substituted respectively for u, v, w. Making this substitution in equation (2.01), we have—

$$\left\{ \frac{\partial}{\partial t} + X \frac{\partial}{\partial u} + Y \frac{\partial}{\partial v} + Z \frac{\partial}{\partial w} + u \frac{\partial}{\partial x} + v \frac{\partial}{\partial y} + w \frac{\partial}{\partial z} \right\} (vf)$$

$$= \iiint v^{2} (f^{(1)'} f^{(2)'} - f^{(1)} f^{(2)}) V du_{2} dv_{2} dw_{2} p dp de. \quad (2.03)$$

^{*} Boltzmann, 'Vorlesungen über Gastheorie,' I., s. 98-115.

[†] Jeans, 'Dynamical Theory of Gases' (3rd ed.), 1921, p. 210.

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

There is no need to retain the suffix attached to the velocities on the left-hand side of equation (2.01), for it is our purpose to investigate the form of f, and the result is to be applicable to all molecules, whatever their velocity.

§ 3. Consideration of the Fundamental Equation.

Many of the gas phenomena which have been investigated by means of the kinetic theory can be considered without the introduction of external forces, and such is the case also in the problem which we consider in this paper. Putting, therefore, X = Y = Z = 0,* the fundamental equation reduces to

$$\left[\frac{\partial}{\partial t} + u\frac{\partial}{\partial x} + v\frac{\partial}{\partial y} + w\frac{\partial}{\partial z}\right](\nu f) = \nu^2 \iiint (f^{(1)'}f^{(2)'} - f^{(1)}f^{(2)}) \nabla du_2 dv_2 dw_2 p dp d\epsilon. \quad (3.01)$$

It is easily verified that the solution in the steady state is given by

 $f_0 = Ae^{-hmC^2}, \dots \dots \dots \dots \dots$ (3.02)

5

where

$$C^{2} = (u - u_{0})^{2} + (v - v_{0})^{2} + (w - w_{0})^{2} \qquad (3.03)$$

$$= U^2 + V^2 + W^2, \dots$$
 (3.04)

and

$$A = (hm/\pi)^{3/2}$$
. (3.05)

In the steady state ν is a constant, and may be denoted by ν_0 .

In the non-steady state, let us assume that

(i)
$$f = f_0 [1 + F(u, v, w, x, y, z, t)],$$
 (3.06)

where F is a small quantity of the first order. It will be found to be a linear function of the space derivatives of the temperature and mean velocity of the gas, which we shall assume to be quantities of the first order. The number of molecules per unit volume will differ very slightly from that in the normal steady state, and σ will accordingly be a small number.

The integrand of equation (3.01) now becomes

$$f_0^{(1)}f_0^{(2)}\{F^{(1)'}+F^{(2)'}-F^{(1)}-F^{(2)}\}, \dots (3.08)$$

since from considerations of conservation of energy and momentum at an encounter

$$f_0^{(1)'}f_0^{(2)'} = f_0^{(1)}f_0^{(2)}$$
. (3.09)

^{*} The methods used in this paper are not, however, restricted to the case of no external forces. The latter may be introduced provided that they are of the first order, so that products with space derivatives of temperature and mean velocity may be neglected. See also note on p. 6.

The symbols $F^{(1)'}$, $F^{(1)}$, &c., are abbreviations for $F(U_1, V_1, W_1)$, $F(U_1, V_1, W_1)$, &c. If we write

$$u = u_0 + U, \&c.,$$

and put

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + u_0 \frac{\partial}{\partial x} + v_0 \frac{\partial}{\partial y} + w_0 \frac{\partial}{\partial z}, \quad (3.10)$$

equation $(3 \cdot 01)$ takes the form

$$\left[\frac{d}{dt} + \mathbf{U}\frac{\partial}{\partial x} + \mathbf{V}\frac{\partial}{\partial y} + \mathbf{W}\frac{\partial}{\partial z}\right] \left(\nu_0 f_0 e^{\sigma} (1 + \mathbf{F})\right)$$

$$= \nu^2 f_0^{(1)} \iiint f_0^{(2)} \left(\mathbf{F}^{(1)'} + \mathbf{F}^{(2)'} - \mathbf{F}^{(1)} - \mathbf{F}^{(2)}\right) \mathbf{V} du_2 dv_2 dw_2 p dp d\epsilon. \quad (3.11)$$

We propose to denote by D the operators on the left-hand side of the above equation and to put

$$I(F) = \iiint \int_0^{(2)} (F^{(1)'} + F^{(2)'} - F^{(1)} - F^{(2)}) V du_2 dv_2 dw_2 p dp d\epsilon. \quad (3.12)$$

We note, in passing, that

$$I(F+G) = I(F)+I(G)$$
 (3.13)

and

$$I(aF) = aI(F), \dots (3.14)$$

where a is a constant.

The equation (3.11) can now be written*

$$\nu_0 f_0 e^{\sigma} (1 + F) D (\log f_0 e^{\sigma}) + \nu_0 f_0 e^{\sigma} D (F) = \nu^2 f_0 I (F), \quad (3.15)$$

or, using equations (3.02), (3.04) and (3.05), and dividing by $\nu_0 f_0 e^{\sigma}$

$$(1+F) D(\frac{3}{2} \log h - hmC^2 + \sigma) + D(F) = \nu I(F).$$
 (3.16)

Since the left-hand side of this equation consists only of derivatives, it is clear that F, when found, will likewise consist of derivatives. We shall find it convenient to consider separately the group of terms involving derivatives of the same order, and we therefore denote by F₁ the group containing derivatives of the first order, by F₂ that of the second order, and so on. Now, by assumption, F₁ is small, and so, in obtaining it, we may neglect the product of F into the derivatives on the left-hand side of equation (3.16) above, as well as the terms D(F).

^{*} cf. Jeans, loc. cit., pp. 211-213.

[†] If external forces had been introduced, which were not small, D (F) could not so be neglected; for, D (F) would then include terms of the type X $\frac{\partial F}{\partial u}$, which might conceivably be of the first order (cf. note, p. 5).

Hence correct to the first order, we have

$$D\left(\frac{3}{2}\log h - hmC^{2} - \sigma\right) = \left(\frac{3}{2h} - mC^{2}\right)\frac{dh}{dt} + 2hm\Sigma U\frac{du_{0}}{dt} + \frac{d\sigma}{dt} + \left(\frac{3}{2h} - mC^{2}\right)\Sigma U\frac{\partial h}{\partial x} + \Sigma U\frac{\partial \sigma}{\partial x} + 2hm\Xi = \nu I(F_{1}), \quad (3.17)$$

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

where

$$\Xi = \mathbf{U}^{2} \frac{\partial u_{0}}{\partial x} + \mathbf{V}^{2} \frac{\partial v_{0}}{\partial y} + \mathbf{W}^{2} \frac{\partial w_{0}}{\partial z} + \mathbf{U} \mathbf{V} \left(\frac{\partial v_{0}}{\partial x} + \frac{\partial u_{0}}{\partial y} \right) + \mathbf{V} \mathbf{W} \left(\frac{\partial w_{0}}{\partial y} + \frac{\partial v_{0}}{\partial z} \right) + \mathbf{W} \mathbf{U} \left(\frac{\partial u_{0}}{\partial z} + \frac{\partial w_{0}}{\partial z} \right). \quad (3.18)$$

The summation $\Sigma U \frac{du_0}{dt}$ involves three terms formed by cyclical changes of u_0 , v_0 , w_0 , as well as of U, V, W, while the other two summations, also of three terms, involve corresponding changes in the derivatives.

Before attempting to solve this equation, we proceed to show the relation between this equation and Maxwell's equation of transfer, and how, by virtue of the special dynamic properties of collisions, it can be reduced to a much simpler form.

§ 4. The Rate of Change of Molecular Properties due to Collisions.

Suppose that Q represents any function of the velocity components of a molecule or, briefly, a molecular property. The rate of change of the sum of Q taken over all the molecules in the volume element dx dy dz, usually denoted by $\Delta Q dx dy dz$, may be calculated in two ways.

We may find the number of collisions of a given type per unit time and volume, multiply the result by the change produced in Q at each of these collisions, then integrate over the whole range of velocities. This is the method used by MAXWELL, who thereby finds

$$\Delta Q = \nu^2 \iiint (Q' - Q) f^{(1)} f^{(2)} V du_1 dv_1 dw_1 du_2 dv_2 dw_2 p dp d\epsilon. \quad (4.01)$$

The result can be obtained otherwise if we find the rate of increase by collision of molecules entering a given state (that is, whose velocities enter the prescribed limits u, v, w and u + du, v + dv, w + dw, multiply the result by Q, then integrate the expression over the whole range of velocities. Remembering the definition of I(F), it is evident that $\nu^2 f_0^{(1)}$ I (F) $du_1 dv_1 dw_1 dx dy dz dt$ represents the increase in such molecules by collision.

We deduce, therefore, that

$$\Delta Q = \nu^2 \iiint Q f_0^{(1)} I(F) du_1 dv_1 dw_1. \quad . \quad . \quad . \quad . \quad (4.02)$$

A simple analytical proof might also be given that the expressions in the above two equations are equal.

