This projection will be (Fig. 3)

$$\mathrm{Proj}(\Delta\Omega)=\frac{v_1}{|v|}\Delta S_1+\frac{v_2}{|v|}\Delta S_2, \tag{37}$$

where ΔS_j is the surface element whose normal points in the direction of v_j. But because of the orthogonality we have $\Delta\Omega=s_j\Delta S_j$ for any j, so that we may replace ΔS_1 and ΔS_2 in the denominator of (36) by $\Delta\Omega/s_1$ and $\Delta\Omega/s_2$, respectively.

The expression (36) for the mean segment will then take the form

$$\bar{l}=v\bigg/\left(\frac{v_1}{s_1}+\frac{v_2}{s_2}\right), \tag{38}$$

where the denominator is just the sum of the reciprocal passage times $1/t_1=v_1/s_1$, and $1/t_2=v_2/s_2$. The extension to more dimensions is now immediate, and so we have generally

$$\frac{1}{T_{\mathrm{coinc}}}=\sum\frac{1}{t_j}, \tag{39}$$

as was to be shown.

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Time-Correlation Functions in the Statistical Mechanics of Transport Processes*

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A kinetic equation governing the time dependence of the correlation function of flux is established for dilute gases and is integrated to yield a relation between the correlation time and the transport cross section. The spectrum of the binary collision operator is determined for spherically symmetric forces between molecules, which, for the hard-core model, consists of two discrete values in the classical limit; hence it is shown that the question of validity of approximating the correlation function by an exponential decay depends upon the type of intermolecular force and the temperature of the system. Approximate eigenvalues of the master collision operator are obtained corresponding to the fluxes of viscosity and thermal conduction, and their relations to the macroscopic transport coefficients are derived. These relations lead to a new approach to the transport properties of dilute gases, which is different from Enskog-Chapman's method, but yields the same results in the classical limit. An expansion formula for the canonical transformation describing the motion of dilute gases is obtained and is employed to clarify the assumption of random *a priori* phases in the momentum representation for spatially uniform gases; this is done by formulating the quantum-mechanical equivalent of Brout's idea in the classical derivation of the master equation.

1. INTRODUCTION

THE typical examples of the molecular theory of transport phenomena, such as the viscosity of dilute gases and the electrical conductivity of metals, are usually based on the Maxwell-Boltzmann integro-differential equation for the velocity distribution function of molecules[1] or its modification. The extension of the kinetic method to the treatment of transport phenomena in dense gases and degenerate quantum gases has not been made in the general case.

On the other hand, according to the recent theories of transport processes,[2,3] we can obtain molecular expressions for transport coefficients or kinetic coefficients which are valid over the same region as the thermodynamics of irreversible processes.[4] The most remarkable feature of the theories is the formulation of the transport coefficients in terms of the correlation functions of the equilibrium fluctuations of the corresponding dynamical fluxes F,

$$\Psi_{F,F}(t)=\tfrac{1}{2}\langle FF(t)+F(t)F\rangle, \tag{1.1}$$

where the angular brackets mean the average over the canonical ensemble of the system, and $F(t)$ is the value of F after time t and should, in the quantum-mechanical case, be read as the Heisenberg operator. For example, the coefficient of shear viscosity of isotropic fluids can be expressed as[3,5,6]

$$\eta=(1/VkT)\int_0^\infty dt\,\Psi_{F,F}(t), \tag{1.2}$$

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[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, Cambridge, 1939).

[2] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[3] H. Mori, J. Phys. Soc. Japan 11, 1029 (1956).

[4] S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951).

[5] M. S. Green, J. Chem. Phys. 22, 398 (1954).

[6] In the classical limit, Eq. (1.2) agrees with Green's expression[5] except that the average in (1.1) is made with the canonical ensemble whereas, in his expression, with the micro-canonical ensemble. The latter situation causes a serious difference in the

with

$$F=\sum_{i=1}^{N} p_{ix}p_{iy}/m_i+\sum_{i<j}^{N}\sum^{N} (r_{ij})_x(F_{ij})_y, \qquad (1.3)$$

p_{ix} and $(r_{ij})_x$ being the x components of the momentum of molecule i and the relative coordinate between i and j, and $(F_{ij})_y$ the y component of the intermolecular force between i and j. T is the temperature, V the volume, N the number of molecules, and k the Boltzmann constant.

