

## The Statistical Mechanical Theory of Transport Processes II. Transport in Gases

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## The Statistical Mechanical Theory of Transport Processes

## II. Transport in Gases

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By means of the methods developed in the first paper of this series, SMTI, the Maxwell-Boltzmann integro-differential equation, underlying the well-developed Chapman-Enskog theory of transport phenomena in gases of low density, is derived from the principles of statistical mechanics. The derivation supplements and clarifies the usual physical argument employed to establish this important equation.

THE molecular theory of transport in gases of low density is based upon the Maxwell-Boltzmann integro-differential equation, the consequences of which have been developed by Chapman, Enskog, and other investigators.<sup>1</sup> Rigorous mathematical methods, due principally to Enskog, applied to the solution of the Maxwell-Boltzmann equation, have yielded adequate and detailed theories of diffusion, viscous flow, heat conduction, and related phenomena in gases of sufficiently low density to be amenable to binary collision analysis. Little remains to be done along these lines.

The Maxwell-Boltzmann equation is customarily derived by means of a physical argument which, though plausible, leaves certain points rather obscure. The passage from "fine-grained" to "coarse-grained" distribution functions is glossed over and the role of multiply periodic states of motion is not clarified. In order to complete the molecular theory of transport in gases, an analytical derivation of the Maxwell-Boltzmann integro-differential equation from the principles of statistical mechanics is much to be desired. We shall here undertake such a derivation on the basis of the statistical mechanical theory of transport processes outlined in the first paper of this series,<sup>2</sup> SMTI.

We begin with Liouville's equation,

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{l=1}^N \left\{ \frac{\mathbf{p}_l}{m_l} \cdot \nabla_{\mathbf{R}_l} f^{(N)} + (\mathbf{X}_l + \mathbf{F}_l) \cdot \nabla_{\mathbf{p}_l} f^{(N)} \right\} = 0, \quad (1)$$

$$\mathbf{F}_l = \sum_{i=1}^N \mathbf{F}_{il},$$

for the distribution function  $f^{(N)}$  in the phase space  $(\mathbf{p}_1, \mathbf{p}_N, \mathbf{R}_1, \mathbf{R}_N)$  of systems of  $N$  molecules. Here  $\mathbf{X}_l$  is the external force acting on molecule  $l$  and  $\mathbf{F}_l$ , the total intermolecular force, assumed the sum of contributions  $\mathbf{F}_{il}$ , each depending only on the relative configuration of molecules  $i$  and  $l$ . The distribution function  $f_i^{(1)}$  in the 6-phase space of an individual molecule is given by

$$f_i^{(1)}(\mathbf{p}_i, \mathbf{R}_i; t) = \int \int f^{(N)}(\mathbf{p}_i, \mathbf{R}_i, \mathbf{P}, \mathbf{Q}; t) d\mathbf{P} d\mathbf{Q}, \quad (2)$$

where the integration extends over  $(\mathbf{P}, \mathbf{Q})$  the residual phase space of the other  $N-1$  molecules of the system. The distribution function  $\bar{f}_i^{(1)}$  averaged over an interval of time  $\tau$  subsequent to the instant  $t$  is defined by the relation,

$$\bar{f}_i^{(1)}(\mathbf{p}_i, \mathbf{R}_i; t) = \frac{1}{\tau} \int_0^\tau f_i^{(1)}(\mathbf{p}_i, \mathbf{R}_i; t+s) ds. \quad (3)$$

<sup>1</sup> See Chapman and Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, 1939).

<sup>2</sup> J. G. Kirkwood, *J. Chem. Phys.* **14**, 180 (1946).

It is this distribution function  $\bar{f}_i^{(1)}$ , "coarse-grained" in time, which we shall find to satisfy the Maxwell-Boltzmann equation when the influence of collisions involving more than two molecules is neglected and  $\tau$  is selected as large relative to the duration of a representative collision. We surmise that an alternative description based upon a distribution function "coarse-grained" in phase space<sup>3</sup> might be constructed, but such a description is not necessary.