As we shall now have occasion to consider in some detail the integrals (4.01) and (4.02), and as the form of f, which it is our purpose to find, cannot depend on the magnitude of the mean velocities, it will be more convenient and simpler if, from this point, we suppose that $u_0 = v_0 = v_0 = 0$ at the point under consideration. We shall then put

$$I(F) = \iiint f_0^{(2)} (F^{(1)'} + F^{(2)'} - F^{(1)} - F^{(2)}) V dU_2 dV_2 dW_2 p dp d\epsilon . \quad (4.021)$$

and

8

$$\Delta \mathbf{Q} = \nu^2 \iiint \mathbf{Q} f_0^{(1)} \mathbf{I} (\mathbf{F}) d\mathbf{U}_1 d\mathbf{V}_1 d\mathbf{W}_1. \qquad (4.022)$$

This expression for ΔQ is evidently obtained by multiplying the right-hand side of equation (3.17) by $\nu Q f_0$ and then integrating over the range of velocities U, V, and W. If, therefore, we carry out this operation on the whole equation, we shall obtain a new equation which will give the rate of change of molecular properties due to collisions. Putting

$$\overline{\mathbf{Q}} = \iiint \mathbf{Q} f_0 d\mathbf{U} d\mathbf{V} d\mathbf{W}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.023)$$

we obtain the equation,

$$\overline{\left(\frac{3}{2h} - mC^{2}\right)} Q \frac{dh}{dt} + 2hm\Sigma \overline{UQ} \frac{du_{0}}{dt} + \overline{Q} \frac{d\sigma}{dt} + \overline{Q} \frac{d\sigma}{dt} + \Sigma \overline{\left(\frac{3}{2h} - mC^{2}\right)} Q \overline{U} \frac{\partial h}{\partial x} + \Sigma \overline{UQ} \frac{\partial \sigma}{\partial x} + 2hm\overline{Q\Xi} = \Delta Q/\nu, \quad (4.03)$$

the summations being of the same type as those used and explained in the preceding

For purposes of calculating ΔQ by this formula we shall require the following results:

$$\overline{\mathbf{U}^{2}\mathbf{C}^{2s}} = \frac{1}{3}\overline{\mathbf{C}^{2(s+1)}}, \quad \overline{\mathbf{U}^{4}\mathbf{C}^{2(s-1)}} = \frac{1}{5}\overline{\mathbf{C}^{2(s+1)}}, \quad \overline{\mathbf{V}^{2}\mathbf{W}^{2}\mathbf{C}^{2(s-1)}} = \frac{1}{15}\overline{\mathbf{C}^{2(s+1)}}, \quad . \quad (4.04)$$

$$\overline{\mathbf{C}^{2s}} = 1 \cdot 3 \cdot 5 \dots (2s+1) (2hm)^{-s}, \dots (4.05)$$

while, if either p, q or r is odd,

Equation (3.17) and (4.03) can now be reduced by a consideration of certain special cases. For ΔQ is zero, when Q is equal to 1, U or U^2 , since there can clearly be no change in the numbers or in the momentum or in the energy of the molecules

THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

contained in any element of volume owing to their mutual collisions. We deduce the equations of continuity of motion, and of energy, viz.:—

$$\frac{1}{\nu}\frac{d\nu}{dt} + \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} = 0, \quad (4.07)$$

$$\rho \, \frac{du_0}{dt} + \frac{\partial p}{\partial x} = 0, \qquad (4.08)$$

and

$$3\left(-\frac{1}{h}\frac{dh}{dt} + \frac{1}{\nu}\frac{d\nu}{dt}\right) + 5\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right) = 0. \quad (4.09)$$

From equations (4.07) and (4.09) the law of adiabatic expansion, $p_{\rho}^{-5/3} = \text{constant}$, can readily be deduced.

Using equations (4.07), (4.08) and (4.09), and changing from the variable h to T, we find that equation (3.17) reduces to

$$(hmC^{2} - \frac{5}{2}) \frac{1}{T} \left(U \frac{\partial T}{\partial x} + V \frac{\partial T}{\partial y} + W \frac{\partial T}{\partial z} \right)$$

$$+ 2hm \left\{ \left(U^{2} - \frac{C^{2}}{3} \right) \frac{\partial u_{0}}{\partial x} + \left(V^{2} - \frac{C^{2}}{3} \right) \frac{\partial v_{0}}{\partial y} + \left(W^{2} - \frac{C^{2}}{3} \right) \frac{\partial w_{0}}{\partial z} + UV \left(\frac{\partial v_{0}}{\partial x} + \frac{\partial u_{0}}{\partial y} \right) \right.$$

$$+ VW \left(\frac{\partial w_{0}}{\partial y} + \frac{\partial v_{0}}{\partial z} \right) + WU \left(\frac{\partial u_{0}}{\partial z} + \frac{\partial w_{0}}{\partial x} \right) \right\} = \nu I (F_{1}), \quad (4.10)$$

which is the equation obtained by Enskog by a different method.* Similarly, equation (4.03) becomes

$$\overline{(hmC^{2}-\frac{5}{2})} \overline{QU} \frac{1}{T} \frac{\partial T}{\partial x} + \overline{(hmC^{2}-\frac{5}{2})} \overline{QV} \frac{1}{T} \frac{\partial T}{\partial y} + \overline{(hmC^{2}-\frac{5}{2})} \overline{QW} \frac{1}{T} \frac{\partial T}{\partial z}
+ 2hm \left\{ \overline{\left(U^{2}-\frac{C^{2}}{3}\right)} \overline{Q} \frac{\partial u_{0}}{\partial x} + \overline{\left(V^{2}-\frac{C^{2}}{3}\right)} \overline{Q} \frac{\partial v_{0}}{\partial y} + \overline{\left(W^{2}-\frac{C^{2}}{3}\right)} \overline{Q} \frac{\partial w_{0}}{\partial z} + \overline{UVQ} \left(\frac{\partial v_{0}}{\partial x} + \frac{\partial u_{0}}{\partial y}\right)
+ \overline{VWQ} \left(\frac{\partial w_{0}}{\partial y} + \frac{\partial v_{0}}{\partial z}\right) + \overline{WUQ} \left(\frac{\partial u_{0}}{\partial z} + \frac{\partial w_{0}}{\partial x}\right) \right\} = \Delta Q/\nu. \quad (4.11)$$

The latter is the new equation referred to in § 1, which gives a formula for the easy calculation of the rate of change of any molecular property due to collision. It is easily seen, for example, that

$$\Delta \mathbf{C}^{2s} = 0, \qquad \Delta \mathbf{U} \mathbf{C}^{2s} = \frac{1 \cdot 3 \cdot 5 \dots (2s+3) s}{3 \cdot (2hm)^{s+1}} \frac{\nu}{\mathbf{T}} \frac{\partial \mathbf{T}}{\partial x}.$$

When Q is an odd function, ΔQ involves only the space derivatives of temperature, while if Q is even, ΔQ involves only the space derivatives of the mean velocity.

* Enskog (1917), loc. cit., equation (53), p. 35.

VOL. CCXXIII.—A.

§ 5. The Form of F_1 .

From the fundamental equation (4.10), we can now proceed to investigate the form of the function F_1 . Since the terms on the left-hand side of this equation are independent of each other, we may, following Enskog, express the solution in the following way:—

$$F_1 = F_{1x} + F_{1y} + F_{1z} + F_{1xx} + F_{1yy} + F_{1zz} + F_{1xy} + F_{1yz} + F_{1zx} \qquad (5.01)$$

where

$$\left(hmC^{2} - \frac{5}{2}\right)\frac{\mathrm{U}}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial x} = \nu \mathrm{I}\left(\mathrm{F}_{1x}\right), \&c., \qquad (5.02)$$

$$2hm\left(\mathbf{U}^{2}-\frac{\mathbf{C}^{2}}{3}\right)\frac{\partial u_{0}}{\partial x}=\nu\mathbf{I}\left(\mathbf{F}_{1xx}\right), \&c., \qquad (5.03)$$

$$2hm UV \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y}\right) = \nu I (F_{1xy}), \&c., (5.04)$$

and we have used the fact that

$$I(F_{1}) = I(F_{1x}) + I(F_{1y}) + I(F_{1z}) + I(F_{1xx}) + I(F_{1yy}) + I(F_{1zz}) + I(F_{1xy}) + I(F_{1yz}) + I(F_{1xz}) (5.05)$$

Putting

$$\mathbf{F}_{1x} = \frac{1}{\nu \mathbf{T}} \frac{\partial \mathbf{T}}{\partial x} \pi_x, \qquad (5.06)$$

$$\mathbf{F}_{1xx} = \frac{2hm}{\nu} \frac{\partial u_0}{\partial x} \, \pi_{xx}, \qquad (5.07)$$

$$\mathbf{F}_{1xy} = \frac{2hm}{\nu} \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right) \pi_{xy}, \qquad (5.08)$$

we have

$$\left(hmC^2 - \frac{5}{2}\right)U = I(\pi_x), \text{ (three equations)} (5.09)$$

$$\left(\mathrm{U}^2 - \frac{\mathrm{C}^2}{3}\right) = \mathrm{I}\left(\pi_{xx}\right), \quad \text{(three equations)} \quad . \quad . \quad . \quad (5.10)$$

$$UV = I(\pi_{ry}), \text{ (three equations)}...$$
 (5.11)

Now it has been shown* that the values of π_x , π_{xx} and π_{xy} , &c., which satisfy these equations are

$$\pi_x = \text{UP}_1 (C^2) (5.12)$$

$$\pi_{xx} = \left(\mathbf{U}^2 - \frac{\mathbf{C}^2}{3}\right) \mathbf{P}_2 (\mathbf{C}^2) \dots \dots \dots \dots (5.13)$$

where P₁ and P₂ are undetermined functions, the form of which we shall consider presently.

^{*} Enskog, loc. cit., pp. 37-41; Jeans' 'Dynamical Theory of Gases' (1921), pp. 229-230.

THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

We may, therefore, write

$$F_{1} = \frac{1}{\nu T} \left(U \frac{\partial T}{\partial x} + V \frac{\partial T}{\partial y} + W \frac{\partial T}{\partial z} \right) P_{1} (C^{2})$$

$$+ \frac{2hm}{\nu} \left\{ \left(U^{2} - \frac{C^{2}}{3} \right) \frac{\partial u_{0}}{\partial x} + \left(V^{2} - \frac{C^{2}}{3} \right) \frac{\partial v_{0}}{\partial y} + \left(W^{2} - \frac{C^{2}}{3} \right) \frac{\partial w_{0}}{\partial z} + UV \left(\frac{\partial v_{0}}{\partial x} + \frac{\partial u_{0}}{\partial y} \right) \right.$$

$$+ VW \left(\frac{\partial w_{0}}{\partial y} + \frac{\partial v_{0}}{\partial z} \right) + WU \left(\frac{\partial u_{0}}{\partial z} + \frac{\partial w_{0}}{\partial x} \right) \right\} P_{2} (C^{2}). \quad (5.15)$$

Hence, in a normal gas, in which the first order derivatives in f are sufficient, we may write

$$f = f_{0} \left[1 + \frac{1}{\nu T} \left(U \frac{\partial T}{\partial x} + V \frac{\partial T}{\partial y} + W \frac{\partial T}{\partial z} \right) P_{1} (C^{2}) \right]$$

$$+ \frac{2hm}{\nu} \left\{ \left(U^{2} - \frac{C^{2}}{3} \right) \frac{\partial u_{0}}{\partial x} + \left(V^{2} - \frac{C^{2}}{3} \right) \frac{\partial v_{0}}{\partial y} + \left(W^{2} - \frac{C^{2}}{3} \right) \frac{\partial w_{0}}{\partial z} + UV \left(\frac{\partial v_{0}}{\partial x} + \frac{\partial u_{0}}{\partial y} \right) \right.$$

$$+ VW \left(\frac{\partial w_{0}}{\partial y} + \frac{\partial v_{0}}{\partial z} \right) + WU \left(\frac{\partial u_{0}}{\partial z} + \frac{\partial w_{0}}{\partial x} \right) \left. \right\} P_{2} (C^{2})$$

$$(5.16)$$

By reason of the definition of f, we must have

$$\iiint Uf(U, V, W) dU dV dW = 0, \text{ (three equations)}. (5.18)$$

and hence

$$\iiint \mathbf{F_1} f_0 d\mathbf{U} d\mathbf{V} d\mathbf{W} = \iiint \mathbf{U} \mathbf{F_1} f_0 d\mathbf{U} d\mathbf{V} d\mathbf{W} = 0. \quad . \quad . \quad (5.19)$$