By determining the time dependence of the correlation functions, therefore, we may calculate the transport coefficients. Interesting studies along such a line have been carried out in several important cases.[5,7,8]

Green's[5] investigation of classical dilute gases is based on the assumption that the temporal development of a conditional average value of the flux $F(t)$ in the correlation function is governed, in a certain manner, by the linearized Maxwell-Boltzmann equation. Thus, although he has shown the consistency of his approach with the kinetic theory based upon the Enskog-Chapman solution of the Maxwell-Boltzmann equation, the molecular picture of the time-dependence of the correlation functions has not been clarified.

In Kubo-Tomita's[7] theory of magnetic resonance absorption and Nakano's[8] method of calculating electrical conductivity, it has been assumed that the correlation function decays exponentially in time, and the relaxation time has been calculated by the second-order perturbation theory. It is necessary, however, to discuss the physical aspect and the limit of validity of this approximation, which will be seen to depend upon the Hamiltonian and the thermodynamic state of the system concerned.

The principal purpose of the present paper is, therefore, to investigate the time dependence of the correlation functions of fluxes from the standpoint of molecular dynamics. As a typical example, we consider the viscosity and the thermal conductivity in nondegenerate quantum gases of one component with spherically symmetric forces between molecules.

We set up in Sec. 2 two problems which are the main subjects of the following sections; one is to establish a kinetic equation for the diagonal elements of the Heisenberg operator of the flux, and the other is to determine the spectrum of the binary and master collision operators in the kinetic equation. These subjects are essential to the analysis of the relaxation processes in momentum space and their relations to the macroscopic transport coefficients. In Sec. 3, the spectrum of the binary collision operator is obtained, and the fluxes of viscosity and thermal conduction are shown to be approximate eigenfunctions of the master collision operator. On the basis of these results, the time dependence of the correlation functions of fluxes and the relaxation processes in momentum space are investigated. In Sec. 4, Enskog and Chapman's expressions for the viscosity and the thermal conductivity are derived from the corresponding eigenvalues of the master collision operator, and it is pointed out that our theory may be regarded as a generalization of Maxwell and Boltzmann's original theory of transport in dilute gases. Sections 5 and 6 are devoted to establish the above-mentioned kinetic equation from the principles of statistical mechanics. A linear operator governing the change in time of the Heisenberg operator is introduced, and an expansion formula for it is obtained. This enables us to derive the kinetic equation without the repeated use of the assumption of random *a priori* phases.

2. PRELIMINARY DISCUSSIONS

We first present a simple and practically convenient method of obtaining a kinetic equation for the correlation function and a molecular expression for the relaxation time.

In gases of low density, the contribution due to the intermolecular part to the viscosity flux, (1.3), may be neglected in comparison with that due to the first part:

$$F=\sum_{i=1}^{N} p_{ix}p_{iy}/m. \qquad (2.1)$$

Therefore, by neglecting the interaction energy in the Hamiltonian in the Boltzmann factor, the correlation function can be written as

$$\Psi_{F,F}(t)=\langle\{F_{\mathbf{p}}\langle\mathbf{p}|F(t)|\mathbf{p}\rangle\}\rangle, \qquad (2.2)$$

where

$$\langle B\rangle=\sum\nolimits_{\mathbf{p}}B\exp(-E_{\mathbf{p}}/kT)/\sum\nolimits_{\mathbf{p}}\exp(-E_{\mathbf{p}}/kT), \qquad (2.3)$$

where $F_{\mathbf{p}}$ and $E_{\mathbf{p}}$ are, respectively, the eigenvalues of F and the kinetic energy H_0 corresponding to the eigenstate of the total momentum, $\mathbf{p}=(\mathbf{p}_1,\cdots,\mathbf{p}_N)$, and $\langle\mathbf{p}|F(t)|\mathbf{p}\rangle$ are the diagonal elements of the Heisenberg operator $F(t)$ in the momentum representation.

The Heisenberg operators at different times are related to each other as

$$F(t)=U(s)^{\dagger}F(t_0)U(s), \quad U(s)=\exp(sH/i\hbar), \qquad (2.4)$$

where H is the total Hamiltonian of the system, $U(s)^{\dagger}$ the Hermitean conjugate of $U(s)$, and $t=t_0+s$. In order to obtain a kinetic equation for the diagonal elements of the Heisenberg operator, we make use of the postulate of random *a priori* phases[9] in the following manner.

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calculation of the transport coefficients; for example, the 2nd term of the flux of thermal conduction (3.23) is missing in his corresponding expression. Equations (1.2) and (3.24) will be proved exactly, in a forthcoming paper, with the assumption that the macroscopic motion of the fluids can be described by one velocity, one temperature, and one mass-density field.

[7] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[8] H. Nakano, Progr. Theoret. Phys. (Japan) **15**, 77 (1956); **17**, 145 (1957).