Integration of both sides of Eq. (1) over the residual phase space ( $\mathbf{P}$ ,  $\mathbf{Q}$ ) of all molecules except  $i$  and construction of the time average lead to the following equations, Eqs. (49) and (51) of SMTI, for the distribution function  $\bar{f}_i^{(1)}$ ,

$$\begin{aligned} \frac{\partial \bar{f}_i^{(1)}}{\partial t} + \frac{\mathbf{p}_i}{m_i} \cdot \nabla_{\mathbf{R}_i} \bar{f}_i^{(1)} + \mathbf{X}_i \cdot \nabla_{\mathbf{p}_i} \bar{f}_i^{(1)} &= \sum_{l=1}^N N_l \nabla_{\mathbf{p}_i} \cdot \boldsymbol{\Omega}_{li}^{(1)}, \\ \nabla_{\mathbf{p}_i} \cdot \boldsymbol{\Omega}_{li}^{(1)} &= \int \cdots \int (\nabla_{\mathbf{p}_i} \cdot \mathbf{K}_{li}) f_i^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}; t) f_l^{(1)}(\mathbf{p}_{l0}, \mathbf{R}_{l0}; t) d\mathbf{p}_{i0} d\mathbf{R}_{i0} d\mathbf{p}_{l0} d\mathbf{R}_{l0}, \\ \mathbf{K}_{li} &= -\frac{1}{\tau} \int_0^\tau \int \mathbf{F}_{li}(t+s) \delta(\mathbf{p}_{i0} + \Delta \mathbf{p}_i - \mathbf{p}_i) \delta(\mathbf{R}_{i0} + \Delta \mathbf{R}_i - \mathbf{R}_i) (1 + \vartheta_{li}) \\ &\quad \times f^{(2/N)}(\mathbf{p}_{i0} \cdots \mathbf{R}_{l0}/\mathbf{P}_0, \mathbf{Q}_0; t) d\mathbf{P}_0 d\mathbf{Q}_0 ds, \\ (1 + \vartheta_{li}) &= \frac{f_{il}^{(2)}(\mathbf{p}_{i0} \cdots \mathbf{R}_{l0}; t)}{f_i^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}; t) f_l^{(1)}(\mathbf{p}_{l0}, \mathbf{R}_{l0}; t)}, \end{aligned} \quad (4)$$

where the symbols have the same significance as in SMTI.  $f^{(2/N)}(\mathbf{p}_{i0} \cdots \mathbf{R}_{l0}/\mathbf{P}_0, \mathbf{Q}_0; t)$  is the relative probability density in the residual phase space ( $\mathbf{P}_0$ ,  $\mathbf{Q}_0$ ) of the remaining  $N-2$  molecules, if the specified pair,  $i$  and  $l$ , are situated at the point,  $\mathbf{p}_{i0}$ ,  $\mathbf{R}_{i0}$ ,  $\mathbf{p}_{l0}$ ,  $\mathbf{R}_{l0}$ , in the phase space of that pair. The correlation function in pair space,  $(1 + \vartheta_{li})$ , was denoted by  $\varphi_{li}$  in STMI. If  $\vartheta_{li}$  is a short range function of the intermolecular distance in a sense presently to be made more precise, that part of  $\mathbf{K}_{li}$  arising from  $\vartheta_{li}$  makes negligible contribution to  $\boldsymbol{\Omega}_{li}^{(1)}$  for sufficiently large  $\tau$ .

We shall assume that the force  $\mathbf{F}_{li}$  exerted by molecule  $l$  on molecule  $i$  has a finite range  $R_0$ , vanishing for intermolecular distances  $R_{li}$  greater than  $R_0$ . For short range intermolecular forces of the van der Waals type, this is not an essential limitation, since an  $R_0$  of molecular order of magnitude may be chosen beyond which such intermolecular forces are of negligible magnitude. If for relative initial configurations of the pair  $il$ , for which  $\mathbf{F}_{li}$  differs from zero in the subsequent interval  $\tau$ , the probability of configurations of the remaining  $N-2$  molecules, for which their contribution to the force on  $i$  also differs from zero, is negligible, it is sufficient to use the *binary collision* approximation,

$$\partial(\Delta \mathbf{p}_i)/\partial s = \mathbf{F}_{li} \quad (5)$$

in the evaluation of the integrals  $\mathbf{K}_{li}$  and  $\nabla_{\mathbf{p}_i} \cdot \boldsymbol{\Omega}_{li}^{(1)}$ . The condition for the validity of the approximation is that the ratio of the probability that three or more molecules are situated in region of 3-configuration space, of linear dimension of the order of magnitude of the range of intermolecular force  $R_0$ , to the probability that two molecules are situated in the region, be zero. For distributions departing but slightly from statistical equilibrium, this condition is normally fulfilled in the limit of zero density (the assumption of *molecular chaos*). If we make the additional assumption that  $f_i^{(1)}$  and  $f_l^{(1)}$  have only macroscopic dependence on  $\mathbf{R}_i$  and  $\mathbf{R}_l$ ,