This latter equation places a restriction on P₁ (C²), thus

$$\overline{\mathrm{U^2P_1}(\mathrm{C^2})} = 0$$
, (three equations) . . . (5.20)

11

$$\overline{C^2P_1(C^2)} = 0. (5.21)$$

 \S 6. Determination of the Functions $P_{1}\left(C^{2}\right)$ and $P_{2}\left(C^{2}\right)$

We have seen (equation 4.02) that

$$\Delta \mathbf{Q} = \nu^2 \iiint \mathbf{Q} f_0^{(1)} \mathbf{I} \left(\mathbf{F}_1 \right) d\mathbf{U}_1 d\mathbf{V}_1 d\mathbf{W}_1.$$

If we now introduce the notation

[G, H] =
$$\iiint_{C} G f_0^{(1)} I(H) dU_1 dV_1 dW_1, \quad . \quad . \quad . \quad (6.01)$$

we have

$$\Delta Q = \nu^2 [Q, F_1].$$
 (6.02)

Using equation (3.13), it is clear that

$$[Q, F+G+H+\&c.] = [Q, F]+[Q, G]+[Q, H]+\&c.$$
 (6.03)

and hence, using the expansion for F₁ above, we obtain

$$\Delta Q = \nu^2 [Q, F_{1x}] + \nu^2 [Q, F_{1y}] + \nu^2 [Q, F_{1z}] + \nu^2 [Q, F_{1xx}] + \&c. \qquad (6.04)$$

so that equation (4.11) becomes

$$\Sigma \overline{(hmC^{2} - \frac{5}{2})} \overline{QU} \frac{1}{T} \frac{\partial T}{\partial x} + 2hm\Sigma \overline{\left(U^{2} - \frac{C^{2}}{3}\right)} Q \frac{\partial u_{0}}{\partial x}$$

$$= \Delta Q/\nu$$

$$= \Sigma [Q, UP_{1}(C^{2})] \frac{1}{T} \frac{\partial T}{\partial x} + 2hm\Sigma \left[Q, \left(U^{2} - \frac{C^{2}}{3}\right) P_{2}(C^{2})\right] \frac{\partial u_{0}}{\partial x} (6.05)$$

In this equation, as in (4.10), the individual terms are independent of each other, and therefore we may equate the coefficients of like derivatives on each side of the equation. We thus obtain.

$$(\overline{hmC^2-\frac{5}{2})}$$
 QU = [Q, UP₁(C²)], (three equations) . . . (6.06)

$$\left(\overline{\mathbf{U}^2 - \frac{\mathbf{C}^2}{3}}\right)\mathbf{Q} = \left[\mathbf{Q}, \left(\mathbf{U}^2 - \frac{\mathbf{C}^2}{3}\right)\mathbf{P}_2\left(\mathbf{C}^2\right)\right], \text{ (three equations)}.$$
 (6.07)

$$\overline{\text{UVQ}} = [Q, \text{UVP}_2(C^2)].$$
 (three equations). . . (6.08)

These equations are independent and are to hold for all values of Q. If we assume that P₁ (C²) and P₂ (C²) can be expanded in powers of C², whose coefficients are independent of the velocities U₁, V₁, W₁, U₂, V₂, W₂, we have an infinite number of constants to determine. For this purpose, we propose to adopt the method first used by Chapman* in his 1915 memoir; that is, we choose an infinite number of convenient forms of Q, thus getting an infinite number of equations to determine the unknowns. The simplest forms which suggest themselves are $Q = UC^{2s}$ for equation (6.06) and $Q = U^2C^{2s}$ for equation (6.07), letting s, in each case, assume all integral values from 0 to ∞ .

We then get

$$\frac{1.3.5...(2s+3)s}{3(2hm)^{s+1}} = [UC^{2s}, UP_1(C^2)], (6.09)$$

and

$$\frac{4}{45} \frac{1 \cdot 3 \cdot 5 \dots (2s+5)}{(2hm)^{s+2}} = \left[U^2 C^{2s}, \left(U^2 - \frac{C^2}{3} \right) P_2 (C^2) \right] . \qquad (6.10)$$

where, in equation (6.09), the factor s is to be omitted when s = 0.

^{*} Chapman, 'Phil. Trans.,' A, 1915, vol. 216, p. 279.

Chapman was led to equations which are equivalent to (6.09) and (6.10) in his treatment of the same problem by means of Maxwell's equation of transfer.* He evaluated the integrals on the right-hand side, and thus arrived in each case at an

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

infinite system of equations to determine the unknown constants.†

§ 7. COEFFICIENT OF VISCOSITY AND HEAT CONDUCTION.

We use the notation

$$\overline{\mathbf{Q}} = \iiint \mathbf{Q} f \, d\mathbf{U} \, d\mathbf{V} \, d\mathbf{W} \quad . \quad . \quad . \quad . \quad . \quad (7.01)$$

to distinguish the mean value of Q taken over the molecules in the unsteady state, from that taken with respect to the normal velocity distribution function f_0 . Thus the system of pressures at a point is given by

$$P_{xx} = \rho \widetilde{U}^2$$
, $P_{xy} = \rho \widetilde{U} \widetilde{V}$, &c. (7.02)

Using equation (5.16), we thus obtain

The corresponding hydrodynamical equations of pressure in a viscous fluid of coefficient of viscosity μ are

$$P_{xx} = p - \frac{2}{3}\mu \left\{ 2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right\}, \qquad (7.05)$$

$$P_{xy} = -\mu \left\{ \frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right\}. \quad (7.06)$$

Hence, by comparison,

When the constants in P_2 (C²) have been determined as indicated in § 6, the numerical value of μ can be computed, as has been done by Chapman and Enskog in the memoirs already quoted. It will suffice to leave the values of μ in the form of the last equation (7.07).

^{*} Chapman (1915), loc. cit.

[†] Снарман (1915), рр. 311-312.

Similarly, we can find the coefficient of heat conduction by a consideration of the transfer of energy. Thus, the transfer of energy across unit area of a plane perpendicular to the axis of x is given by

$$q_{x} = \frac{1}{2}\rho \overrightarrow{\mathbf{U}}\overrightarrow{\mathbf{C}}^{2} = \frac{m}{2T} \overline{\mathbf{U}^{2}}\overrightarrow{\mathbf{C}}^{2}P_{1}(\overrightarrow{\mathbf{C}}^{2})\frac{\partial \mathbf{T}}{\partial x}$$

$$= \frac{m}{6T} \overline{\mathbf{C}^{4}}P_{1}(\overrightarrow{\mathbf{C}}^{2})\frac{\partial \mathbf{T}}{\partial x}. \qquad (7.08)$$

Now if 3 is the coefficient of conduction of heat, the flow of heat across unit area of the same plane is $-\Im \partial T/\partial x$, so that the flow of energy is $-\Im \partial T/\partial x$, where J is the mechanical equivalent of heat. Confining ourselves to dynamical measure, we have, on comparison with (7.08)

$$\vartheta = -\frac{m}{6T}\overline{\mathrm{C}^4\mathrm{P}_1(\mathrm{C}^2)}. \qquad (7.09)$$

We shall require \Im in this form later in the work.

§ 8. Consideration of the Second-Order Derivatives in the Velocity Distribu-TION FUNCTION.

(a) The Fundamental Equations.

In normal gases it is sufficient to obtain the development of F to the first order only, but in rarefied gases second-order terms may become important. For, the coefficients of the first and second-order derivatives respectively contain (λ/l) and $(\lambda/l)^2$, where λ is the mean free path of a molecule and l is comparable with the scale of length within which the temperature and mean velocity vary appreciably. In normal gases $(\lambda/l)^2$ can be neglected in comparison with (λ/l) , but we now proceed to consider cases where λ is of the same order as l.

Correct to the first order, we were able to neglect the series of terms D (F) in equation (3.16), but now this is no longer permissible. We shall, however, obtain the equation correct to the second-order derivatives if we substitute F_1 for F in D(F), since the operator D consists entirely of first-order derivatives. Neglecting products of derivatives, the Boltzmann integral equation accordingly takes the form,

$$\left(\frac{3}{2h} - mC^{2}\right)\frac{dh}{dt} + 2hm\Sigma U\frac{du_{0}}{dt} + \frac{d\sigma}{dt} + \left(\frac{3}{2h} - mC^{2}\right)\Sigma U\frac{\partial h}{\partial x} + \Sigma U\frac{\partial\sigma}{\partial x} + 2hm\Xi + D\left(F_{1}\right) = \nu I\left(F\right), \quad (8.01)$$

where, as before,

$$D \equiv \frac{d}{dt} + U \frac{\partial}{\partial x} + V \frac{\partial}{\partial y} + W \frac{\partial}{\partial z}. \qquad (8.02)$$

Since F₁ contains all the derivatives of the first order, it is clear that there will be no change in F_1 due to the addition of second-order terms. We may substitute for F_1 in equation (8.02) then precisely the solution obtained in equation (5.15).

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

From the resulting equation, the form of F could be determined by methods analogous to those used in § 5 above. For every derivative on the left-hand side of the equation there would correspond a term containing a like derivative in the expansion of F. to carry out this process at the present stage would have the disadvantage of introducing into F more derivatives than are necessary, since there are certain relations between the latter, as represented, for example, by the equation of continuity. difficulty was avoided and the work reduced to a minimum in the case of a normal gas, considered above, by forming the ΔQ equation, deducing from it the equation of continuity, the equation of motion and the equation of energy, and then using them to reduce the equations to a simpler form. We shall, therefore, adopt the same method in the present more extended problem.

Generalizing equation (4.03), we obtain the following form for the equation of transfer,

$$\left(\frac{3}{2h} - mC^{2}\right)Q\frac{dh}{dt} + 2hm\Sigma\overline{UQ}\frac{du_{0}}{dt} + \frac{d\sigma}{dt} + \left(\frac{3}{2h} - mC^{2}\right)\Sigma UQ\frac{\partial h}{\partial x} + \Sigma\overline{UQ}\frac{\partial\sigma}{\partial x} + 2hm\overline{Q\Xi} + \overline{QD}(\overline{F}_{1}) = \Delta Q/\nu. \quad (8.03)$$

(b) Special Cases.

