

Transport Phenomena in Einstein-Bose and Fermi-Dirac Gases. I

E. A. UEHLING AND G. E. UHLENBECK, *University of Michigan*

(Received February 13, 1933)

The theory of gases in nonstationary states, given by Lorentz and Enskog, is generalized for the quantum statistics to give the hydrodynamical equations and the distribution function in first and second approximation, and formal expressions for the viscosity and heat conductivity coefficients. These results are valid for all statistics and for all degrees of degeneration. Two essential points contribute to this generality: (a) Exact expressions independent of statistics and degeneration can be given for the coordinate and time derivatives of the coefficient A of the equilibrium distribution function in terms of the pressure and temperature gradients and time derivatives, though a closed expression for this coefficient as a function

of v and T is known only in limiting cases; (b) The function W of the general equation of state for ideal gases in all statistics

$$pv = (RT/M)W(v^3T)$$

is adiabatically invariant. Numerical values of the viscosity and heat conductivity coefficients, which should come out of the formal theory on the introduction of special assumptions about the molecular forces, have not yet been obtained. It is our hope that these results, when found, may furnish an experimental test of the existence of Einstein-Bose statistics in real gases, as is required by theory.

INTRODUCTION

§1

One may distinguish broadly two methods of treating the problem of viscosity and heat conductivity of an ideal gas. The first of these is an inexact method according to which an equilibrium distribution function is considered to be descriptive of the state within the gas, subject only to the condition that the five quantities, the density, the temperature, and the three components of mass velocity are functions of position. The conception of the mean free path is fundamental in this theory.

According to the second and more nearly exact method, which is due mainly to Maxwell and Chapman on the one hand, and to Lorentz and Enskog¹ on the other, one recognizes the fact that the above assumption regarding the equilibrium distribution function is not valid, since

the latter does not fulfill the fundamental Boltzmann continuity equation. We propose to generalize this method so as to include the Einstein-Bose and the Fermi-Dirac as well as the Maxwell-Boltzmann statistics.

§2

In this generalization we will follow Lorentz and Enskog, rather than Maxwell and Chapman. An understanding of the method used may be obtained from a consideration of the electron theory of metals of Lorentz.² The essential points in this theory follow.

The fundamental Boltzmann equation in this case, where one assumes the existence of a steady state, the dependence on one coordinate only, and elastic collisions between the electrons and fixed ions with no interaction among the electrons themselves, takes the form:

$$r_x \frac{\partial f}{\partial x} + X \frac{\partial f}{\partial r_x} = nR^2 r \int \{f(r_x' r_y' r_z') - f(r_x r_y r_z)\} \cos \vartheta d\Omega, \quad (1)$$

where ϑ is the angle between the direction of the line of centers in collision and the electron velocity r ; $d\Omega$ is the element of solid angle within which the direction of the line of centers must lie; n is

¹ Maxwell, *Collected Works II*, p. 1; Lorentz, *Theory of Electrons*, Note 29, p. 266, Ges. Abh. I, p. 72, *Vorträge über die kinetische Theorie der Materie und Electricität*, p. 185; Chapman, *Phil. Trans.* **216 A**, 279 (1915); **217 A**, 115

(1916); Enskog, *Kinetische Theorie der Vorgänge in mässig verdünnten Gasen*, *Dissertation*, Upsala, 1917. Also see Jeans, *Dynamical Theory of Gases*, Chapters VIII and IX.

² Lorentz, Reference 1.

the number of ions per unit volume; R is the sum of the radii of the electron and ion; and X is the acceleration due to the external electric field. Primes denote quantities which are to be taken after collision.

In the determination of the distribution function which fulfills this equation one can distinguish the following steps:

(a) *The principle of solution.* One assumes:

$$f = f^{(0)}(1 + \varphi), \tag{2}$$

where $f^{(0)}$ is the equilibrium distribution function, and φ is a small perturbation term. Introducing (2) into (1), and retaining only first order quantities, one obtains, since $f^{(0)}$ is a function only of r :

$$r_x \frac{\partial f^{(0)}}{\partial x} + X \frac{\partial f^{(0)}}{\partial r_x} = nR^2 r f^{(0)} \int (\varphi' - \varphi) \cos \vartheta d\Omega. \tag{3}$$

(b) *Conditions imposed on φ .* Eq. (3) is in an inhomogeneous integral equation of the second kind with a symmetric kernel. Because the homogeneous equation has a solution (namely $\varphi_1 = \text{const.}$), the necessary condition that the inhomogeneous equation has a solution is that the left member of the equation is orthogonal to φ_1 . This condition is identically fulfilled. To make the solution of (3) perfectly definite, one may impose on φ the auxiliary condition:

$$\int \varphi d\Omega = 0. \tag{4}$$

One finds that this implies:

$$\int f^{(0)} \varphi dr_x dr_y dr_z = \int r^2 f^{(0)} \varphi dr_x dr_y dr_z = 0,$$

which means physically, that the density and temperature are determined by the mean values formed with the equilibrium distribution function

$$\frac{\partial f}{\partial t} + D(f) = \int d\phi_1 \int g w(\vartheta g) d\Omega \{ f' f_1' (1 + \theta f) (1 + \theta f_1) - f f_1 (1 + \theta f') (1 + \theta f_1') \}, \tag{6}$$

³ A well-known defect of the Lorentz theory is that it gives no account of the Joulian heat, since only elastic collisions between the electrons and immovable ions are considered. This is probably the reason, also, for the

just as in the equilibrium state.