$$|\nabla_{\mathbf{R}_i} \log f_i^{(1)}| = 0(1/L_i), \quad |\nabla_{\mathbf{R}_l} \log f_l^{(1)}| = 0(1/L_l), \quad (6)$$

where  $L_i$  and  $L_l$  are macroscopic lengths large relative to the range of intermolecular force, then to terms of order  $0(R_0/L_i)$ , we may replace  $\delta(\mathbf{R}_{i0} + \Delta \mathbf{R}_i - \mathbf{R}_i)$  by  $\delta(\mathbf{R}_{i0} - \mathbf{R}_i)$  in the integral defining  $\mathbf{K}_{li}$  and  $\mathbf{R}_{l0}$  by  $\mathbf{R}_{i0}$  as the configurational argument of  $f_l^{(1)}$  in the integral defining  $\nabla_{\mathbf{p}_i} \cdot \boldsymbol{\Omega}_{li}^{(1)}$ , Eq. (4).

<sup>3</sup> See Tolman, *Statistical Mechanics* (Oxford University Press, 1938), Chapter VI, Oxford VI.

We now proceed to evaluate  $\mathbf{K}_{il}$  and  $\nabla_{\mathbf{p}_i} \cdot \Omega_{il}^{(1)}$  of Eq. (4) with the use of Eq. (5) and the other assumptions stated in the preceding paragraph. Changing configuration variables from  $\mathbf{R}_{i0}$  and  $\mathbf{R}_{l0}$  to  $\mathbf{R}_{i0}$  and  $\mathbf{R}_{il}^0$ , the relative configuration of  $i$  and  $l$ , and using the properties of the delta functions  $\delta(\mathbf{p}_{i0} + \Delta\mathbf{p}_i - \mathbf{p}_i)$  and  $\delta(\mathbf{R}_{i0} - \mathbf{R}_i)$ , we obtain from Eqs. (4) and (5),

$$\begin{aligned} \nabla_{\mathbf{p}_i} \cdot \Omega_{il}^{(1)} &= \int \int \int \psi_{li} f_i^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_i; t) f_l^{(1)}(\mathbf{p}_{l0}, \mathbf{R}_i; t) d\mathbf{p}_{i0} d\mathbf{p}_{l0} d\mathbf{R}_{il}^0 / \tau, \\ \psi_{li} &= (1 + \vartheta_{li}) \int_0^\tau \frac{\partial(\Delta\mathbf{p}_i)}{\partial s} \cdot \nabla_{\Delta\mathbf{p}_i} \delta(\mathbf{p}_{i0} + \Delta\mathbf{p}_i - \mathbf{p}_i) ds \\ &= (1 + \vartheta_{li}) \{ \delta(\mathbf{p}_{i0} + \Delta\mathbf{p}_i(\tau) - \mathbf{p}_i) - \delta(\mathbf{p}_{i0} - \mathbf{p}_i) \}, \end{aligned} \quad (7)$$

where the integration of  $f^{(2/N)}$  over the residual configuration space  $(\mathbf{P}_0, \mathbf{Q}_0)$  has been carried out to give unity, since, by Eq. (5), the other factors of the integrand of the expression defining  $\mathbf{K}_{il}$  are independent of  $\mathbf{P}_0$  and  $\mathbf{Q}_0$ , depending only on the Lagrange coordinates of the pair  $il$ , and  $f^{(2/N)}$  is normalized to unity.

If the integral,  $\int \vartheta_{li} d\mathbf{R}_{il}^0$ , is bounded, it is possible to choose  $\tau$  of sufficient magnitude to make contributions to  $\nabla_{\mathbf{p}_i} \cdot \Omega_{il}^{(1)}$ , arising from the deviation  $\vartheta_{li}$ , of the pair correlation function from unity, as small as desired, and we may write,