[9] R. C. Tolman, *The Principles of Statistical Mechanics* (Clarendon Press, Oxford, England, 1938), Chap. XI; D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954), Appendix I.

The value of $\langle \mathbf{p}|F(t)|\mathbf{p}\rangle$ depends upon all the matrix elements of $F(t_0)$ at a previous time. If, however, we may neglect the contribution due to the off-diagonal elements of $F(t_0)$, then Eq. (2.4) leads to

$$\langle \mathbf{p}|F(t)|\mathbf{p}\rangle=\textstyle\sum_{\mathbf{p}'}W(\mathbf{p}',\mathbf{p};s)\langle \mathbf{p}'|F(t_0)|\mathbf{p}'\rangle, \tag{2.5}$$

where we have defined

$$W(\mathbf{p}',\mathbf{p};s)=|\langle \mathbf{p}'|U(s)|\mathbf{p}\rangle|^2, \tag{2.6}$$

with the corresponding matrix element of the $U(s)$ in the momentum representation. $W(\mathbf{p}',\mathbf{p};t)$, $(t>0, \mathbf{p}'\neq\mathbf{p})$, expresses the transition probability of the system from state $\mathbf{p}$ to state $\mathbf{p}'$ after time t.[10] By taking the unit operator instead of F in Eq. (2.5), we obtain the conservation law of probability,

$$1=W(\mathbf{p},\mathbf{p};s)+\sum_{\mathbf{p}'(\neq\mathbf{p})}W(\mathbf{p}',\mathbf{p};s), \tag{2.7}$$

which is inserted into (2.5) to give

$$\begin{aligned}\langle \mathbf{p}|F(t)|\mathbf{p}\rangle=\langle \mathbf{p}|F(t_0)|\mathbf{p}\rangle+\sum_{\mathbf{p}'(\neq\mathbf{p})}W(\mathbf{p}',\mathbf{p};\mathbf{s})\\ \times\{\langle \mathbf{p}'|F(t_0)|\mathbf{p}'\rangle-\langle \mathbf{p}|F(t_0)|\mathbf{p}\rangle\},\end{aligned} \tag{2.8}$$

which describes the change in time of the diagonal elements in terms of their increments due to the transition processes. We note here that Eq. (2.8) is rigorous when $t_0=0$, because F is a diagonal matrix in the momentum representation and therefore the use of the assumption of random *a priori* phases is unnecessary in this case.

Now we consider a dilute gas whose molecular motion can be analyzed in terms of binary collisions. The intermolecular interaction is assumed to be a spherically symmetric force of short range. The mean free time and the mean collision time are denoted, respectively, by τ_f and τ_0, and we assume that $\tau_0\ll\tau_f$ (the assumption of instantaneous collisions). In a time much shorter than the mean free time, each molecule collides with at most one other molecule. By a binary collision between i and j, the state $\mathbf{p}$ is transformed to

$$\begin{aligned}A_{ij}(\mathbf{l})\mathbf{p}=(\mathbf{p}_1,\cdots,\mathbf{p}_i+(\mathbf{p}_j-\mathbf{p}_i)\cdot\mathbf{ll},\cdots,\\ \mathbf{p}_j-(\mathbf{p}_j-\mathbf{p}_i)\cdot\mathbf{ll},\cdots,\mathbf{p}_N),\end{aligned} \tag{2.9}$$

where $\mathbf{l}$ is the unit vector in the perihelion direction. The corresponding transition probability can be expressed in terms of the usual scattering cross section,[11] because, according to the definition of the binary collision, the wave packets of i and j do not overlap those of the other molecules; namely,

$$\begin{aligned}W(\mathbf{p}',\mathbf{p};t)=w(\mathbf{p}_{ij}',\mathbf{p}_{ij};t)N!\left[\frac{(2\pi\hbar)^3}{V}\right]^{N-1}\\ \times\delta(\mathbf{p}_{cij}'-\mathbf{p}_{cij})\prod_{k(\neq i,j)}\delta(\mathbf{p}_k'-\mathbf{p}_k),\\ w(\mathbf{p}_{ij}',\mathbf{p}_{ij};t)\left(\frac{V}{(2\pi\hbar)^3}\right)d\mathbf{p}_{ij}'\\ =\left(\frac{t}{V}\right)\left(\frac{2p_{ij}}{m}\right)\sigma(p_{ij},\theta)\delta(E_{ij}'-E_{ij})d\Omega dE_{ij}',\end{aligned} \tag{2.10}$$