(1) Q = 1. In this case we find

$$\frac{d\sigma}{dt} + \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} + \frac{1}{3vT} \overline{\mathbf{C}^2 \mathbf{P_1} (\mathbf{C}^2)} \nabla^2 \mathbf{T} = 0,$$

and since $\overline{C^2P_1(C^2)} = 0$ from equation (5.21), we obtain the equation of continuity in the same form as before, viz:

$$\frac{d\sigma}{dt} + \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} = 0. (8.04)$$

(2) Q = U. In this case, we find from equation (8.03) an equation corresponding to (4.08), viz.:—

$$2hm\frac{du_0}{dt} - \frac{1}{h}\frac{\partial h}{\partial x} + \frac{\partial \sigma}{\partial x} + 2hm\overline{\mathrm{UD}(\mathrm{F}_1)} = 0. \quad . \quad . \quad . \quad . \quad (8.05)$$

Now

$$\overline{\mathrm{UD}\left(\mathrm{F}_{1}\right)} = \frac{\overline{\mathrm{C}^{2}\mathrm{P}_{1}\left(\mathrm{C}^{2}\right)}}{3\nu\mathrm{T}}\frac{d}{dt}\left(\frac{\partial\mathrm{T}}{\partial x} + \frac{\partial\mathrm{T}}{\partial y} + \frac{\partial\mathrm{T}}{\partial z}\right) + \frac{2hm}{\nu}\overline{\mathrm{U}\left(\mathrm{U}\frac{\partial}{\partial x} + \mathrm{V}\frac{\partial}{\partial y} + \mathrm{W}\frac{\partial}{\partial z}\right)}\mathrm{P}_{2}\left(\mathrm{C}^{2}\right)\Theta, \quad (8.051)$$

where

$$\begin{split} \Theta \equiv & \left(\mathbf{U^2} - \frac{\mathbf{C^2}}{3} \right) \frac{\partial u_0}{\partial x} + \left(\mathbf{V^2} - \frac{\mathbf{C^2}}{3} \right) \frac{\partial v_0}{\partial y} + \left(\mathbf{W^2} - \frac{\mathbf{C^2}}{3} \right) \frac{\partial w_0}{\partial z} + \mathbf{U} \mathbf{V} \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right) \\ & + \mathbf{V} \mathbf{W} \left(\frac{\partial w_0}{\partial y} + \frac{\partial v_0}{\partial z} \right) + \mathbf{W} \mathbf{U} \left(\frac{\partial u_0}{\partial z} + \frac{\partial w_0}{\partial x} \right), \quad . \quad (8.052) \end{split}$$

if products of derivatives be systematically neglected.*

*
$$E.g.$$
, instead of $\frac{d}{dt} \left(\frac{1}{\nu T} \frac{\partial T}{\partial x} \right)$, we are able to write $\frac{1}{\nu T} \frac{d}{dt} \left(\frac{\partial T}{\partial x} \right)$.

The coefficient of the first group of terms on the right of equation (8.051) is zero by virtue of equation (5.20), and by the use of equations (7.03) and (7.04), we are then able to write

$$\overline{\mathrm{UD}\left(\mathbf{F}_{1}\right)} = \frac{1}{\rho} \left\{ \frac{\partial \left(\mathbf{P}_{xx} - p\right)}{\partial x} + \frac{\partial \mathbf{P}_{xy}}{\partial y} + \frac{\partial \mathbf{P}_{xz}}{\partial z} \right\} \qquad (8.053)$$

Hence equation (8.05) becomes

$$2hm\frac{du_0}{dt} - \frac{1}{h}\frac{\partial h}{\partial x} + \frac{\partial \sigma}{\partial x} + \frac{2hm}{\rho} \left\{ \frac{\partial \left(\mathbf{P}_{xx} - \mathbf{p} \right)}{\partial x} + \frac{\partial \mathbf{P}_{xy}}{\partial y} + \frac{\partial \mathbf{P}_{xz}}{\partial z} \right\} = 0, \quad . \quad (8.054)$$

or

$$\frac{du_0}{dt} + \frac{1}{\rho} \left\{ \frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{xy}}{\partial y} + \frac{\partial P_{xz}}{\partial z} \right\} = 0, \quad (8.06)$$

with the similar equations obtained from ΔV and ΔW . These are the new equations of motion, correct to the second-order derivatives.

(3) $Q = C^2$. Lastly, remembering that ΔC^2 is zero, we find

$$\frac{3}{2hm} \left\{ \frac{1}{T} \frac{dT}{dt} + \frac{d\sigma}{dt} \right\} + \frac{5}{2hm} \left\{ \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right\} + \frac{\overline{C^4 P_1(C^2)}}{3\nu T} \nabla^2 T = 0, \quad (8.07)$$

or, using equation (8.04) and (7.09),

$$\frac{1}{T}\frac{dT}{dt} = \frac{2}{3}\frac{d\sigma}{dt} - \frac{2hm}{9\nu T}\overline{C^4P_1(C^2)}\nabla^2T$$

$$= \frac{2}{3}\frac{d\sigma}{dt} + \frac{4}{3}\frac{9h}{\nu}\nabla^2T, \quad (8.08)$$

9 being the coefficient of heat conduction.

We can also write the equation in the form

$$\rho \frac{d\mathbf{T}}{dt} = \frac{2}{3}\mathbf{T} \frac{d\rho}{dt} + \frac{9}{\mathbf{C}_{v}} \nabla^{2}\mathbf{T}, \qquad (8.09)$$

since, in a monatomic gas, the specific heat at constant volume is given, in dynamical units, by*

$$C_v = \frac{3}{2} \frac{R}{m} = \frac{3}{4hTm}.$$
 (8.10)

Equation (8.09) may be referred to as the equation of energy, or, following MAXWELL, the equation of temperature. It is seen to be the same as that obtained by Jeans† and Chapmant by other methods, except in so far as the latter include products of

^{*} Jeans, 'Dynamical Theory of Gases' (1921), p. 185, equation (472); Maxwell, 'Papers,' vol. 2, p. 65, equation (111).

[†] Jeans, loc. cit., p. 245 (the second term of the r.h.s. should be multiplied by a factor T).

[‡] Chapman, 'Phil. Trans.' A, (1915), equation (246).

derivatives. It is identical with the equation obtained by MAXWELL,* but the latter is able to substitute $5\mu/2$ for \Im/C_v in the case of the special molecular model which he considered.

(c) The Simplified Forms of the Fundamental Equations.

By means of equations (8.04), (8.054) and (8.09), we are now able to eliminate certain of the derivatives from the fundamental F-equation (8.01), and to write it in the form:

$$(hmC^{2} - \frac{5}{2}) \sum \frac{\mathbf{U}}{\mathbf{T}} \frac{\partial \mathbf{T}}{\partial x} + 2hm\Theta - \frac{2hm}{\rho} \sum \mathbf{U} \mathbf{P}_{x} + (hmC^{2} - \frac{3}{2}) \frac{9}{C_{v}\rho \mathbf{T}} \nabla^{2} \mathbf{T} + \mathbf{D} \left(\mathbf{F}_{1}\right) = \nu \mathbf{I} \left(\mathbf{F}\right), \quad (8.11)$$

where
$$\mathbf{P}_{x} \equiv \frac{\partial \left(\mathbf{P}_{xx} - p\right)}{\partial x} + \frac{\partial \mathbf{P}_{xy}}{\partial y} + \frac{\partial \mathbf{P}_{xz}}{\partial z}$$
. (8.111)

and P_y , P_z denote expressions obtained by cyclical changes of x, y and z. summations involve appropriate changes of U, V and W, as well as of x, y and z; and the symbol in the second term has already been defined, equation (8.052).

In a similar way we obtain an analogous form for the Q-equation (8.03),

$$\overline{\left(hmC^{2}-\frac{5}{2}\right)\Sigma\frac{\overline{UQ}}{T}\frac{\partial T}{\partial x}+2hm\overline{Q\Theta}-\frac{2hm}{\rho}\Sigma\overline{UQ}\mathbf{P}_{x}} + \overline{\left(hmC^{2}-\frac{3}{2}\right)Q}\frac{\Im}{C_{n}\rho T}\nabla^{2}T + \overline{QD}(\overline{F}_{1}) = \Delta Q/\nu \quad . \quad (8.12)$$

The two equations (8.11) and (8.12) are sufficient to determine the precise form of F as far as second-order derivatives, if the value of F_1 be substituted from equation (5.15) in the term $D(F)_1$ on the left-hand side. On the left-hand side of these equations there are still derivatives of the first order. If, however, we write

$$I(F) = I(F_1) + I(F_2),$$

in accordance with equation (3.13), and use equation (4.10), we are able to reduce equation (8.11) so that it contains second-order derivatives only. In fact, we find

$$-\frac{2hm}{\rho} \sum \mathbf{U} \mathbf{P}_x + (hm\mathbf{C}^2 - \frac{3}{2}) \frac{9}{\mathbf{C}_v \rho \mathbf{T}} \nabla^2 \mathbf{T} + \mathbf{D} (\mathbf{F}_1) = \nu \mathbf{I} (\mathbf{F}_2). \quad . \quad . \quad . \quad . \quad . \quad (8.13)$$

(d) The Form of
$$F_2$$
.

The procedure is now exactly the same as that used in § 5 to determine the form of Thus, we note, as before, that the derivatives on the left-hand side of the above

* Maxwell, 'Papers,' vol. 2, p. 700, equation (52).

equation (8.13) are independent, and for every derivative on the left there must be a corresponding derivative on the right. Proceeding as in the case of (5.01), we can write

$$F_{2} = \Sigma F_{2x} + \Sigma F_{2} (T)_{xx} + \Sigma F_{2} (T)_{tx} + \Sigma F_{2xx} + \Sigma F_{2} (u_{0})_{xx} + \Sigma F_{2} (v_{0})_{xx} + \Sigma F_{2} (w_{0})_{xx}, \quad (8.14)$$

where ΣF_{2x} and $\Sigma F_{2}(T)_{tx}$ involve three terms each, and

$$\sum F_{2xx} = F_{2xx} + F_{2yy} + F_{2zz} + F_{2xy} + F_{2yz} + F_{2zz}. (8.15)$$

with similar meanings for $\Sigma F_2(T)_{xx}$, $\Sigma F_2(u_0)_{xx}$, &c.