(c) *Reduction of the left member.* Introducing

$$f^{(0)} = A(x) e^{-h(x)r^2}$$

where $h(x) = m/2kT(x)$, one obtains for the left member:

$$r_x (d \ln A / dx - r^2 dh / dx - 2hX) A e^{-hr^2}. \tag{5}$$

(d) *"Ansatz" for φ and its verification.* The form of the left member suggests the solution:

$$\varphi = r_x \chi(r),$$

which fulfills condition (4). Introducing this expression into the right member of (3), one finds upon integration that the latter becomes proportional to r_x , giving the final result:

$$\chi(r) = \frac{1}{\pi n R^2} \left(r^2 \frac{dh}{dx} - \frac{d \ln A}{dx} + 2hX \right) \frac{1}{r},$$

from which all further conclusions regarding the heat and electric conductivity follow.³

This description is intended to show only the analogy between the method of the Lorentz theory of metals and the generalized Enskog theory of gases. Points (a) to (d) of the Lorentz theory given in §2 correspond to points §5 to §8 in the theory of gases generalized to include the quantum statistics which is to follow. A *strict* analogy does not exist. One would have to consider in the Lorentz theory also nonstationary states, and extend the theory of gases to include also mixtures in order to see the former as a special case of the latter.

THE GENERAL HYDRODYNAMICAL EQUATIONS

§3

For Einstein-Bose and Fermi-Dirac gases in a nonsteady state, one may write the general Boltzmann equation in the form:

following difficulty. If one attempts to find the next approximation to the distribution function, one obtains an integral equation of the same type as (3). But now the left member is *not* orthogonal to the solution of the homo-

where

$$D(f) = r_\alpha(\partial f/\partial x_\alpha) + X_\alpha(\partial f/\partial r_\alpha). \quad (7)$$

In these expressions $r_i(r_x r_y r_z)$ are the three components of the absolute velocity, $X_i(XYZ)$ are the three components of the external force per unit mass, and the usual summation convention has been used.⁴ The function $w(\vartheta g)d\Omega$ represents the effective cross section for a collision which changes the direction of the relative velocity g of two molecules by the angle ϑ , such that this velocity after collision g' lies within an element of solid angle $d\Omega = \sin \vartheta d\vartheta d\varphi$, where φ is the azimuthal angle about g . The subscript 1 denotes functions and variables pertaining to the second molecule in the collision, over which the integration takes place, and the primes denote functions and variables which are to be taken after the collision. The differential $d\phi$ has the usual interpretation:

$$d\phi = VG(m/h)^3 dr_x dr_y dr_z, \quad (8)$$

where G is an eventual weight-factor, and V is included for dimensional reasons, but is to be considered as having the value unity to agree with the meaning of f as giving the number of particles per phase cell in coordinate-momenta space of which the space part has unit volume.

Eq. (6) includes (namely for $\theta=0$) the Boltzmann equation of the classical statistics⁵ as a special case. It differs from the latter in the Einstein-Bose statistics ($\theta=+1$) and in the Fermi-Dirac statistics ($\theta=-1$) only in the "collision" term of the right member. The essential points of difference in this term are: (1) the use of the appropriate "Stoszzahlansatz," and (2) the necessity of determining the transition probability function, $w(\vartheta g)$, quantum-mechanically, and of taking into account the identity of the molecules in this determination, as was first done by N. F. Mott in his theory of collisions between two electrons.⁶ That the "streaming" terms of the left member need not be changed in the quantum theory, has been proved in general by Nordheim

and Kikuchi.⁷ As usual, the principle of microscopic reversibility has been used in the derivation of the collision term in Eq. (6).

Just as in the classical case⁸ one can derive from Eq. (6) a general transport equation for a function $F(xyzr_x r_y r_z t)$. Specializing F to be successively m , mr_x , mr_y , mr_z , and $\frac{1}{2}mr^2$, one obtains the *general hydrodynamical equations*:

$$\left. \begin{aligned} d\rho/dt + \rho(\partial u_\alpha/\partial x_\alpha) &= 0, & a \\ \rho(du_i/dt) &= \rho X_i - \partial p_{i\alpha}/\partial x_\alpha, & b \\ \rho \frac{d(Q/\rho)}{dt} + \frac{\partial q_\alpha}{\partial x_\alpha} &= -p_{\alpha\beta} S_{\alpha\beta}, & c \end{aligned} \right\} \quad (9)$$

where $u_i(uvw)$ and $q_i(q_x q_y q_z)$ are the components of the mass-velocity and heat current, respectively:

$$(a) u_i = \bar{r}_i, \quad (b) q_i = \frac{1}{2}\rho \overline{U_i U^2} \quad (10)$$

and where, furthermore

$$U_i = r_i - u_i; \quad U^2 = U_x^2 + U_y^2 + U_z^2 \quad (11)$$

denotes the relative velocity. The functions p_{ij} and S_{ij} are the components of the stress and the rate of pure strain tensors, respectively:

$$(a) p_{ij} = \rho \overline{U_i U_j}, \quad (b) S_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \quad (12)$$

Finally, Q denotes the energy of heat motion per unit volume:

$$Q = \frac{1}{2}\rho U^2 = \frac{1}{2}(p_{xx} + p_{yy} + p_{zz}) = 3p/2 \quad (13)$$

and d/dt denotes the total time derivative:

$$d/dt = \partial/\partial t + u_\alpha(\partial/\partial x_\alpha). \quad (14)$$

§4

One obtains the hydrodynamical equations in *first approximation* by calculating the ten mean value quantities, (10b), (12a) and (13) with the aid of the equilibrium distribution function $f^{(0)}$. Since the latter depends only on U^2 , one obtains⁹:

$$p_{ij} = p\delta_{ij}, \quad q_i = 0,$$

⁷ Nordheim and Kikuchi, *Zeits. f. Physik* **60**, 652 (1930).

⁸ Compare Enskog, reference 1, pp. 14-19; Jeans, reference 1, Chapter IX.