where $\mathbf{p}_{ij}$, $\mathbf{p}_{cij}$, and E_{ij} are, respectively, the relative and center-of-mass momenta and the relative kinetic energy, and $d\Omega$ the element of solid angle in the direction of scattering (θ,φ), and $\sigma(p_{ij},\theta)$ the scattering cross section in which the symmetry effect due to the collision of identical particles has been taken into account. The dE_{ij}' should be of the order of magnitude of $\hbar/t$. Therefore, by taking into consideration all possible binary encounters, Eq. (2.8) leads to

$$\langle \mathbf{p}|F(t)|\mathbf{p}\rangle=(1-\tau\Lambda)\langle \mathbf{p}|F(t-\tau)|\mathbf{p}\rangle, \tag{2.11}$$

for such a short time interval that $\tau_0\ll\tau\ll\tau_f$. Here, we have defined the following collision integral operators familiar in the kinetic theory of dilute gases[12]:

$$\begin{aligned}\Lambda=\sum_{i=1}^{N}\sum_{j=i+1}^{N}\Lambda_{ij},\\ \Lambda_{ij}g(\mathbf{p})=-(1/V)\int_0^{2\pi}d\varphi\int_0^{\pi}d\theta\,\sin\theta\frac{2p_{ij}}{m}\sigma(p_{ij},\theta)\\ \times\{g(A_{ij}(\mathbf{l})\mathbf{p})-g(\mathbf{p})\},\end{aligned} \tag{2.12}$$

which will be called, respectively, the master and binary collision operators. The condition $\tau_0\ll\tau$ means that the majority of collisions concerned start and end during the time interval τ so that the change of the diagonal elements in τ can be described sufficiently in terms only of the scattering cross section. Thus, with the use of the assumption of random *a priori* phases in the above manner and the assumption of instantaneous collisions, we obtain

$$\langle \mathbf{p}|F(t)|\mathbf{p}\rangle=\exp(-t\Lambda)\,F_{\mathbf{p}}, \tag{2.13}$$

which is substituted into (2.2) to give[13]

$$\Psi_{F,F}(t)=\langle F_{\mathbf{p}}\exp(-t\Lambda)\,F_{\mathbf{p}}\rangle. \tag{2.14}$$

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[10] The density matrix $\rho(t)$ satisfies $\rho(t)=U(t)\rho(0)U(t)^{\dagger}$. Therefore, under the initial condition $\langle \mathbf{p}'|\rho(0)|\mathbf{p}\rangle=P(\mathbf{p})\delta_{\mathbf{p}',\mathbf{p}}$, we obtain an equation for the density matrix analogous to (2.5), which gives $\langle \mathbf{p}|\rho(t)|\mathbf{p}\rangle=W(\mathbf{p},\mathbf{p}_0;t)$, if $P(\mathbf{p})=\delta_{\mathbf{p},\mathbf{p}_0}$. From this, the foregoing follows.

[11] D. Bohm, *Quantum Theory* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1951).

[12] M. Kac, *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability* (University California Press, California, 1956), Vol. 3, p. 171.

[13] We note here that Eq. (2.14) is valid only for $t>0$ and does not satisfy the relation $\Psi_{F,F}(t)=\Psi_{F,F}(-t)$, which is obtained from (1.1) with the aid, in the classical case, of the Liouville theorem and, in the quantum-mechanical case, of the identity $\mathrm{Tr}AB=\mathrm{Tr}BA$. In order to clarify the origin of this inequality of the direction of time axis, we consider (2.11) with $t=\tau$. Since (2.8) is rigorous when $t_0=0$, the origin is in the procedure of obtaining

When the average de Broglie wavelength of molecules becomes of the order of magnitude of the average molecular distance at very low temperatures, then multiple collisions appear so that the binary collision approximation may be invalid.

Next we consider a formal condition under which these equations can be expressed approximately in terms of one relaxation time. We introduce an average value of the master collision operator for the viscosity flux,

$$\lambda_v = \langle F_{\mathrm{p}} \Lambda F_{\mathrm{p}} \rangle / \langle F_{\mathrm{p}}^2 \rangle, \tag{2.15}$$

which is positive.[14] Then, the correlation function (2.14) can be written as

$$\Psi_{F,F}(t) = \langle F_{\mathrm{p}}^2 \rangle \exp(-t\lambda_v)[1+\mu(t)], \tag{2.16}$$

where we have defined

$$\mu(t) = \sum_{n=2}^{\infty} (-t)^n \mu_n / n!, \tag{2.17}$$

with the nth moment about the average value;

$$\mu_n = \langle F_{\mathrm{p}} (\Lambda - \lambda_v)^n F_{\mathrm{p}} \rangle / \langle F_{\mathrm{p}}^2 \rangle. \tag{2.18}$$