The symbols are defined by the following equations,

$$\nu I(\mathbf{F}_{2x}) = -\frac{2hm}{\rho} U\mathbf{P}_x, \qquad (8.16)$$

$$\nu I (F_2 (T)_{xx}) = \frac{1}{\nu T} \left\{ U^2 P_1 (C^2) + (hmC^2 - \frac{3}{2}) \frac{\Im \nu}{C_{\nu} \rho} \right\} \frac{\partial^2 T}{\partial x^2}, \quad . \quad . \quad (8.17)$$

$$\nu I (F_2(T)_{tx}) = \frac{1}{\nu T} UP_1(C^2) \frac{d}{d\bar{t}} \left(\frac{\partial T}{\partial x} \right), \qquad (8.18)$$

$$\nu I(F_{2xx}) = \frac{2hm}{\nu} \left(U^2 - \frac{C^2}{3} \right) P_2(C^2) \frac{d}{dt} \left(\frac{\partial u_0}{\partial x} \right), \qquad (8.19)$$

$$\nu I (F_{2xy}) = \frac{2hm}{\nu} UVP_2(C^2) \frac{d}{dt} \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right), \qquad (8.20)$$

$$\nu I(\mathbf{F}_{2}(u_{0})_{xx}) = \frac{2hm}{\nu} U\left(U^{2} - \frac{\mathbf{C}^{2}}{3}\right) \mathbf{P}_{2}\left(\mathbf{C}^{2}\right) \frac{\partial^{2} u_{0}}{\partial x^{2}}, \quad (8.21)$$

$$\nu I\left(F_{2}\left(u_{0}\right)_{xy}\right) = \frac{2hm}{\nu} \left\{V\left(U^{2} - \frac{C^{2}}{3}\right) + U^{2}V\right\} \frac{\partial^{2}u_{0}}{\partial x \partial y}, \quad (8.22)$$

with corresponding equations for $F_2(v_0)_{xx}$, &c.

Equation (8.16) can be solved by the method of Enskog,* but, in order to solve equations (8.17) to (8.20) it is necessary to generalize the latter's work. It is not difficult to establish the following results:—

If I (
$$\pi$$
) is equal respectively to U Φ (C²), $\left(U^{2}-\frac{C^{2}}{3}\right)\Phi$ (C²), or U² Φ_{1} (C²) + Φ_{2} (C²), then π is equal to U Ψ (C²), $\left(U^{2}-\frac{C^{2}}{3}\right)\Psi$ (C²), or $\left(U^{2}-\frac{C^{2}}{3}\right)\Psi_{1}$ (C²) + Ψ_{2} (C²).

^{*} See note on p. 10 above, § 5.

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

In each case Ψ (C²) is a function of C², whose form the equation does not disclose. In the last case, Ψ_2 (C²) is subject to the conditions,

19

$$\iiint C^{2}\Psi_{2}(C^{2}) f_{0} dU dV dW = 0 (8.24)$$

The only part of F_2 which will be used in the subsequent investigation is that which is even in U, V and W. Now it is evident from a consideration of dimensions, that if I (G) is equal to an odd function of U, V, W, then G must likewise be an odd function. There is, therefore, no need for us to solve equations (8.21) and (8.22), for F_2 (u_0)_{cx}, &c., will be odd functions of U, V, W. Using E_2 to denote the even portion of F_2 , we have

$$E_2 = \Sigma F_2 (T)_{xx} + \Sigma F_{2xx}$$
 (8.25)

in the notation of equation (8.15); and, using the theorems enunciated above to solve equations (8.17), &c., we have

$$F_{2}(T)_{xx} = \frac{1}{\nu^{2}T} \left\{ \left(U^{2} - \frac{C^{2}}{3} \right) Q_{1}(C^{2}) + R(C^{2}) \right\} \frac{\partial^{2}T}{\partial x^{2}}, \quad (8.26)$$

$$F_{2}(T)_{xy} = \frac{1}{\nu^{2}T} 2UVQ_{1}(C^{2}) \frac{\partial^{2}T}{\partial x \partial y}, \qquad (8.27)$$

$$\mathbf{F}_{2xx} = \frac{2hm}{\nu^2} \left(\mathbf{U}^2 - \frac{\mathbf{C}^2}{3} \right) \mathbf{Q}_2 \left(\mathbf{C}^2 \right) \frac{d}{dt} \left(\frac{\partial u_0}{\partial x} \right), \quad (8.28)$$

$$F_{2xy} = \frac{2hm}{\nu^2} UVQ_2 (C^2) \frac{d}{dt} \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right). \qquad (8.29)$$

By the use of the F-equation (8.13), we have now ascertained the nature of the terms in E_2 ; but for a complete solution it is necessary to know the three functions, Q_1 (C^2), Q_2 (C^2) and R (C^2), and for this purpose we have recourse to the Q-equation (8.12).

(e) Equations to determine the Coefficients in E2.

In § 4 it was established that

$$\Delta Q = \nu^2 \iiint Q f_0^{(1)} I(F) dU_1 dV_1 dW_1, \qquad (8.291)$$

where I (F) represents the quintuple integral (4.021). For the sake of brevity, we may write, as in equation (6.02),

$$\Delta Q = \nu^2 [Q, F].$$

Now F consists of a number of terms, the nature of which have already been found, equations (5.15) and (8.14). Using these results, and applying the theorem stated in equation (6.03), we obtain the following expansion for ΔQ ,

$$\Delta Q/\nu^{2} = [Q, F_{1}] + [Q, F_{2}]
= [Q, F_{1}] + \Sigma [Q, F_{2x}] + \Sigma [Q, F_{2}(T)_{xx}] + \Sigma [Q, F_{2}(T)_{tx}]
+ \Sigma [Q, F_{2xx}] + \Sigma [Q, F_{2}(u_{0})_{xx}] + \Sigma [Q, F_{2}(v_{0})_{xx}] + \Sigma [Q, F_{2}(w_{0})_{xx}] .$$
(8.292)

We have now two expressions for ΔQ , the present one in terms of octuple integrals and another in terms of mean values, equation (8.12). Both expressions contain the same derivatives, and since the latter are independent, the two results may be compared term by term.

Thus, comparing the terms containing $\partial^2 T/\partial x^2$, we obtain the following equation,

$$\frac{1}{\nu T} \left\{ \overline{\mathbf{U}^{2} \mathbf{P}_{1} \left(\mathbf{C}^{2}\right) \mathbf{Q}} + \left(\overline{hm} \mathbf{C}^{2} - \frac{3}{2} \right) \mathbf{Q} \frac{\partial \nu}{\mathbf{C}_{\nu} \rho} \right\} \frac{\partial^{2} \mathbf{T}}{\partial x^{2}} = \nu \left[\mathbf{Q}, \mathbf{F}_{2} \left(\mathbf{T} \right)_{xx} \right], \quad . \quad (8.293)$$

or, substituting the value of $F_2(T)_{xx}$ from (8.26), we get

$$\left\{ \overline{\mathbf{U}^{2}\mathbf{P}_{1}\left(\mathbf{C}^{2}\right)\mathbf{Q} + \left(\overline{hm\mathbf{C}^{2} - \frac{3}{2}\right)\mathbf{Q}} \, \frac{\mathcal{G}_{\nu}}{\mathbf{C}_{\nu}\rho} \right\} = \left[\mathbf{Q}, \left(\mathbf{U}^{2} - \frac{\mathbf{C}^{2}}{3}\right)\mathbf{Q}_{1}\left(\mathbf{C}^{2}\right)\right] + \left[\mathbf{Q}, \, \mathbf{R}\left(\mathbf{C}^{2}\right)\right]. \quad (8.294)$$

A comparison of the coefficients of $\partial^2 T/\partial y^2$ and $\partial^2 T/\partial z^2$ results in two similar equations. By using these in conjunction with (8.294), and by writing the left-hand side of the latter in the form

$$\left(\overline{U^{2}-\frac{C^{2}}{3}}\right)P_{1}\left(C^{2}\right)Q+\overline{\frac{C^{2}}{3}P_{1}\left(C^{2}\right)Q}+\overline{\left(hmC^{2}-\frac{3}{2}\right)Q}\,\frac{\vartheta_{\nu}}{C_{\nu}\rho},$$

it is easily established that

$$\left[Q, \left(U^{2} - \frac{C^{2}}{3}\right) Q_{1}(C^{2})\right] = \overline{\left(U^{2} - \frac{C^{2}}{3}\right) P_{1}(C^{2}) Q_{1}}, \quad (8.30)$$

and

$$[Q, R(C^2)] = \overline{\frac{C^2}{3}P_1(C^2)Q} + \overline{(hmC^2 - \frac{3}{2})Q} \overline{Q} \frac{\vartheta_{\nu}}{C_{\nu}\rho}. \qquad (8.31)$$

Similarly we find, on comparing coefficients of $\frac{d}{dt} \left(\frac{du_0}{dx} \right)$,

$$\left[Q, \left(U^2 - \frac{C^2}{3} \right) Q_2(C^2) \right] = \left(\overline{U^2 - \frac{C^2}{3}} \right) P_2(C^2) Q. \quad . \quad . \quad . \quad (8.32)$$

Other equations could be obtained in like manner, but the equations here given will be sufficient to determine the functions which occur in E2. In fact, for the particular application which we wish to make of E_2 , it will only be necessary to determine $Q_1(C^2)$

21

and $Q_2(C^2)$. We assume that the latter functions can be expressed as power series in C². No attempt will be made to establish any convergency conditions necessary in the course of the analysis, but the subsequent numerical calculations indicate that the series are rapidly convergent.

The equations (8.30) and (8.32) are true whatever function of U, V, W, the symbol Q may represent. But the use which we wish to make of the equations is to evaluate the coefficients of $Q_1(C^2)$ and $Q_2(C^2)$. Now, in general, the latter are infinite in number, and an infinite number of linear relations between them will be necessary for a complete solution. Any value of Q, substituted in the equations, will give a linear relation between the coefficient of Q_1 (C2) and Q_2 (C2), provided the octuple integral can be evaluated. form of Q which we shall adopt, however, will obviously be that which makes the octuple integral $\left[Q, \left(U^2 - \frac{C^2}{3}\right) P_2\left(C^2\right)\right]$ easiest to evaluate. Now we have already indicated in § 6 that, in the evaluation of the velocity distribution function for a normal gas, it is necessary to find the integral $\left[U^2C^{2s}, \left(U^2 - \frac{C^2}{3}\right)P_2\left(C^2\right)\right]$. This has already been done by Chapman (loc. cit.). We shall, therefore, choose U^2C^{2s} as our form of Q for both the We may obtain then as many relations as we require by equations (8.30) and (8.32). giving to s different values.

We thereupon obtain as the system of equations determining $Q_1(C^2)$ and $Q_2(C^2)$,

$$\left[U^{2}C^{2s}, \left(U^{2} - \frac{C^{2}}{3} \right) Q_{1} \left(C^{2} \right) \right] = \overline{U^{2}C^{2s} \left(U^{2} - \frac{C^{2}}{3} \right) P_{1} \left(C^{2} \right)}
= \frac{4}{45} \overline{C^{2s+4}P_{1} \left(C^{2} \right)}, \dots (8.33)$$

and

$$\left[U^{2}C^{2s}, \left(U^{2} - \frac{C^{2}}{3}\right)Q_{2}\left(C^{2}\right)\right] = \frac{4}{45}\overline{C^{2s+4}P_{2}\left(C^{2}\right)}, \quad (8.34)$$

where s is to assume all integral values from zero to infinity.