$$\begin{aligned} \nabla_{\mathbf{p}_i} \cdot \Omega_{il}^{(1)} &= \int \int \int \{ \delta(\mathbf{p}_i' - \mathbf{p}_i) - \delta(\mathbf{p}_{i0} - \mathbf{p}_i) \} f_i^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_i; t) f_l^{(1)}(\mathbf{p}_{l0}, \mathbf{R}_i; t) d\mathbf{p}_{i0} d\mathbf{p}_{l0} d\mathbf{R}_{il}^0 / \tau + O(\tau_k / \tau), \\ \mathbf{p}_i' &= \mathbf{p}_i + \Delta\mathbf{p}_i(\tau) \end{aligned} \quad (8)$$

where  $\tau_k$  is a time interval of finite magnitude determined by the correlation integral,  $\int \vartheta_{li} d\mathbf{R}_{il}^0$ . Since the initial distribution is arbitrary there is no *a priori* reason for  $\vartheta_{il}$  to be short range in the sense that the correlation integral is finite, but it may generally be expected to be so for distributions departing but slightly from statistical equilibrium. The requirement that it be so may be regarded as an auxiliary part of the assumption of *molecular chaos* which must be satisfied for the present analysis to be valid. We shall presently show that the volume in relative configuration space for which  $\Delta\mathbf{p}_i(\tau)$  is non-vanishing becomes proportional to  $\tau$  and that  $\nabla_{\mathbf{p}_i} \cdot \Omega_{il}^{(1)}$  becomes independent of  $\tau$  for sufficiently large  $\tau$ .

We now need to consider in detail the solutions of Eq. (5), the equation of motion for a binary collision. Since these solutions are, of course, well known,<sup>1</sup> only the results will be summarized. The reduced mass  $m_{il}$  and the relative momentum  $\mathbf{p}_{il}^0$  are defined as

$$\begin{aligned} 1/m_{il} &= 1/m_i + 1/m_l, \\ \mathbf{p}_{il} &= \frac{m_{il}}{m_l} \mathbf{p}_l - \frac{m_{il}}{m_i} \mathbf{p}_i. \end{aligned} \quad (9)$$

Pairs for which the initial Lagrange coordinate  $R_{il}^0$  is greater than the range of intermolecular force occupy aperiodic orbits. The relative momentum remains constant and equal to  $\mathbf{p}_{il}^0$  until a sphere of radius  $R_0$  with origin, say in molecule  $i$ , is penetrated. If the initial configuration allows the penetration of this sphere, the collision is completed in a time  $\tau_c$ , dependent on the collision parameters, the relative momentum receives a finite increment,  $\Delta\mathbf{p}^*$ , and subsequently remains constant and equal to  $\mathbf{p}_{il}'$ . The scalar magnitude  $p_{il}'$  is equal to  $p_{il}^0$ . By conservation of total linear momentum,  $\mathbf{p}_{i0}$  and  $\mathbf{p}_{l0}$  experience increments  $-\Delta\mathbf{p}^*$  and  $+\Delta\mathbf{p}^*$ , respectively. Summarizing, we have

$$\begin{aligned} \Delta\mathbf{p}^* &= \mathbf{p}_{il}' - \mathbf{p}_{il}^0, \quad \Delta\mathbf{p}_i = -\Delta\mathbf{p}_l = \Delta\mathbf{p}^*, \quad \Delta\mathbf{p}^* = 2p_{il}^0 \cos(\chi/2)\mathbf{e}, \\ \chi/2 &= \int_a^\infty \frac{b p_{il}^0 dR/R^2}{[(1 - b^2/R^2)p_{il}^0{}^2 - 2m_{il}V_{il}(R)]^{1/2}}, \quad b p_{il}^0 = |\mathbf{R}_{il}^0 \times \mathbf{p}_{il}^0|, \end{aligned} \quad (10)$$

where  $a$  is the greatest positive root of the equation

$$(1 - b^2/a^2)p_{il}^2 - 2m_{il}V_{il}(a) = 0.$$

$V_{il}$  is the potential of the intermolecular force,  $\mathbf{e}$  is a unit vector in the direction of the apse line drawn from molecule  $i$  to the orbit perihelion, and  $b$  is the impulse parameter.