If all the moments μ_n, $(n \geqq 2)$, vanish, then the correlation function decays exponentially to zero. The necessary and sufficient condition for this is the requirement that F_{p} be an eigenfunction of the master collision operator and λ_v be the corresponding eigenvalue,

$$\Lambda F_{\mathrm{p}} = \lambda_v F_{\mathrm{p}}. \tag{2.19}$$

This condition will be shown to be satisfied rigorously by the Maxwell model of intermolecular force in the classical limit. In general, especially in the quantum-mechanical cases, Eq. (2.19) cannot be satisfied exactly. It is nautral, however, to consider that the deviation $\mu(t)$ may be neglected as the first approximation;

$$|\mu(t)| \ll 1. \tag{2.20}$$

Then, substitution of (2.16) into (1.2) gives

$$\eta = \frac{(\langle F_{\mathrm{p}}^2 \rangle / VkT)}{\lambda_v} \tag{2.21}$$

for the viscosity coefficient of dilute gases. The straightforward calculation of (2.21) will be shown to yield, in the classical limit, Enskog and Chapman's expression for the viscosity in the first approximation.[1]

As has been seen in the above, the crucial points about the correlation function to be investigated further are the following:

(I) *the eigenvalue problem of the master collision operator*;
(II) *the physical meaning and the limit of validity of the assumption of random a priori phases in the momentum representation.*

These problems themselves are of great interest and have been, respectively, investigated in a number of papers. The question (I) is closely correlated to the eigenvalue problem of the collision operator in the linearized Maxwell-Boltzmann equation[15] which has been solved for the Maxwell molecules in the classical case. The spectrum of the master collision operator has been investigated by Kac,[12] but has not been obtained even for his simplified model, a kind of one-dimensional Maxwell model. Our particular intention is to obtain the eigenvalues of Λ and Λ_{ij} which give the relaxation times of the fluxes of viscosity and thermal conduction, and to know how the eigenvalues depend upon the type of intermolecular force and the thermodynamic state of the system.

The problem (II) is a central subject of the recent investigations of the statistical mechanics of transport processes. Van Hove[16] has clarified this question by deriving a kinetic equation with the requirement of the postulate of random *a priori* phases at the initial time only. His derivation is based on the recognition of the fact that the perturbation responsible for the irreversible behavior possesses remarkable properties which result from the largeness of the system. The classical counterpart of this situation has been established by Prigogine and Brout.[17] These derivations, however, are based on perturbation techniques which may become invalid if the interactions between particles of the system include forces of repulsion as the hard-core or Lennard-Jones' potential. As has been pointed out before, the derivation of (2.13) does not need the assumption of random *a priori* phases if t is a short time interval in which successive binary collisions do not occur. This means that the assumption of random *a*

Eq. (2.10) which is valid only for $t>0$. Thus the inequality turns out to be due to the adiabatic approximation in the theory of collision (see reference 30), which is introduced so that the states before and after collision can be expressed by definite eigenfunctions of the kinetic Hamiltonian, and, therefore, which is related essentially to the process of interaction of the quantum-mechanical system with a classically describable system, an apparatus of measuring the kinetic Hamiltonian, in the theory of quantum-mechanical observation (See reference 11, Secs. 18.9, 22.14). Such relation to the process of observation is important to clarify the statistical-mechanical picture of kinetic equations. In the present paper, we shall not consider it further. It should be emphasized, however, that the assumption of random *a priori* phases introduced just before (2.5) has no primary relation to the inequality of the direction of time.

[14] With the aid of microscopic reversibility (6.24), we obtain

$$\langle g(\mathbf{p}) \Lambda g(\mathbf{p}) \rangle = \frac{1}{2V} \sum_{i<j} \left\langle \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \times \left(\frac{2p_{ij}}{m}\right) \sigma(p_{ij},\theta) \{ g(A_{ij}\mathbf{p}) - g(\mathbf{p}) \}^2 \right\rangle.$$

[15] L. Boltzmann, *Vorlesungen über Gas Theorie* (J. A. Barth, Leipzig, 1895). A review on such problems in the kinetic theory of gases is given by G. E. Uhlenbeck, Higgins lectures given at Princeton University, 1954 (unpublished).

[16] L. Van Hove, Physica 21, 517 (1955).