⁹ The equation: $Q=3p/2$ or $pv=2\epsilon/3$, where ϵ is the energy per unit mass, and v is the specific volume, follows, also, from an application of the general virial theorem to an ideal gas. It is, itself, often called the virial theorem.

geneous equation as a consequence of which the inhomogeneous equation has *no* solution. In the theory of gases one does *not* encounter an analogous difficulty.

⁴ Greek letters are used for dummy indices.

⁵ Compare e.g., Jeans, *Dynamical Theory of Gases*, p. 210.

⁶ Proc. Roy. Soc. **A126**, 259-267 (1930).

whereupon (9) reduces to:

$$\left. \begin{aligned} d\rho/dt + \rho(\partial u_\alpha/\partial x_\alpha) &= 0, & \text{a} \\ \rho(du_i/dt) &= \rho X_i - (\partial p/\partial x_i), & \text{b} \\ \frac{d}{dt} \left(\frac{p}{\rho} \right) &= -\frac{2}{3} \frac{p}{\rho} \frac{\partial u_\alpha}{\partial x_\alpha}. & \text{c} \end{aligned} \right\} \quad (15)$$

The energy equation (15c) can be put into another form by introducing the equation of state:

$$p/\rho = (RT/M)W(T\rho^{-3}), \quad (16)$$

which holds in all statistics. M denotes the molecular weight, ρ is the density, and W is a function of the argument $T\rho^{-3}$ which is a different function for the different statistics, but is in each case an *adiabatic invariant*.¹⁰ The latter property makes it possible to remove W from the differential operator d/dt when (16) is introduced into (15c). Thus the energy equation becomes:

$$\frac{dT}{dt} = -\frac{2}{3}T(\partial u_\alpha/\partial x_\alpha). \quad (15c')$$

where

$$\chi = \varphi/(1 + \theta f^{(0)}) \quad (19)$$

$$I(\chi) = \int d\phi_1 \int g w(\vartheta g) d\Omega \cdot f^{(0)} f_1^{(0)} (1 + \theta f^{(0)'}) (1 + \theta f_1^{(0)'}) (\chi + \chi_1 - \chi' - \chi_1'). \quad (20)$$

One can show that Eq. (18) has the following properties: (a) It is reducible to the form of an inhomogeneous integral equation of the second kind¹²; (b) the kernel of this equation is symmetric; (c) the kernel is invariant with respect to rotations in U_i -space. Furthermore, the operator I has certain properties, which will be required

In Note 1 it will be shown that an expression for the velocity of sound in first approximation, that is, neglecting viscosity and heat conductivity, follows immediately from (15).

THE NONSTEADY STATE DISTRIBUTION FUNCTION

§5. The principle of solution of the Boltzmann equation

In order to proceed with the theory of gases, one needs to know the deviation of the actual distribution function from the equilibrium state. For this determination one must obtain a solution of Eq. (6). As in the Lorentz theory outlined in §2, one assumes a solution of the form:

$$f = f^{(0)}(1 + \varphi), \quad (17)$$

which, upon introduction into Eq. (6) and simplification with the aid of the principle of detailed balancing,¹¹ yields the inhomogeneous integral equation:

$$\partial f^{(0)}/\partial t + D(f^{(0)}) = -I(\chi) \quad (18)$$

later. Using the notation:

$$[F, G] = \int FI(G)d\phi,$$

one finds by the same reasoning as is used in deriving the H -theorem:

$$[F, G] = \frac{1}{4} \int d\phi \int d\phi_1 \int g w(\vartheta g) d\Omega \cdot f^{(0)} f_1^{(0)} (1 + \theta f^{(0)'}) (1 + \theta f_1^{(0)'}) \cdot (F + F_1 - F' - F_1')(G + G_1 - G' - G_1'), \quad (21)$$

from which follows:

$$\left. \begin{aligned} [F, G] &= [G, F], & \text{a} \\ [F, G+H] &= [F, G] + [F, H], & \text{b} \\ [F, bG] &= b[F, G], & \text{c} \\ [F, F] &\cong 0, & \text{d} \end{aligned} \right\} \quad (22)$$

where b is a function independent of all variables of integration.

¹⁰ Uhlenbeck and Uehling, Phys. Rev. **39**, 1014 (1932).

¹¹ This principle follows, as is well known, from the previously assumed principle of microscopic reversibility and a generalized H -theorem. Comp. Nordheim, Proc. Roy. Soc. **A119**, 689 (1928); Pauli, Sommerfeld Festschrift, p. 30.

¹² This reduction is accomplished by a series of transformations of variables, in a manner analogous to that used by Enskog in the classical case (Reference 1, pp. 140-148).

§6. Conditions imposed on φ

Consider the homogeneous equation following from (18):

$$I(\psi) = 0. \quad (18a)$$

Multiplying with $\psi d\phi$ and integrating, one obtains: $[\psi, \psi] = 0$. From the properties of this operator this equality exists only if:

$$\psi + \psi_1 - \psi' - \psi_1' = 0. \quad (23)$$

Eq. (23), according to the number, momentum and energy conservation theorems, has as its solution a linear combination of the functions¹³:

$$\psi_1 = 1; \psi_2 = r_x; \psi_3 = r_y; \psi_4 = r_z; \psi_5 = r^2. \quad (24)$$

In order, therefore, that the inhomogeneous Eq. (18) may have a solution, the left member must be orthogonal to the five functions (24). As consequences of this orthogonality one finds that the five parameters ρ , T , u , v and w on which the equilibrium distribution function $f^{(0)}$ depends, must, for the purpose of solution of Eq. (18), be functions of x , y , z and t which fulfill the hydrodynamical equations in *first* approximation (15).¹⁴ To make the solution of Eq. (18) definite one may impose on φ or χ the five conditions:

$$\int \psi_i f^{(0)} \varphi d\phi = \int \psi_i f^{(0)} (1 + \theta f^{(0)}) \chi d\phi = 0, \quad (i=1, 2, \dots, 5) \quad (25)$$

which interpreted physically express the fact that the parameters ρ , T , u , v and w of the equilibrium distribution function may be interpreted physically as the density, temperature, and the three components of mass velocity, re-

spectively, just as in the equilibrium state. One can show, in a manner analogous to that used by Enskog in the classical case (reference 1, p. 27-31), that if one has determined the arbitrary constants in the general solution of Eq. (18) such that the conditions (25) are fulfilled, at the time $t=0$, they will remain fulfilled for all values of the time.