§ 9. Stresses in a Rarefied Gas.

As in § 7, we have

$$P_{xx} = \rho \ddot{U}^2$$
, and $P_{xy} = \rho \ddot{U}\ddot{V}$,

so that, using the expression for f correct to the second-order derivatives,

$$P_{xx} = p - \frac{2}{3}\mu \left\{ 2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right\} + P'_{xx}, \qquad (9.01)$$

$$P_{xy} = -\mu \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right) + P'_{xy}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.02)$$

where*

$$P'_{xx} = \frac{\rho}{\nu^{2}T} \left\{ \overline{U^{2}Q_{1}(C^{2}) \Sigma \left(U^{2} - \frac{C^{2}}{3}\right)} \frac{\partial^{2}T}{\partial x^{2}} + \overline{U^{2}R_{1}(C^{2})} \nabla^{2}T \right\}$$

$$+ \frac{2hm\rho}{\nu^{2}} \overline{U^{2}Q_{2}(C^{2}) \Sigma \left(U^{2} - \frac{C^{2}}{3}\right)} \frac{d}{dt} \left(\frac{\partial u_{0}}{\partial x}\right)$$

$$= \frac{2\rho}{45\nu^{2}T} \overline{C^{4}Q_{1}(C^{2})} \left(2 \frac{\partial^{2}T}{\partial x^{2}} - \frac{\partial^{2}T}{\partial y^{2}} - \frac{\partial^{2}T}{\partial z^{2}}\right)$$

$$+ \frac{4hm\rho}{45\nu^{2}} \overline{C^{4}Q_{2}(C^{2})} \frac{d}{dt} \left(2 \frac{\partial u_{0}}{\partial x} - \frac{\partial v_{0}}{\partial y} - \frac{\partial w_{0}}{\partial z}\right), \qquad (9.03)$$

$$\mathbf{P}'_{xy} = \frac{2\rho}{45\nu^{2}\Gamma} \overline{\mathbf{C}^{4}\mathbf{Q}_{1}(\mathbf{C}^{2})} \frac{\partial^{2}\Gamma}{\partial x \partial y} + \frac{2hm}{15\nu^{2}} \overline{\mathbf{C}^{4}\mathbf{Q}_{2}(\mathbf{C}^{2})} \frac{d}{dt} \left(\frac{\partial v_{0}}{\partial x} + \frac{\partial u_{0}}{\partial y} \right) . \quad . \quad (9.04)$$

In the above we have used the fact that $\overline{C^2R(C^2)}$ is zero by virtue of (8.24). evaluate the stresses, therefore, all that we require is the numerical value of $\overline{C^4Q_1(C^2)}$ and $\overline{\mathrm{C}^4\mathrm{Q}_2\left(\mathrm{C}^2\right)}$.

- § 10. Evaluation of $\overline{C^4Q_1\left(C^2\right)}$ and $\overline{C^4Q_2\left(C^2\right)}$ for Particular Molecular Models.
 - (a) The System of Equations to Determine the Functions Q_1 (C^2) and Q_2 (C^2).

If we suppose Q₁ (C²) and Q₂ (C²) expanded as power series, the equations given above for their determination, equations (8.33) and (8.34), will involve octuple integrals of the type $\left[U^2C^{2s}, \left(U^2 - \frac{C^2}{3} \right)C^{2r} \right]$. This integral has been evaluated by Chapman in a recent memoir,† and we shall abbreviate our own work by using the same notation and by referring the reader to the original paper for its interpretation. Thus, we write;

$$\left[U^{2}C^{2s}, \left(U^{2} - \frac{C^{2}}{3} \right) C^{2r} \right] = -\frac{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2s+5) \cdot 1 \cdot 3 \cdot 5 \cdot \dots \cdot (2r+5)}{3\nu C_{0} \left(2hm \right)^{r+s+2}} \cdot \frac{4}{4 \cdot 5} \cdot c_{rs}, \quad (10.01)$$

where c_{rs} is a number whose value can be calculated when the law of molecular interaction is known. In the following analysis, we shall regard c_{rs} as a known constant. The symbol C_0 is the same as that used by Chapman (C. 142), (C. 147), (C. 170), and is equal to ν^{-1} multiplied into a function of the absolute temperature. The form of

- * 16th Feb., 1922.—The summations included in P'_{xx} are of the same type as the expression for θ , equation (8.052).
- † Chapman, 'Phil. Trans.,' A (1915), vol. 216, pp. 279-348. As we shall now have occasion to make repeated references to this paper, we shall abbreviate them by prefixing to the equation the letter C. Thus equation (137) in the paper cited will be written (C. 137).
 - ‡ (C. 77), (C. 80), (C. 135), (C. 137) and (C. 131). See also (C. 144).

the function depends on the molecular model considered. If we write Q₁ (C²) and Q_2 (C^2) in the following way,

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

$$Q_{1}(C^{2}) = \sum_{r=0}^{\infty} \frac{(2hm)^{r}}{1 \cdot 3 \cdot 5 \dots (2r+5)} \delta_{r} C^{2r}, \dots (10.02)$$

$$Q_{2}(C^{2}) = \sum_{r=0}^{\infty} \frac{(2hm)^{r}}{1 \cdot 3 \cdot 5 \dots (2r+5)} \epsilon_{r} C^{2r}, \qquad (10.03)$$

we find that equations (8.33) and (8.34) become

$$\sum_{r=0}^{\infty} \delta_r c_{rs} = -\frac{3\nu C_0 (2hm)^{s+2}}{1 \cdot 3 \cdot 5 \dots (2s+5)} \overline{C^{2s+4} P_1(C^2)} . \qquad (10.04)$$

$$(s = 0, 1, 2 \dots \infty).$$

and

$$\sum_{r=0}^{\infty} \epsilon_r c_{rs} = -\frac{3\nu C_0 (2hm)^{s+2}}{1 \cdot 3 \cdot 5 \dots (2s+5)} \overline{C^{2s+4} P_2(C^2)} \cdot \cdot \cdot \cdot (10.05)$$

$$(s = 0, 1, 2 \dots \infty).$$

Our next step will be the calculation of $\overline{C^{2s+4}P_i(C^2)}$ and $\overline{C^{2s+4}P_2(C^2)}$, and for this purpose we now proceed to the statement of a useful theorem in determinants, proved and used by Enskog* in his recent memoir on the kinetic theory of gases.

(b) Theorem on Determinants.

If a series of quantities δ_0 , δ_1 , δ_2 , ... δ_n are determined by a system of linear equations

$$C_{00} \, \delta_0 + C_{10} \, \delta_1 + C_{20} \, \delta_2 + \dots + C_{n0} \, \delta_n = \alpha_0,$$

$$C_{01} \, \delta_0 + C_{11} \, \delta_1 + C_{21} \, \delta_2 + \dots + C_{n1} \, \delta_n = \alpha_1,$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$C_{0n} \, \delta_0 + C_{1n} \, \delta_1 + C_{2n} \, \delta_2 + \dots + C_{nn} \, \delta_n = \alpha_n,$$

then any other linear expression of the same quantities can be expressed in the following way:-

$$m_0 \, \delta_0 + m_1 \, \delta_1 + m_2 \, \delta_2 + \ldots + m_n \, \delta_n = rac{igcup_0 \, \delta_0 + m_1 \, \delta_1 + m_2 \, \delta_2 + \ldots + m_n \, \delta_n}{igcup_{\mathrm{C}_{00}} \, igcup_0 \, igcup_$$

* Enskog, loc. cit., 1917, Anhang 1.

(c) Evaluation of
$$\overline{C^{2s+4}P_1(C^2)}$$
 and $\overline{C^{2s+4}P_2(C^2)}$.

In order to avail ourselves further of the work done by Chapman and to facilitate reference, we shall adopt for P₁ (C²) and P₂ (C²) the same notation as the writer referred We have, then, on a comparison of equation (5.15) with his equation (C. 73),

$$P_{1}(C^{2}) \equiv -B_{0\nu} \sum_{r=0}^{\infty'} \frac{(2hm)^{r}}{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2r+3) r} \beta_{r-1} C^{2r}, \quad . \quad . \quad . \quad (10.06)$$

$$P_2(C^2) \equiv -3C_0 \nu \sum_{r=0}^{\infty} \frac{(2hm)^r}{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2r+5)} \gamma_r C^{2r}, \quad \dots \quad (10.07)$$

where, of course, β_r and γ_r are constants; C_0 has already been explained, and $B_0 = \frac{9}{4} C_0$ (cf. C. 170).

From the equations (5.21) and (6.09) we find as the equations to determine β_r ,

$$\beta_{-1} + \sum_{r=0}^{\infty} \frac{\beta_r}{r+1} = 0, \quad . \quad . \quad . \quad . \quad . \quad (10.08)$$

where

$$b_{rs} = -\frac{3B_0 \nu (2hm)^{r+s+2}}{1 \cdot 3 \cdot 5 \cdot \dots (2s+5)(s+1) \cdot 1 \cdot 3 \cdot 5 \cdot \dots (2r+5)(r+1)} [UC^{2(s+1)}, UC^{2(r+1)}], (10.10)$$

and may accordingly be regarded as known.* The quantities b_{rs} are, in fact, pure numbers, depending only on the molecular mass and on the force constant of the molecules.

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

Similarly, the system of equations (6.10) connecting the coefficients γ_r becomes

$$\sum_{r=0}^{\infty} \gamma_r c_{rs} = 1, \qquad (10.11)$$

$$(s = 0, 1, 2 \dots \infty)$$

25

in the notation of equation (10.01).

By means of the determinantal theorem given above we shall now be able to use equations (10.09) and (10.11) to evaluate any linear expression of β_r and of γ_r , such as, for example, the expressions $C^{2s+4}P_1(C^2)$ and $C^{2s+4}P_2(C^2)$. We shall content ourselves with the calculation of the latter functions for the special cases s=0, 1 and 2. It will be evident later why these three cases are sufficient.