[17] R. Brout and I. Prigogine, Physica 22, 621 (1956); I. Prigogine, Can. J. Phys. 34, 1236 (1956).

priori phases is related to successions of binary collisions. The second purpose of the present paper is to clarify this situation, which will be done by formulating exactly Brout's[18] idea in the classical derivation of the master equation to the quantum-mechanical case.

3. EIGENFUNCTIONS AND EIGENVALUES OF THE COLLISION OPERATORS

We first determine the spectrum of the binary collision operator. From (2.1) and (2.12), we obtain

$$\Lambda_{ij}F_{\mathbf{p}}=\Lambda_{ij}(p_{ix}p_{iy}+p_{jx}p_{jy})/m. \tag{3.1}$$

It is worth while to notice here that m_i+m_j, $\mathbf{p}_i+\mathbf{p}_j$ and $p_i^2+p_j^2$ are eigenfunctions of the binary collision operator Λ_{ij} and the corresponding eigenvalues are zero according to the laws of conservation of mass, momentum, and energy in binary collision. Using the relative and center-of-mass momenta, we have

$$\begin{aligned} \mathbf{p}&=(\mathbf{p}_j-\mathbf{p}_i)/2, & \mu&=m/2,\\ \mathbf{p}^c&=\mathbf{p}_i+\mathbf{p}_j, & M&=2m, \end{aligned} \tag{3.2}$$

$$(p_{ix}p_{iy}+p_{jx}p_{jy})/m=p_xp_y/\mu+p_x{}^cp_y{}^c/M. \tag{3.3}$$

Equation (3.1) can be written as

$$\Lambda_{ij}F_{\mathbf{p}}=\Lambda_{ij}\psi_{ij}, \tag{3.4}$$

with

$$\psi_{ij}=p_xp_y/\mu, \tag{3.5}$$

which will be shown to be an eigenfunction of Λ_{ij}. Denoting the spherical angular coordinates of $\mathbf{p}$ by (Θ,Φ), Eq. (3.5) is written as

$$\psi_{ij}=(ip^2/12\mu)[Y_{2,2}{}^*(\Theta,\Phi)-Y_{2,2}(\Theta,\Phi)] \tag{3.6}$$

in terms of the spherical harmonics[11,19]

$$Y_{m,l}(\Theta,\Phi)=P_l{}^{|m|}(\cos\Theta)\exp(im\Phi) \tag{3.7}$$

$$=Y_{-m,l}{}^*(\Theta,\Phi). \tag{3.8}$$

If the relative momentum after collision is denoted by $\mathbf{p}'=(p,\Theta',\Phi')$, then Eq. (3.4) may be written as

$$\Lambda_{ij}\psi_{ij}=\frac{1}{V}\int_0^{2\pi}d\theta\,\sin\theta\,\frac{p}{\mu}\sigma(p,\theta)\times\int^{\pi}d\varphi\{\psi_{ij}(\Theta,\Phi)-\psi_{ij}(\Theta',\Phi')\}, \tag{3.9}$$

where we have expressed in $\psi_{ij}(\Theta,\Phi)$ its angular dependence explicitly.

In order to calculate the integral with respect to φ, let us now consider a spherical harmonic of degree l,

$$Y_l(\Theta,\Phi)=\sum_{m=-l}^{l}C_mY_{m,l}(\Theta,\Phi), \tag{3.10}$$

where the C_m's are constants which may be functions of the invariants of the collision, such as μ, $\mathbf{p}^c$, and p^2. Let the axes of coordinates be rotated so that the new z axis passes through the direction of $\mathbf{p}$ and the angular coordinates of $\mathbf{p}'$ become the scattering angle (θ,φ) in the new coordinate system. Then, according to the transformation $(\Theta',\Phi')\rightarrow(\theta,\varphi)$, the $Y_l(\Theta',\Phi')$ goes into a new function of θ and φ which is a spherical harmonic of the same degree l. This can be seen easily from the fact that spherical harmonics are eigenfunctions of the square of the quantum-mechanical angular momentum[11] which is invariant to a rotation of the coordinate system. Therefore, we can expand $Y_l(\Theta',\Phi')$ as

$$Y_l(\Theta',\Phi')=\sum_{m=-l}^{l}D_mY_{m,l}(\theta,\varphi). \tag{3.11}$$

The coefficients D_m depend upon the angle and direction of rotation. If we put $\theta=0$, then $Y_{0,l}(\theta,\varphi)=1$ and $Y_{m,l}(\theta,\varphi)=0$, $(m\neq0)$, so that $D_0=Y_l(\Theta,\Phi)$. Thus, integration of (3.11) with respect to φ gives

$$\frac{1}{2\pi}\int_0^{2\pi}d\varphi\,Y_l(\Theta',\Phi')=P_l(\cos\theta)Y_l(\Theta,\Phi). \tag{3.12}$$