§7. Introduction of new variables and reduction of the left member

One may introduce the equilibrium distribution function:

$$f^{(0)} = \frac{1}{(1/A) \exp(m/2kT) U^2 - \theta} \quad (26)$$

into the left member of Eq. (18). The five parameters, ρ , T , u , v and w on which this function depends are defined by the equations:

$$\left. \begin{aligned} \rho &= m \int f^{(0)} d\phi, \\ u_i &= \frac{1}{\rho} \int m r_i f^{(0)} d\phi, \\ \epsilon &= \frac{3p}{2\rho} = \frac{3RT}{2M} W(T\rho^{-1}) \\ &= \frac{1}{\rho} \int \frac{1}{2} m U^2 f^{(0)} d\phi. \end{aligned} \right\} \quad (27)$$

Transforming, also, to dimensionless variables $\xi_i (\xi \eta \zeta)$ where $\xi_i = (r_i - u_i) c^{\frac{1}{2}}$; $r^2 = \xi^2 + \eta^2 + \zeta^2$ and $c = m/2kT$, Eq. (18) becomes:

$$\frac{f^{(0)2}}{A e^{-r^2}} \left[\frac{d \ln A}{dt} + \frac{\tau^2}{T} \frac{dT}{dt} + \frac{1}{c^{\frac{1}{2}}} \xi_\alpha \left\{ \frac{\partial \ln A}{\partial x_\alpha} - 2c \left(X_\alpha - \frac{\partial u_\alpha}{\partial t} \right) + \frac{\tau^2}{T} \frac{\partial T}{\partial x_\alpha} \right\} + 2\xi_\alpha \xi_\beta \frac{\partial u_\alpha}{\partial x_\beta} \right] = -I(\chi). \quad (28)$$

Now one may prove, as is done in Note 3, that in all statistics and for all degrees of degeneration the following relations exist:

$$\left. \begin{aligned} \frac{d \ln A}{dt} &= \frac{dW}{dt} + W \left(\frac{1}{\rho} \frac{d\rho}{dt} - \frac{3}{2} \frac{1}{T} \frac{dT}{dt} \right) & \text{a} \\ \frac{\partial \ln A}{\partial x_i} &= \frac{p}{nkT} \left(\frac{1}{p} \frac{\partial p}{\partial x_i} - \frac{5}{2} \frac{1}{T} \frac{\partial T}{\partial x_i} \right) & \text{b} \end{aligned} \right\} \quad (29)$$

Since W is adiabatically invariant, and since it

has been proved that a solution of Eq. (18) exists only if ρ and T fulfill the hydrodynamical equations (15a) and (15c') in first approximation, one finds that $d \ln A / dt$ vanishes. Furthermore, one obtains from (15b) and (29b) the result:

¹³ That (24) are the only solutions of (23), one can prove strictly for spherically symmetric molecules (compare Jeans, Reference 1, p. 25), to which this theory is restricted.

¹⁴ See Note 2 for the proof of this result.

$$\frac{\partial \ln A}{\partial x_i} - 2c \left(X_i - \frac{du_i}{dt} \right) = - \frac{5}{2} \frac{p}{nkT} \frac{1}{T} \frac{\partial T}{\partial x_i}.$$

Introducing also the value of dT/dt from (15c') the equation

$$\frac{f^{(0)2}}{Ae^{-\tau^2}} \left\{ \frac{1}{c^{\frac{1}{2}}} \frac{1}{T} \xi_\alpha \frac{\partial T}{\partial x_\alpha} \left(\tau^2 - \frac{5}{2} \frac{p}{nkT} \right) + \left(\xi_\alpha \xi_\beta - \frac{\tau^2}{3} \delta_{\alpha\beta} \right) \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \right\} = -I(\chi) \quad (30)$$

is obtained.¹⁵

Dimensionless variables and functions will be introduced, also, into the operator $I(\chi)$. One may decompose the transition probability function in the following arbitrary manner

$$w(\vartheta\gamma) = \frac{1}{4} s^2 \cdot \sigma(\gamma) \cdot u(\vartheta\gamma),$$

where

$$g = \gamma(2/c)^{\frac{1}{2}},$$

s is a constant having the dimensions of a length and in the case of spherical molecules being the actual collision radius, $\sigma(\gamma)$, is a dimensionless function, and $u(\vartheta\gamma)$ is a dimensionless probability function representing the scattering into an ele-

ment of solid angle per unit angle divided by the average scattering per unit solid angle. In the case of a classical collision between two spherical molecules the functions σ and u are simply unity. In the case of a classical collision between molecules repelling inversely as the ν th power of the distance, where $\nu > 1$, u is independent of γ , and σ depends on γ and on the temperature T . Finally introducing the variables ξ_i , the differential becomes

$$d\phi_1 = VG(m/h)^3 c^{-\frac{1}{2}} dw_1; \quad dw_1 = d\xi_1 d\eta_1 d\zeta_1.$$

In these variables and functions

$$I(\chi) = (2^{\frac{1}{2}} s^2 A^2 VG/c^2) (m/h)^3 I'(\chi), \quad (31)$$

where

$$I'(\chi) = \frac{1}{4A^2} \int dw_1 \int d\Omega \cdot \gamma \sigma^2(\gamma) u(\vartheta\gamma) (\chi + \chi_1 - \chi' - \chi'_1) \cdot f^{(0)} f_1^{(0)} (1 + \theta f^{(0)'}) (1 + \theta f_1^{(0)'}) \quad (32)$$

One finds that the bracket expression $[F, G]$ defined with the operator I' has the same properties (22) as the expression defined with the operator I .