For certain regions of the relative configuration space, the molecules occupy aperiodic orbits only partially traversed in the interval  $\tau$ , or multiply periodic orbits with bounded  $\Delta\mathbf{p}_i$ . We now proceed to specify the several regions more precisely. To do this we select a cylindrical coordinate system in the relative Lagrange configuration space  $(z, b, \epsilon)$  with origin in molecule  $i$  and  $z$  axis antiparallel to  $\mathbf{p}_{il}^0$ . The radial coordinate  $b$  is the impulse parameter and  $\epsilon$  its azimuth. Unless the conditions,

$$(R_0^2 - b^2)^{\frac{1}{2}} \leq z \leq (p_{il}^0/m_{il})\tau + (R_0^2 - b^2)^{\frac{1}{2}}, \quad 0 \leq b \leq R_0, \quad (11)$$

are satisfied, the sphere  $R_0$  is not penetrated in the interval  $\tau$ , the momentum increment  $\Delta\mathbf{p}_i$  remains zero, and the integrand, Eq. (8), vanishes. For those coordinates lying in filaments of volume,

$$(p_{il}^0/m_{il})(\tau - \tau_c)bdbd\epsilon, \quad (R_0^2 - b^2)^{\frac{1}{2}} \leq z \leq (p_{il}^0/m_{il})(\tau - \tau_c) + (R_0^2 - b^2)^{\frac{1}{2}}, \quad (12)$$

a complete collision is experienced in  $\tau$  with momentum increments given by Eq. (10). In filaments of volume,

$$(p_{il}^0/m_{il})\tau_c bdbd\epsilon, \quad (p_{il}^0/m_{il})(\tau - \tau_c) + (R_0^2 - b^2)^{\frac{1}{2}} < z \leq (p_{il}^0/m_{il})\tau + (R_0^2 - b^2)^{\frac{1}{2}}, \quad (13)$$

partially completed collisions occur in the interval  $\tau$ . In filaments of volume,

$$2(R_0^2 - b^2)^{\frac{1}{2}}bdbd\epsilon, \quad -(R_0^2 - b^2)^{\frac{1}{2}} \leq z < +(R_0^2 - b^2)^{\frac{1}{2}}, \quad (14)$$

within the sphere  $R_0$ , partially completed collisions may be completed or multiply periodic orbits may be traversed in the interval  $\tau$ . Possible singular behavior being excluded, the integrand of Eq. (8) remains finite for the regions specified by Eqs. (13) and (14).

Carrying out the configurational integration in Eq. (8) with the aid of Eqs. (12), (13), and (14), we obtain,

$$\nabla_{\mathbf{p}_i} \cdot \mathbf{\Omega}_{li}^{(1)} = \int \dots \int \frac{p_{il}^0}{m_{il}} \{ \delta(\mathbf{p}_i' - \mathbf{p}_i) - \delta(\mathbf{p}_{i0} - \mathbf{p}_i) \} f_l^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_i; t) f_l^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_i; t) d\mathbf{p}_{i0} d\mathbf{p}_{i0} bdbd\epsilon + 0(\bar{\tau}_c/\tau),$$

$$\mathbf{p}_i' = \mathbf{p}_{i0} - \Delta\mathbf{p}^*, \quad (15)$$

where  $\bar{\tau}_c$  is a finite time of the order of magnitude of the mean collision duration or of  $\tau_c$ , whichever is the greater. Thus if  $\tau$  is selected large relative to  $\bar{\tau}_c$ , only completed collisions in aperiodic orbits contribute to  $\nabla_{\mathbf{p}_i} \cdot \mathbf{\Omega}_{li}^{(1)}$ . Since incomplete collisions and motion in multiply periodic orbits correspond to regions of relative configuration space of finite volume independent of  $\tau$ , their contributions may be made as small as desired.

It should be remarked that  $\tau$  cannot be allowed to approach infinity, since for systems confined to a finite domain of phase space, there will exist Poincaré cycle periods within which each orbit will be traversed in the reverse sense to any desired degree of accuracy, canceling its initial contribution to  $\nabla_{\mathbf{p}_i} \cdot \mathbf{\Omega}_{li}^{(1)}$ . The thermodynamic irreversibility implied by the non-vanishing of the right-hand side of Eq. (15) would then fail.