This result means that a spherical harmonic is an eigenfunction of the binary collision operator, because substitution of $Y_l(\Theta,\Phi)$ for $\psi_{ij}(\Theta,\Phi)$ in (3.9) leads to

$$\Lambda_{ij}Y_l(\Theta,\Phi)=\lambda_{ij}{}^{(l)}Y_l(\Theta,\Phi), \tag{3.13}$$

where

$$\lambda_{ij}{}^{(l)}=\frac{2\pi}{V}\int_0^{2\pi}d\theta\,\sin\theta\,\frac{p}{\mu}\sigma(p,\theta)\{1-P_l(\cos\theta)\}. \tag{3.14}$$

Since the absolute value of the Legendre polynomial is not larger than unity, the eigenvalues are always positive or, for the trivial case, zero;

$$\lambda_{ij}{}^{(0)}=0,\quad \lambda_{ij}{}^{(l)}>0,\quad (l\geqq1). \tag{3.15}$$

For the rigid elastic molecule with a force range a, these become in the classical limit

$$\begin{aligned}\lambda_{ij}{}^{(0)}&=0,\\ \lambda_{ij}{}^{(l)}&=(\pi a^2/V)(p/\mu),\quad (l\geqq1),\end{aligned} \tag{3.16}$$

since $\sigma(p,\theta)=\frac{1}{4}a^2$. The quantum-mechanical case is not so simple because the cross section depends upon the angle and wavelength in a complicated manner.[11] Another special example is the Maxwell molecules in the classical case. In this case the eigenvalues become independent of the relative momentum, because $\{p\sigma(p,\theta)\}$ becomes a function of θ only.[1]

By making use of the above results, approximate eigenfunctions and eigenvalues of the master collision operator can be obtained readily. Equation (3.6) is a spherical harmonic of the second degree so that (3.13) gives

$$\Lambda_{ij}\psi_{ij}=\lambda_{ij}{}^{(2)}\,\psi_{ij}. \tag{3.17}$$

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[18] R. Brout, Physica 22, 509 (1956).

[19] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1271.

We now assume that, on the average, the deviation of the eigenvalue $\lambda_{ij}^{(2)}$ is small from some average value of it with respect to the relative momentum, $((\lambda_{ij}^{(2)}))$. Then, from (2.12), (3.4), and (3.17), we obtain approximately

$$\Lambda F_{\mathbf{p}}=\lambda_v F_{\mathbf{p}}, \tag{3.18}$$

with

$$\lambda_v=\tfrac{1}{2}N((\lambda_{ij}^{(2)})), \tag{3.19}$$

where we have put the total momentum, $\mathbf{P}=\sum_{i=1}^N \mathbf{p}_i$, to be zero in the equation

$$\sum_{i<j}\psi_{ij}=\tfrac{1}{2}N\{F_{\mathbf{p}}-P_xP_y/mN\}, \tag{3.20}$$

because the total momentum is invariant to collisions between molecules and expresses the uniform translation of the whole system so that it is of no primary importance to the discussion of the law of motion of $F(t)$. Equation (3.18) is inserted into (2.13) to lead to

$$\langle\mathbf{p}|F(t)|\mathbf{p}\rangle=F_{\mathbf{p}}\exp(-t\lambda_v). \tag{3.21}$$

Equation (3.18) shows that the viscosity flux (2.1) is an approximate eigenfunction of the master collision operator and its eigenvalue is given by (3.19). According to (3.21), the inverse of the eigenvalue, $\tau_v=1/\lambda_v$, turns out to be the relaxation time for the diagonal elements of the viscosity flux to decay in time. In the case of the Maxwell molecules and the classical limit $\hbar\rightarrow 0$, since $\lambda_{ij}^{(2)}$ becomes independent of the relative momentum, the assumption introduced before (3.18) is exactly satisfied so that (3.18) and (3.21) become exact and the exact eigenvalue is given by

$$\lambda_v=3\pi A(\alpha/2m)^{\frac{1}{2}}(N/V), \tag{3.22}$$

where $A=0.436$ and the intermolecular force has been taken to be α/r^5. Equation (3.22) agrees with the inverse of the relaxation time computed by Maxwell.[15,20]