§8. The "Ansatz" for χ and its verification

Since it is linear, and the integration in $I'(\chi)$ is over only the velocity components ξ_i , Eq. (30) may be decomposed by choosing for the solution:

$$\chi = - \frac{c^{\frac{1}{2}}}{2^{\frac{1}{2}} s^2 A VG} \left(\frac{h}{m} \right)^3 \frac{1}{T} \frac{\partial T}{\partial x_\alpha} \pi_\alpha - \frac{c^2}{2^{\frac{1}{2}} s^2 A VG} \left(\frac{h}{m} \right)^3 \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \pi_{\alpha\beta}, \quad (33)$$

where π_i and $\pi_{ij} = \pi_{ji}$ are nine new unknown functions, which fulfill respectively the nine integral equations:

$$\left. \begin{aligned} \frac{f^{(0)2}}{A^2 e^{-\tau^2}} \xi_i \left(\tau^2 - \frac{5}{2} \frac{p}{nkT} \right) &= I'(\pi_i), & \text{a} \\ \frac{f^{(0)2}}{A^2 e^{-\tau^2}} \left(\xi_i \xi_j - \frac{\tau^2}{3} \delta_{ij} \right) &= I'(\pi_{ij}). & \text{b} \end{aligned} \right\} \quad (34)$$

In a manner analogous to the Lorentz theory

¹⁵ In the classical case, $p = nkT$ and $f^{(0)} = Ae^{-\tau^2}$; the left member of this equation then agrees completely with the result of Enskog. (Reference 1, Eq. 53.)

(see d in §2), one can show that π_i and π_{ij} have the forms:

$$\left. \begin{aligned} \pi_i &= \xi_i \chi_a(\tau), & \text{a} \\ \pi_{ij} &= (\xi_i \xi_j - \tau^2 \delta_{ij}/3) \chi_b(\tau). & \text{b} \end{aligned} \right\} \quad (35)$$

The problem is reduced in this way to the determination of the two unknown functions $\chi_a(\tau)$ and $\chi_b(\tau)$. The procedure differs, however, from that in the Lorentz theory in that it is not possible in this case to obtain closed expressions for these functions. They may be obtained only by a method of successive approximations after definite assumptions regarding the nature of the

molecular interactions have been introduced; i.e., after the functions $\sigma(\gamma)$ and $u(\vartheta\gamma)$ have been specified.

One can prove that the functions π_i and π_{ij} have the forms given by (35) as follows. One verifies that the left members of both (34a and b) are orthogonal to the five functions ψ_i of (24), and, therefore, orthogonal as well to the functions

$$\psi_1=1; \psi_2=\xi; \psi_3=\eta; \psi_4=\zeta; \psi_5=\tau^2, \quad (24a)$$

which as before represent the solutions of the homogeneous equation. The forms of π_i and π_{ij} may be made definite by imposing on both the five conditions:

$$\int \psi_i f^{(0)}(1+\theta f^{(0)})\pi d\omega=0 \quad (36)$$

as consequences of which χ will fulfill conditions (25). As further consequences of conditions (36) Eqs. (34a and b) each have one and only one solution. Finally, one uses the fact that Eqs. (34a and b) have properties analogous to those of Eq. (18) discussed in §5; namely: (a) they are linear integral equations of the second kind, (b) the kernel is symmetric, (c) the kernel is *invariant with respect to rotations in ξ_i -space*. In fact, one can show that:

$$I'(\pi)=k(\tau)\pi(\xi_i)+\int d\omega'\pi(\xi_i')K(\tau\tau'\epsilon), \quad (37)$$

where ϵ is the angle between the two vectors

$$f=f^{(0)}\left[1-\frac{c^{\frac{1}{2}}f^{(0)}e^{\tau^2}}{2^{\frac{1}{2}}S^2A^2VG}\left(\frac{h}{m}\right)^3\frac{1}{T}\frac{\partial T}{\partial x_\alpha}\xi_\alpha\chi_\alpha(\tau)-\frac{c^2f^{(0)}e^{\tau^2}}{2^{\frac{1}{2}}S^2A^2VG}\left(\frac{h}{m}\right)^3\left(\frac{\partial u_\alpha}{\partial x_\beta}+\frac{\partial u_\beta}{\partial x_\alpha}\right)\left(\xi_\alpha\xi_\beta-\frac{\tau^2}{3}\delta_{\alpha\beta}\right)\chi_b(\tau)\right]. \quad (40)$$

This expression reduces to that of Enskog¹⁷ for the Maxwell-Boltzmann statistics in which: (1) the equilibrium distribution function is $f^{(0)}=Ae^{-\tau^2}$; (2) $\chi_\alpha(\tau)$ and $\chi_b(\tau)$ are determined by Eqs. (34a and b) with $p=nkT$, $\theta=0$, and classical values of $\sigma(\gamma)$ and $u(\varphi\gamma)$; (3) account is taken of

¹⁶ A second method is by means of the resolvent of (37). One can show that the resolvent as well as the kernel is a function only of τ , τ' and ϵ . Writing down the formal solutions of (34a and b) and using (38) one finds again that the solutions must have the form (35).