Using equation (10.08), we find

$$\overline{C^{4}P_{1}(C^{2})} = -B_{0}\nu (2hm)^{-2} \sum_{r=0}^{\infty} \frac{2r+5}{r} \beta_{r-1}$$

$$= -B_{0}\nu (2hm)^{-2} 2 \sum_{r=0}^{\infty} \beta_{r} \qquad (10.12)$$

Similarly, we find

$$\overline{C^{6}P_{1}(C^{2})} = \overline{C^{4}P_{1}(C^{2})} (2hm)^{-1}7\mathbf{B}_{1}, \qquad (10.13)$$

$$\overline{\mathbf{C}^{8}\mathbf{P}_{1}(\mathbf{C}^{2})} = \overline{\mathbf{C}^{4}\mathbf{P}_{1}(\mathbf{C}^{2})}(2hm)^{-2}7.9\mathbf{B}_{2}, \dots (10.14)$$

where

$$\mathbf{B}_{1} = \sum_{r=0}^{\infty} 2(r+7)\beta_{r} \div 7\sum_{r=0}^{\infty} \beta_{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10.15)$$

$$\mathbf{B}_{2} = \sum_{r=0}^{\infty} (4r^{2} + 50r + 189) \beta_{r} \div 7.9. \sum_{r=0}^{\infty} \beta_{r}. \qquad (10.16)$$

The corresponding values of $C^{2s+4}P_2$ (C2) are

$$\overline{C^{4}P_{2}(C^{2})} = -3C_{0}\nu(2hm)^{-2}\sum_{r=0}^{\infty}\gamma_{r}, \qquad (10.17)$$

$$\overline{C^{6}P_{2}(C^{2})} = \overline{C^{4}P_{2}(C^{2})}(2hm)^{-1}7\mathbf{C}_{1}, \quad . \quad . \quad . \quad . \quad (10.18)$$

$$\overline{\mathbf{C}^{8}\mathbf{P}_{2}(\mathbf{C}^{2})} = \overline{\mathbf{C}^{4}\mathbf{P}_{2}(\mathbf{C}^{2})}(2hm)^{-2}7.9.\mathbf{C}_{2}, \quad . \quad . \quad . \quad (10.19)$$

where

$$\mathbf{C}_1 = \sum_{r=0}^{\infty} (2r+7)\gamma_r \div 7\sum_{r=0}^{\infty} \gamma_r, \dots$$
 (10.20)

$$\mathbf{C}_{2} = \sum_{r=0}^{\infty} (2r+7) (2r+9) \gamma_{r} \div 7.9. \sum_{r=0}^{\infty} \gamma_{r}. \qquad (10.21)$$

The numerators and denominators of B and C can be calculated by means of equations (10.09) and (10.11) if we put in the determinantal expansion of § 10 (b), $m_r = 1, (r + 7), \&c.$

The functions $\overline{C^{2s+4}P_1(C^2)}$ can also be expressed in terms of the physical constants of the gas, for we have seen in § 7 that

$$\overline{\mathbf{C}^4\mathbf{P}_1(\mathbf{C}^2)} = -\frac{6\mathbf{T}\mathfrak{R}}{m}, \qquad (10.22)$$

$$\overline{C^{4}P_{2}(C^{2})} = -\frac{15\nu\mu}{\rho 2hm}.$$
 (10.23)

Substituting the values of $\overline{C^{2s+4}P_1(C^2)}$, &c., thus obtained in equations (10.04) and (10.05), and making use of the determinantal theorem, § 10 (b), we find

$$\overline{C^{4}Q_{1}(C^{2})} = (2hm)^{-2} \sum_{r=0}^{\infty} \delta_{r} = \frac{6\nu C_{0}T\vartheta}{5m} q_{b}, \qquad (10.24)$$

and

$$\overline{C^4Q_2(C^2)} = (2hm)^{-2} \sum_{r=0}^{\infty} \epsilon_r = \frac{3\nu^2 C_0 \mu}{\rho 2hm} q_c, \qquad (10.25)$$

where

and q_c represents the numerical expression obtained when C_1 , C_2 , &c., are substituted for B_1 , B_2 , &c., in the expression for q_b .

§ 11. Expressions for the Stresses in a Rarefied Gas for Particular Molecular Models.

(a) General Expressions.

Using the expressions for $\overline{C^4Q_1(C^2)}$ and $\overline{C^4Q_2(C^2)}$ just obtained, we have, on substitution in equation (9.03)

$$P'_{xx} = \frac{4}{75}C_0 \Im q_b \left(2\frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2} - \frac{\partial^2 T}{\partial z^2} \right) + \frac{2}{15}C_0 \mu q_o \frac{d}{dt} \left(2\frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right). \quad (11.01)$$

By equating the two expressions previously obtained for $\overline{C^4P_2}$ ($\overline{C^2}$) [equations (10.17) and (10.23)], we find

$$C_0 = \frac{10hm}{\rho} \frac{\mu}{\Sigma \gamma_r}, \quad \dots \quad (11.02)$$

THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

and, on substitution in the above expression, we find the following expressions for the stresses in the gas [equations (9.01) and (9.02)],

$$P_{xx} = p - \frac{2}{3}\mu \left\{ 2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right\} + \frac{4}{15} \frac{\mu \vartheta}{p} j \left(2 \frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2} - \frac{\partial^2 T}{\partial z^2} \right) + \frac{2}{3} \frac{\mu^2}{p} k \frac{d}{dt} \left(2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right). \qquad (11.03)$$

$$P_{xy} = -\mu \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right) + \frac{4}{5} \frac{\mu \partial}{\rho} j \frac{\partial^2 T}{\partial x \partial y} + \frac{\mu^2}{\rho} k \frac{d}{dt} \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right). \qquad (11.04)$$

The quantities j and k are numbers which depend on the molecular model chosen, and are defined by the equations,

$$j = q_b \div \sum_{r=0}^{\infty} \gamma_r \quad . \quad (11.05)$$

27

(b) Consideration of Particular Molecular Models.

The calculation of j and k used above depends entirely on the values of b_{rs} and c_{rs} and these can only be worked out numerically when the law of interaction between any two molecules is known. If the molecules are point centres of force varying as r^{-n} , expressions for b_{rs} and c_{rs} can be obtained from the paper by Chapman, in which the viscosity and thermal conduction of a monatomic gas were considered, and to which repeated references have already been made. As the work is there given in full,* there is no need to quote the general results here. We shall content ourselves with considering two special cases. First, we shall consider the particular case of molecules which are point centres of force varying inversely as the fifth power (Maxwellian molecules), and, secondly, molecules which are rigid elastic spheres. The latter case is, of course, a special case of the n^{th} power law, being obtained by making n infinite.

Case I. Maxwellian Molecules (r^{-5}) .—From the memoir cited we find that in this particular case the work is very much simplified, for

$$b_{r0} = c_{r0} = 1.$$
 (11.07)

Hence from our equations (10.09) and (10.11) we have, at once

$$\sum_{r=0}^{\infty} \beta_r = \sum_{r=0}^{\infty} \gamma_r = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.08)$$

* Chapman (1915), loc. cit. § 9. † (C. 190.)

In this special case, therefore, we find from equations (10.26), (10.25), (11.05) and (11.06)

The expressions for the stresses in a gas composed of molecules of this kind are then

$$P_{xx} = p - \frac{3}{3}\mu \left\{ 2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right\} + \frac{4}{15} \frac{\mu \Im}{p} \left(2 \frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2} - \frac{\partial^2 T}{\partial z^2} \right) + \frac{3}{3} \frac{\mu^2}{p} \frac{d}{dt} \left(2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right), \quad \dots$$
 (11.10)

$$\mathbf{P}_{xy} = -\mu \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right) + \frac{4}{5} \frac{\mu \partial}{p} \frac{\partial^2 \mathbf{T}}{\partial x \partial y} + \frac{\mu^2}{p} \frac{d}{dt} \left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right). \quad . \quad . \quad (11.11)$$

Case II. Rigid Elastic Spheres.—In this case the numerical work is by no means so simple, for the numbers b_{rs} and c_{rs} are not so easily evaluated and there is no special relation which enables us to find j and k without using the series given in equation (10.26). Having found the values of b_{rs} and c_{rs} , the values of \mathbf{B}_1 , \mathbf{B}_2 , &c., are to be found from equations (10.15), &c., using the appropriate series of the type given in § 10 (b). We are fortunate again in finding that b_{rs} and c_{rs} for $0 \le r \le 3$, $0 \le s \le 3$, have been worked out by Chapman in this special case, and our work is materially lightened by our being able to quote them. We find*

Table I — Values of b_n .

	r=0.	r=1.	r=2.
s = 0	1.000,000	1.071,429	1 · 138,889
s=1	$1 \cdot 071,429$	$1\cdot372,\!449$	1 · 698,696
s=2	1 · 138,889	1 · 698,696	$2 \cdot 402,\!006$

Table II.—Values of c_{rs} .

	r=0.	r=1.	r = 2.
s = 0	1.000,000	1.071,429	1 · 138,889
s = 1	1.071,429	1 • 491,497	1.953,798
s=2	1 · 138,889	1.953,798	3.044,359

^{* (}C. 219) and (C. 220).

29

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

In order to calculate \mathbf{B}_1 , \mathbf{B}_2 , &c., it is necessary to evaluate each of the series occurring in equations (10.12), (10.15), (10.16), (10.17), (10.20) and (10.21). The latter can be obtained as accurately as we please by increasing the number of the terms in the series of the type § 10 (b). As the series are found to converge very rapidly, we have taken the calculations as far as the third term. The following table shows the result of taking one, two and three terms respectively:—

Table III.—Values of $\sum_{c}^{\infty} \beta_{r}$, &c.

	$\overset{\circ}{\underset{0}{\Sigma}}\!eta_{r}.$	$\sum_{0}^{\infty} 2 (r+7) \beta_{r}.$	$\sum_{0}^{\infty} (4r^2 + 50r + 189)\beta_r.$	$\sum_{0}^{\infty} \gamma_{r}$.	$\sum_{0}^{\infty} (2r+7) \gamma_{r}.$	$\sum_{0}^{\infty} (2r+7)(2r+9) \gamma_{r}.$
1st approx.	1.000,00	14.000,00	189·000,00	1.000,00	7.000,00	63.000,00
2nd approx.	1.022,72	13.681,82	$176 \cdot 113,71$	1.014,85	$6 \cdot 688,\!12$	56 • 450,52
3rd approx.	1.024,81	13.669,66	$176 \cdot 651,33$	1.015,87	6.674,92	56.751,28

The corresponding values of B_1 , &c., are then found in accordance with equations (10.15), (10.16), (10.20) and (10.21).

Table IV.—Values of B and C.

	В ₁ .	$\mathrm{B}_2.$	C ₁ .	$\mathbf{C}_2.$
1st approx	2.000,00	3.000,00	1.000,00	1.000,00
2nd approx	1.911,12	$2 \cdot 733,35$	0.941,45	0.882,92
3rd a pprox	1.905,53	$2 \cdot 736,09$	0.938,68	0.886,73
Value used	1.905	$2 \cdot 735$	0.938	0.885

Finally, from equation (10.26) we are able to calculate q_b and q_c to a similar order of approximation, and dividing by $\sum_{j=0}^{\infty} \gamma_{r}$, the corresponding values of j and k are determined.