In order to evaluate the right-hand side of Eq. (15), it is necessary to change variables in the term involving  $\delta(\mathbf{p}_i' - \mathbf{p}_i)$  from  $\mathbf{p}_{i0}$ ,  $\mathbf{p}_{i0}$  to  $\mathbf{p}_i'$  and  $\mathbf{p}_i'$  where

$$\mathbf{p}_i' = \mathbf{p}_{i0} - \Delta\mathbf{p}^*, \quad \mathbf{p}_i' = \mathbf{p}_{i0} + \Delta\mathbf{p}^*. \quad (16)$$

The Jacobian of this transformation is easily shown to be unity. The second term of the integral may be evaluated at once. When the common symbol  $\mathbf{p}_i$  is assigned to the remaining momentum

variables of integration,  $\mathbf{p}_i'$  and  $\mathbf{p}_{i0}$ , the two terms combine to yield,

$$\begin{aligned} \nabla_{\mathbf{p}_i} \cdot \mathbf{\Omega}_{i_i}^{(1)} = & \int_0^{2\pi} \int_0^{R_0} \int \frac{p_{il}}{m_{il}} \{ f_i^{(1)}(\mathbf{p}_i + \Delta \mathbf{p}^*, \mathbf{R}_i; t) f_i^{(1)}(\mathbf{p}_i - \Delta \mathbf{p}^*, \mathbf{R}_i; t) \\ & - f_i^{(1)}(\mathbf{p}_i, \mathbf{R}_i; t) f_i^{(1)}(\mathbf{p}_l, \mathbf{R}_i; t) \} d\mathbf{p}_l b d b d \epsilon, \quad (17) \\ p_{il} = & |\mathbf{p}_l/m_l - \mathbf{p}_i/m_i| m_{il}, \end{aligned}$$

with the neglect of terms,  $0(\bar{\tau}_c/\tau)$ . Substitution of the expressions, Eq. (17), into Eq. (4) and time averaging of both sides over the interval  $\tau$  gives

$$\begin{aligned} \frac{\partial \bar{f}_i^{(1)}}{\partial t} + \frac{\mathbf{p}_i}{m_i} \cdot \nabla_{\mathbf{R}_i} \bar{f}_i^{(1)} + \mathbf{X}_i \cdot \nabla_{\mathbf{p}_i} \bar{f}_i^{(1)} = & \sum_{l=1}^{\nu} N_l \int_0^{2\pi} \int_0^{R_0} \int \frac{p_{il}}{m_{il}} \{ \overline{f_i^{(1)*} f_l^{(1)*}} - \overline{f_i^{(1)} f_l^{(1)}} \} d\mathbf{p}_l b d b d \epsilon, \\ f_i^{(1)*} = & f_i^{(1)}(\mathbf{p}_i + \Delta \mathbf{p}^*, \mathbf{R}_i; t), \quad f_l^{(1)*} = f_l^{(1)}(\mathbf{p}_l - \Delta \mathbf{p}^*, \mathbf{R}_i; t), \end{aligned} \quad (18)$$

since the second time average does not affect the left-hand side of Eq. (4), all terms of which already have only secular dependence on time.

Equation (18) becomes identical with the Maxwell-Boltzmann integro-differential equation (in this equation the symbol  $f_i$  is customarily used to denote the molecular density,  $N_i \bar{f}_i^{(1)}$ , of species  $i$ ) only if

$$\overline{f_i^{(1)} f_l^{(1)}} = \bar{f}_i^{(1)} \bar{f}_l^{(1)}. \quad (19)$$

Equation (19) is not necessarily true, but it is true to terms of the first order for distributions departing but slightly from equilibrium, represented by  ${}^0 f_i^{(1)}$  and  ${}^0 f_l^{(1)}$ , both of which are independent of time. If

$$f_i^{(1)} = {}^0 f_i^{(1)} + \varphi_i^{(1)}, \quad f_l^{(1)} = {}^0 f_l^{(1)} + \varphi_l^{(1)},$$

$$\overline{f_i^{(1)} f_l^{(1)}} = \bar{f}_i^{(1)} \bar{f}_l^{(1)} = {}^0 f_i^{(1)} {}^0 f_l^{(1)} + {}^0 f_i^{(1)} \bar{\varphi}_l^{(1)} + {}^0 f_l^{(1)} \bar{\varphi}_i^{(1)} + 0(\overline{\varphi_i^{(1)} \varphi_l^{(1)}}). \quad (20)$$

Equations (18) and (20) are evidently identical with the Maxwell-Boltzmann equation to terms of the first order for small departures from statistical equilibrium. In all applications, solutions have been limited to terms of the first order. The proposed derivation of this equation from statistical mechanics is therefore complete.

Starting from Eq. (4), we should be able to develop a systematic scheme for taking into account collisions of higher order than binary and thus to obtain transport laws for gases of finite density instead of laws valid only in the limit of vanishing density. This problem is being considered. However, for this purpose, the Brownian motion approximations described in SMTI appear to offer the greatest promise.