¹⁷ Enskog, Reference 1, Eq. (65), p. 41.

ξ_i and ξ_i' , which have the magnitude τ and τ' . This is the essential point in the proof. One may proceed now in different ways. The most simple method perhaps is verification. This is accomplished when one has proved that integrals of the type:

$$\int d\omega'\xi_i'f(\tau\tau'\epsilon)=\xi_iF(\tau) \quad (38a)$$

and of the type:

$$\int d\omega'\left(\xi_i'\xi_j'-\frac{\tau'^2}{3}\delta_{ij}\right)f(\tau\tau'\epsilon) \\ =\left(\xi_i\xi_j-\frac{\tau^2}{3}\delta_{ij}\right)G(\tau). \quad (38b)$$

The proof of these results can be given geometrically (see Note 4).¹⁶

The auxiliary conditions (36) are fulfilled by (35b) identically, and by (35a) when $\chi_\alpha(\tau)$ fulfills:

$$\int \tau^4 f^{(0)}(1+\theta f^{(0)})\chi_\alpha(\tau)d\tau=0. \quad (39)$$

It is always possible to satisfy this condition by adding to $\chi_\alpha(\tau)$ a suitable constant.

§9. The distribution function

In terms of the unknown functions $\chi_\alpha(\tau)$ and $\chi_b(\tau)$ the nonsteady state distribution function may be written with the aid of Eqs. (17), (19), (33), (35a and b) in the following manner:

the weight factor by which the A of Enskog's equations differs from the A used here.

FORMAL EXPRESSIONS FOR THE VISCOSITY AND HEAT CONDUCTIVITY COEFFICIENTS

§10. The heat conductivity coefficient

In order to obtain this coefficient it will be necessary to derive one of the components of the heat current. By using the definition (10b), the expression (40) for the distribution function, and transforming to dimensionless variables, one obtains

$$q_x = -\lambda(\partial T/\partial x), \quad (41)$$

where:

$$\lambda = \frac{m}{(2c)^{\frac{3}{2}}s^2A^2} \frac{1}{T} \int f^{(0)2} e^{\tau^2} \xi^2 \tau^2 \chi_a(\tau) d\tau w. \quad (42)$$

For the purpose of the numerical calculation of this coefficient, one may transform this expression; first, by adding a term which is identically zero by virtue of the auxiliary conditions on $\chi_a(\tau)$, giving

$$\lambda = \frac{m}{(2c)^{\frac{3}{2}}s^2A^2} \frac{1}{T} \int f^{(0)2} e^{\tau^2} \xi \left(\tau^2 - \frac{5}{2} \frac{p}{nkT} \right) \xi \chi_a(\tau) d\tau w$$

and then, by introducing a simplification obtained when one substitutes for a part of the integrand its value given by the integral Eq. (34a) in $\chi_a(\tau)$. Thus, one arrives at the final result:

$$\lambda = \frac{m}{(2c)^{\frac{3}{2}}s^2} \frac{1}{T} [\xi \chi_a(\tau), \xi \chi_a(\tau)]. \quad (43)$$

That λ is always positive follows from the property (22d) of the bracket expressions.

§11. The viscosity coefficient

In order to obtain this coefficient, one may determine either p_{xy} or the deviation of p_{xx} from p . Using the definitions (12a) and (13), introducing the distribution function (40), and transforming to dimensionless variables, one obtains in the latter case:

$$p_{xx} - p = -\frac{2\mu}{3} \left(2 \frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} - \frac{\partial w}{\partial z} \right), \quad (44)$$

where:

$$\mu = \frac{3m}{2^{\frac{3}{2}}c^{\frac{3}{2}}s^2A^2} \int f^{(0)2} e^{\tau^2} \left(\xi^2 - \frac{\tau^2}{3} \right) \left(\xi^2 - \frac{\tau^2}{3} \right) \chi_b(\tau) d\tau w. \quad (45)$$

By using the integral Eq. (34b) for χ_b , this can be written:

$$\mu = \frac{2m}{2^{\frac{3}{2}}c^{\frac{3}{2}}s^2} \left[\left(\xi^2 - \frac{\tau^2}{3} \right) \chi_b(\tau), \left(\xi^2 - \frac{\tau^2}{3} \right) \chi_b(\tau) \right], \quad (46)$$

from which one finds, as in the case of the heat conductivity coefficient, that the viscosity coefficient is always positive.

In the other case one obtains in the same manner:

$$p_{xy} = -\mu \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right), \quad (47)$$

where:

$$\begin{aligned} \mu &= \frac{2m}{(2c)^{\frac{3}{2}}s^2A^2} \int f^{(0)2} e^{\tau^2} \xi^2 \eta^2 \chi_b(\tau) d\tau w \\ &= \frac{2m}{(2c)^{\frac{3}{2}}s^2} [\xi \eta \chi_b(\tau), \xi \eta \chi_b(\tau)]. \end{aligned} \quad (48)$$

A partial integration of these expressions shows that (46) and (48) are identical.