Table V.—Values of j and k (Rigid Elastic Spheres).

	q_b .	$q_c.$	$j\cdot$	k.
1st approx	1.000,00	1.000,00	1.000,00	1.000,00
2nd approx	0.826,68	1.027,34	0.814,58	1.012,31
3rd approx	0.812,82	1.029,44	0.800,12	1.013,35

§ 12. Discussion of the Results.

To Maxwell* belongs the credit of applying first the kinetic theory to a rarefied gas and of demonstrating the existence of temperature stress terms. In order to simplify the mathematics, the model which he considered was that of a gas repelling inversely as the fifth-power law. A further simplification was introduced by the assumption that the velocity distribution function contained terms of the first, second, and third degrees only in U, V and W. Although no justification was given for this step, it can be shown to be legitimate in the case of the special model chosen.† The

method, which Maxwell adopted for the evaluation of the coefficients of the nineteen terms, was similar to that used in his earlier papers. He found, by the use of his equation of transfer, the change in certain functions of the molecular velocities by collisions, e.g., U², U³, UV², &c., and compared the result with that obtained by a direct integration. By choosing as many functions as there were unknowns, a sufficient of equations were obtained to evaluate them.

The result obtained by MAXWELL! for the stress in a gas is, making the necessary changes in the notation,

$$P_{xx} - p = -2\mu \frac{\partial u_0}{\partial x} + \frac{2}{3}\mu \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) + \frac{3\mu^2}{\rho T} \frac{\partial^2 T}{\partial x^2} + \frac{3}{2} \frac{\mu^2}{\rho T} \nabla^2 T. \quad (12.01)$$

An examination of his work, however, reveals that a numerical error has been made in the calculation of the last term, and that a term involving a time derivative has been omitted without any express mention of the fact. The above equation should read

$$P_{xx} - p = -2\mu \frac{\partial u_0}{\partial x} + \frac{2}{3}\mu \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) + \frac{3\mu^2}{\rho T} \frac{\partial^2 T}{\partial x^2} - \frac{\mu^2}{\rho T} \nabla^2 T + \frac{2}{3} \frac{\mu^2}{\rho} \frac{\partial}{\partial t} \left(2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right), \quad (12.02)$$

involving a change in the coefficient of $\nabla^2 T$ and the addition of the last term. evidently in complete agreement with the result obtained in § 11, if we write

$$\beta = \frac{5}{2}\mu C_{v}, \quad C_{v} = \frac{3}{2}\frac{p}{\rho T} \quad . \quad . \quad . \quad . \quad (12.03)$$

- * Maxwell, "On Stresses arising from Inequalities of Temperature in Rarefied Gases," 'Phil. Trans., 1879; Papers, vol. 2, p. 681.
 - † Cf. Jeans, 'Dynamical Theory of Gases' (1921), p. 219.
 - ‡ MAXWELL, loc. cit. ante, p. 700, equation (53).
- § The latter fact has been pointed out by Brillouin and Enskog: Brillouin, 'Annales de Chimie et de Physique,' 7 series, vol. 20, 1900, p. 440; Enskog (1917), loc. cit., p. 123.
 - Cf. (C. 248)-(C. 251); and equation (8.10) above. C_v and S are here measured in *dynamical* units.

The ratio of the coefficient of the last term in equation (12.02) to that of the corresponding temperature derivative is $\frac{2}{5} \frac{m}{R}$ which is of the order 10^{-6} , and is independent of the degree of rarefaction.* MAXWELL was, therefore, justified in neglecting the time derivatives.

ON THE STRESSES IN A NON-UNIFORM RAREFIED MONATOMIC GAS.

Shortly after the appearance of Maxwell's paper, Reynolds published the result of his investigations into the stresses which must result when heat is communicated from a surface to a gas.† The object of his researches was to obtain an explanation of the phenomena of the Radiometer, referred to by him as the "phenomena of impulsion," and not only did he succeed in so doing, but he was led by a more elaborate treatment of the problem to a prediction of the phenomena of thermal transpiration. reasoning by which he arrived at these results was both novel and intricate—too intricate to be described here even in outline. It may be said, however, that his whole investigation involved the assumption that the gas is at all points steady as regards time, and that the molecules are subject to no external forces. The existence of temperature stress terms was established, and a result obtained which was identical in form with MAXWELL'S, but which made the pressure one-third that obtained by the latter. the notation of the present paper, his result takes the form;

$$P'_{xx} = \frac{\mu^2}{\rho T} \frac{\partial^2 T}{\partial x^2}.$$

REYNOLDS was aware of the discrepancy between his result and that of MAXWELL, and made a special point of mentioning it in his paper.\ The present paper, however, confirms Maxwell's result.

Brillouin, in 1900, published a paper on the kinetic theory of a gas in which he gave general expressions for the velocity distribution function of a gas. Recognising that the latter function must be an invariant, he proceeded to write down all possible invariants, first for those of the first-order derivatives, and later for second-order derivatives. As a result, the latter expression is found to contain seventeen groups of terms, excluding those introduced by external forces. A general expression is obtained for the stresses in a gas, which discloses their nature but does not indicate their relative importance. For Brillouin did not attempt to evaluate the unknown functions involved in his expression for the law of distribution of

^{*} Jeans, loc. cit. (1921), p. 119.

[†] REYNOLDS, 'Phil. Trans.,' Part II., 1879. Papers, vol. 1, pp. 257-383.

[‡] It will be recalled that P'xx is used to denote the terms in Pxx involving derivatives of the second

[§] REYNOLDS, loc. cit., p. 367 (footnote).

^{||} Brillouin, loc. cit. ante, p. 30.

molecular velocities. The terms obtained by this writer* are, in the absence of external forces,

$$P_{xx} - p = a \left(2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right) + b \frac{\partial}{\partial t} \left(2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right) + c \left(2 \frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2} - \frac{\partial^2 T}{\partial z^2} \right) + d \left(2 \frac{\partial^2 \sigma}{\partial x^2} - \frac{\partial^2 \sigma}{\partial y^2} - \frac{\partial^2 \sigma}{\partial z^2} \right), \quad (12.04)$$

where a, b, c and d are functions whose nature or value is not given.

The first three groups of terms have been obtained in § 11. As for the last group, we note from equation (4.08) that

$$\frac{\partial \sigma}{\partial x} = -\frac{1}{T} \frac{\partial T}{\partial x} - 2hm \frac{\partial u_0}{\partial t},$$

so that, neglecting products of derivatives, we have

$$\frac{\partial^2 \sigma}{\partial x^2} = -\frac{1}{T} \frac{\partial^2 T}{\partial x^2} - 2hm \frac{\partial}{\partial t} \left(\frac{\partial u_0}{\partial x} \right). \qquad (12.05)$$

The last group is evidently to be included in the second and third.

As was indicated in the introductory paragraph, Enskog, having given a complete solution for normal gases, has attempted to carry his investigations a step further. In the first place he considered a molecular model which had the effect of simplifying the integrations. A molecule is regarded as behaving like a perfectly elastic, infinitely small sphere, whose diameter is not constant, but is a function of the relative velocity of an approaching molecule. Thus, if σ is the diameter, $\sigma \propto V^{-\frac{1}{2}}$. Since in the integrand of equation (4.01) p may be written $\sigma \cos \theta$, it is evident that

$$\nabla p \, dp \propto \sin 2\theta \, d\theta$$

thus introducing a great simplification. Curiously enough the effect is equivalent to Maxwell's assumption of a fifth-power law, and Enskog obtains an expression for the stress in such a gas,† which is identical with our result for Maxwellian molecules. In a consideration of a more general molecular model, viz. that of molecules repelling inversely as the n^{th} power of the distance, Enskog simplifies his work by assuming that the gas is everywhere at rest. Apart from terms involving squares of temperature derivatives, the result obtained ist

$$P'_{xx} = \frac{4}{15} \frac{\mu \Im}{p} \left(2 \frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2} - \frac{\partial^2 T}{\partial z^2} \right). \qquad (12.06)$$

^{*} Brillouin, loc. cit., § 32.

[†] Enskog (1917), loc. cit., p. 122.

[‡] Enskog, p. 127, equations (200) and (204).

The coefficient in equation (12.06) has been worked out by Enskog to the first approximation only and is seen to be in agreement with the result obtained in § 11.

The results for the case of rigid elastic spheres are worked out for the first time in the present paper. From Table IV we deduce that the approximate value of j is in this case approximately 0.8, so that the stress, due to differences of temperature, is

$$P'_{xx} = \frac{1}{7} \frac{6}{5} \frac{\mu \Im}{\rho} \left(2 \frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2} - \frac{\partial^2 T}{\partial z^2} \right). \qquad (12.07)$$

33

An examination of the work in § 11 reveals what a slight change is made in j and k by varying the law of molecular action. Thus, in the case of Maxwellian molecules (n=5), j and k and both equal to unity exactly, while in the case of rigid elastic spheres $(n=\infty)$, j becomes equal to 0.8 while k takes the value 1.013. To a first approximation, the results for the latter model are the same as those for the Maxwellian model, thus showing that to this order of approximation the value of n is immaterial.

Note, added May 25, 1922.—In order to give some idea of the degree of rarefaction, at which the temperature stresses become appreciable, the value of the coefficient $\mu \Im /p$ has been worked out in one or two cases. In the formula (11.03), \Im is measured in dynamical units, so that the value of \Im , as usually given, must be multiplied by J, the mechanical equivalent of heat. The values of \Im and μ , which are given in the table below, are those appropriate to normal temperatures and pressures* and are assumed to hold for very low pressures. The value of J is taken to be $4 \cdot 184 \times 10^7$.

Values of $\Im \mu / p$.

Gas.	ج (heat units).	ે (dynamical units).	μ (c.g.s.).	p (dynes per square centimetre).	$\Im \mu/p$.
Argon	0·00003894	* 1629 • 25	0.000211	1	$0.344 \\ 2.657 \\ 0.458$
Helium	0·0003360	14058 • 28	0.000189	1	
Oxygen	0·0000570	2384 • 88	0.000192	1	

It is evident that the value of $\Im \mu/p$ is in the neighbourhood of unity when p is of the order of one dyne per square centimetre, or about one-millionth of an atmosphere. As Maxwell† pointed out, this is the same order of pressure as is required in a radiometer, and the calculated stress would be sufficient, if it existed alone, to produce a rotation of the cups in such an instrument. There are, however, complications at the surface of a solid immersed in $Qq\theta_0$, a gas, which are not discussed here.

^{*} Jeans, 'Dynamical Theory of Gases' (3rd ed.), 1921, p. 301.

[†] MAXWELL, 'Phil. Trans.,' 1879; 'Scientific Papers,' vol. 2, p. 681.