§12. The hydrodynamical equations in second approximation

The preceding derivation shows that the stress tensor components have the same form in the quantum as in the classical statistics. Eqs. (44) and (47) for these components may be combined in the form:

$$p_{ij} = [p + (2\mu/3)(\partial u_\alpha/\partial x_\alpha)] \delta_{ij} - 2\mu S_{ij}. \quad (49)$$

Introducing these expressions and Eq. (41) for the heat current components into the general hydrodynamical Eq. (9), one obtains the hydrodynamical equations with viscosity and heat conduction:

$$\left. \begin{aligned} & d\rho/dt + \rho(\partial u_\alpha/\partial x_\alpha) = 0, & \text{a)} \\ & \rho \frac{du_i}{dt} = \rho X_i - \frac{\partial p}{\partial x_i} + \frac{1}{3} \frac{\partial^2 u_\alpha}{\partial x_i \partial x_\alpha} + \mu \frac{\partial^2 u_i}{\partial x_\alpha \partial x_\alpha} - \frac{2}{3} \frac{\partial u_\alpha}{\partial x_\alpha} \frac{\partial \mu}{\partial x_i} + 2S_{i\alpha} \frac{\partial \mu}{\partial x_\alpha}, & \text{b)} \\ & \frac{3}{2} \rho \frac{d(p/\rho)}{dt} - \frac{\partial}{\partial x_\alpha} \left(\lambda \frac{\partial T}{\partial x_\alpha} \right) = -pS_{\alpha\alpha} + 2\mu(S_{\alpha\beta}S_{\alpha\beta} - \frac{1}{3}S_{\alpha\alpha}^2). & \text{c)} \end{aligned} \right\} \quad (50)$$

Ordinarily μ may be considered as a constant, since the variations in T and ρ , on which μ depends,¹⁸ are generally small. When this is the case, the last two terms of Eq. (50b) vanish, and this equation then takes the usual form.¹⁹ Introducing $Q=3p/2$ into the energy Eq. (50c), one finds that it gives the rate of increase of heat energy per unit volume due to: (a) conduction of heat from adjacent elements, (b) the work done per unit of time by the internal (scalar) pressure, and (c) the work done in the distortion of the volume element.

§13. Conclusion

The formal part of the theory is now completed. To proceed further, and thus obtain explicit expressions for the viscosity and heat conductivity coefficients as functions of the temperature and density, one must introduce special assumptions regarding the molecular forces. With the introduction of these assumptions, the transition probability function $w(\vartheta\gamma)$ may be determined from the quantum-mechanical collision theory, whereupon the functions $\sigma(\gamma)$ and $u(\vartheta\gamma)$ of the integral equations are completely specified. The integral Eqs. (34) may be solved then numerically. Enskog has developed a method of solution in the classical case which may be extended, also, to the quantum statistics. These questions will be considered in a following paper.

NOTE 1

In order to derive the equation for the velocity of sound from (15), one assumes that the conditions are such that the velocity components and the deviation of the density ρ from its equilibrium value are small quantities of the first order, and that no outside forces exist. Then the density may be written in terms of a condensation factor s : $\rho = \rho_0(1+s)$, where ρ_0 is its equilibrium value. Retaining only quantities of the first order (15a and b) become:

$$\partial s / \partial t = -\partial u_\alpha / \partial x_\alpha, \quad (51)$$

$$\rho_0(\partial u_i / \partial t) = -\partial p / \partial x_i \cong -K(\partial s / \partial x_i), \quad (52)$$

$$\int \psi_i \left[\frac{df^{(0)}}{dt} - \frac{\partial f^{(0)}}{\partial U_\alpha} \frac{du_\alpha}{dt} + U_\alpha \frac{\partial f^{(0)}}{\partial x_\alpha} - U_\beta \frac{\partial f^{(0)}}{\partial U_\alpha} \frac{\partial u_\alpha}{\partial x_\beta} + X_\alpha \frac{\partial f^{(0)}}{\partial U_\alpha} \right] d\phi = 0 \quad (i=1, 2, \dots, 5). \quad (58)$$

If these conditions are valid for the five ψ_i of (24), they must be valid, also, for ψ_i equal to m , mU_x , mU_y , mU_z , and mU^2 . Substituting these values successively into this

¹⁸ Only in the classical case is μ independent of ρ .

¹⁹ See Lamb, *Hydrodynamics*, Fifth Edition, p. 546.

where K is the coefficient of volume elasticity $\rho(d\rho/d\rho)$. Eliminating u_i or s , one obtains the wave equation for s or u_i with the velocity:

$$C^2 = K/\rho_0 = (dp/d\rho)_{\rho=\rho_0}. \quad (53)$$

Now assuming that the frequency is sufficiently high so that one may neglect heat conduction, this differential quotient may be taken under strictly adiabatic conditions. The first order energy equation gives such a determination of this expression. Under the conditions assumed it becomes:

$$\left(\frac{p}{\rho}\right) \frac{\partial u_\alpha}{\partial x_\alpha} = -\frac{3}{2} \frac{\partial}{\partial t} \left(\frac{p}{\rho}\right). \quad (54)$$

Now using Eq. (51), integrating, and solving for p , one obtains:

$$\bar{p} = \frac{1}{3}(\bar{p}/\rho)_0 \rho_0 (1 + 2\rho/\rho_0), \quad (55)$$

from which follows:

$$C^2 = (dp/d\rho)_{\rho=\rho_0} = (5/3)p_0/\rho_0 \quad (56)$$

in accordance with the thermodynamic calculation of $(dp/d\rho)_{\text{adliab.}}$ ²⁰

NOTE 2

From the theory of integral equations the conditions:

$$\int \psi_i [\partial f^{(0)} / \partial t + D(f^{(0)})] d\phi = 0 \quad (i=1, 2, \dots, 5) \quad (57)$$

must exist in order that the inhomogeneous Eq. (18) may have a solution. This follows, also, upon multiplying both sides of (18) by $\psi_i d\phi$ and integrating. The right member then becomes $[\psi_i, \chi]$ which is zero according to (21) and (23).

In Eq. (57) $f^{(0)}$ represents the equilibrium distribution function in the six-dimensional phase space (x_i, r_i) . Since it is a function only of the relative velocities, $U_i = r_i - u_i$, it is convenient to change to axes which move with the volume-element of the gas. The differential quotients then become:

$$\begin{aligned} \frac{\partial f^{(0)}}{\partial t} &= \frac{\partial f^{(0)}}{\partial t} - \frac{\partial u_\alpha}{\partial t} \frac{\partial f^{(0)}}{\partial U_\alpha}, \\ \frac{\partial f^{(0)}}{\partial x_i} &= \frac{\partial f^{(0)}}{\partial x_i} - \frac{\partial u_\alpha}{\partial x_i} \frac{\partial f^{(0)}}{\partial U_\alpha}, \\ \frac{\partial f^{(0)}}{\partial r_i} &= \frac{\partial f^{(0)}}{\partial U_i}, \end{aligned}$$

and Eq. (57) may be written, omitting the primes:

equation, and using (27), one obtains the first order hydrodynamical Eqs. (15).

²⁰ Compare Uhlenbeck and Uehling, *Phys. Rev.* **39**, 1014 (1932).

NOTE 3

From the definitions (27) one obtains

$$\left. \begin{aligned} n = \rho/m &= VG(2\pi mkT/h^2)^{3/2} F_{3/2}, & \text{a) } \\ p = \frac{2}{3}Q &= \frac{2}{3}\epsilon\rho = VGkT(2\pi mkT/h^2)^{3/2} F_{5/2}, & \text{b) } \end{aligned} \right\} \quad (59)$$

where F_s is the Sommerfeld integral:

$$F_s(A) = \frac{1}{\Gamma(s+1)} \int_0^\infty f^{(0)}(z) z^s dz = \frac{1}{\Gamma(s+1)} \int_0^\infty \frac{z^s dz}{(1/A)e^z - \theta}$$

$$z = \tau^2 = (m/2kT)U^2.$$

The result:

$$p/nkT = F_{5/2}/F_{3/2} \quad (60)$$

follows as an immediate consequence of these equations. Also, from the definition of F_s , one obtains the relation:

$$A(dF_s/dA) = F_{s-1}. \quad (61)$$

Considering p and T as functions of the time and the coordinates, one obtains from (59b) the equation

$$\frac{dF_{5/2}}{dt} = F_{5/2} \left(\frac{1}{p} \frac{dp}{dt} - \frac{5}{2} \frac{1}{T} \frac{dT}{dt} \right).$$

On the other hand, Eq. (61) gives:

$$\frac{dF_{5/2}}{dt} = A \frac{d \ln A}{dt} \cdot \frac{dF_{5/2}}{dA} = F_{3/2} \frac{d \ln A}{dt}.$$

Combining these results and using the equation of state (16), one obtains Eq. (29a). In a similar manner one obtains Eq. (29b).

NOTE 4

Interpret $f(\tau\tau'\epsilon)$ as a density distribution in the ξ_i' -space. (See Fig. 1.) This function will have rotational symmetry around the axis OP , the direction of τ , and it will depend only on this direction and not on the special choice of the coordinate axes ξ_i' . To prove (38a) we remark that the left member represents the coordinates of the center of gravity, which, because of the rotational symmetry, must lie on the line OP . Therefore these coordinates, and accordingly the left member of (38a) must be proportional to ξ_i . Since $f(\tau\tau'\epsilon)$ is invariant with respect to rotations of the ξ_i' axis, the proportionality factor must be a function only of τ .

In order to prove (38b) one may consider the integral

$$\int dw' \xi_i' \xi_j' f(\tau\tau'\epsilon) = A_{ij}$$

as representing the moments and products of inertia of the density function $f(\tau\tau'\epsilon)$ in the ξ_i' -space. Because of rotational symmetry, the ellipsoid of inertia is a rotational ellipsoid about the axis OP . Taking O as the center of this ellipsoid, and p and q as the lengths of the main axes, one may write for its equation

$$OR^2/p^2 + RQ^2/q^2 = 1.$$

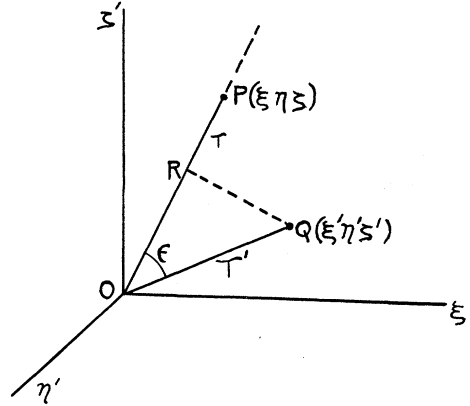


FIG. 1.

Designating the direction cosines of OP by $\lambda_i(\lambda_1\lambda_2\lambda_3)$ one obtains $OR = \lambda_\alpha \xi_\alpha'$, whereupon the equation of the ellipsoid becomes, since $RQ^2 = OQ^2 - OR^2$

$$\left(\lambda_\alpha \lambda_\beta + \frac{p^2}{q^2 - p^2} \delta_{\alpha\beta} \right) \xi_\alpha' \xi_\beta' = \frac{p^2 q^2}{q^2 - p^2}.$$

But the equation of the inertial ellipsoid is also

$$A_{\alpha\beta} \xi_\alpha' \xi_\beta' = \text{const.}$$

Therefore

$$\int dw' \xi_i' \xi_j' f(\tau\tau'\epsilon) \sim \lambda_i \lambda_j + \frac{p^2}{q^2 - p^2} \delta_{ij}$$

$$\sim \xi_i \xi_j + \frac{p^2}{q^2 - p^2} \tau^2 \delta_{ij}$$

$$\int dw' \left(\xi_i \xi_j - \frac{\tau^2}{3} \delta_{ij} \right) f(\tau\tau'\epsilon) \sim \left(\xi_i \xi_j - \frac{\tau^2}{3} \delta_{ij} \right)$$

and the proportionality factor as before can depend only on τ .