We next show that the following quantity is also an eigenfunction of the master collision operator:

$$G=\sum_{i=1}^{N}(p_i^2/2m-h)p_{iz}/m, \tag{3.23}$$

h being the enthalpy for one molecule. This is the z component of the flux of thermal conduction, and the thermal conductivity is given as[5,6]

$$\kappa=(1/VkT^2)\int_0^\infty dt\,\Psi_{G,G}(t). \tag{3.24}$$

In the same way as for (3.4), we obtain

$$\Lambda_{ij}G_{\mathbf{p}}=\lambda_{ij}^{(2)}\phi_{ij} \tag{3.25}$$

with

$$\phi_{ij}=(\mathbf{p}^c\cdot\mathbf{p}p_z-\tfrac{1}{3}p^2p_z^c)/\mu M \tag{3.26}$$

$$=(p^2/6\mu M)[(p_x^c-ip_y^c)Y_{1,2}(\Theta,\Phi)+(p_x^c+ip_y^c)Y_{1,2}^*(\Theta,\Phi)+4p_z^cY_{0,2}(\Theta\,\Phi)]. \tag{3.27}$$

The second term of (3.26) is invariant to collisions and hence gives no contribution to (3.25) but it is added so as to yield (3.27). Equation (3.27) is a spherical harmonic of the second degree so that (3.13) gives

$$\Lambda_{ij}\phi_{ij}=\lambda_{ij}^{(2)}\phi_{ij} \tag{3.28}$$

which leads, in parallel to (3.18), to

$$\Lambda G_{\mathbf{p}}=\lambda_TG_{\mathbf{p}}, \tag{3.29}$$

$$\lambda_T=\tfrac{1}{3}N((\lambda_{ij}^{(2)})), \tag{3.30}$$

where, as in (3.20), the total momentum has been taken to be zero in the equation

$$\sum_{i<j}\phi_{ij}=\tfrac{1}{3}N\{G_{\mathbf{p}}+(P_z/m)(h-\textstyle\sum_i p_i^2/mN)+\mathbf{P}\cdot(\sum_i\mathbf{p}_ip_{iz})/2m^2N\}. \tag{3.31}$$

Thus it turns out that the thermal conduction flux (3.23) is an approximate eigenfunction of the master collision operator and Eq. (3.30) gives its eigenvalue, which is different from that of the viscosity flux;

$$\lambda_T/\lambda_v=2/3. \tag{3.32}$$

In order to calculate these eigenvalues it is necessary to determine the average value $((\lambda_{ij}^{(2)}))$ introduced before (3.18). This can be done in the following way. When $\mathbf{P}\neq 0$, we have, from (3.20), as the extension of (3.18),

$$\Lambda F_{\mathbf{p}}=\lambda_v(F_{\mathbf{p}}-P_xP_y/mN), \tag{3.33}$$

which means that $F_{\mathbf{p}}'=F_{\mathbf{p}}-P_xP_y/mN$ is an eigenfunction of Λ. By multiplying both sides of this equation by $F_{\mathbf{p}}$ and taking the average of it over the canonical ensemble with (2.3), we obtain

$$\langle F_{\mathbf{p}}\Lambda F_{\mathbf{p}}\rangle=\lambda_v(\langle F_{\mathbf{p}}^2\rangle-\langle F_{\mathbf{p}}P_xP_y\rangle/mN). \tag{3.34}$$

On the other hand, we have

$$\langle p_{ix}p_{iy}p_{jx}p_{ky}\rangle=\langle p_{ix}\rangle\langle p_{jx}\rangle\langle p_{iy}p_{ky}\rangle=0,\quad\text{if}\quad i\neq j, \tag{3.35}$$

which gives

$$\langle F_{\mathbf{p}}P_xP_y\rangle/m=\langle F_{\mathbf{p}}^2\rangle. \tag{3.36}$$

Therefore, (3.34) becomes

$$(1/\lambda_v)\langle F_{\mathbf{p}}\Lambda F_{\mathbf{p}}\rangle=\langle F_{\mathbf{p}}^2\rangle(1-1/N), \tag{3.37}$$

which leads, by taking N infinite, to

$$\lambda_v=\langle F_{\mathbf{p}}\Lambda F_{\mathbf{p}}\rangle/\langle F_{\mathbf{p}}^2\rangle, \tag{3.38}$$

which agrees with Eq. (2.15). Equation (3.38) determines, with the aid of (3.19), the average value $((\lambda_{ij}^{(2)}))$, whose explicit form will be given in next section.

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[20] J. C. Maxwell, *The Scientific Papers of J. C. Maxwell* (Dover Publications, New York, 1952), Vol. 2, p. 26.

By making use of the above results, we discuss the time-dependence of the correlation function (2.14). The average over the canonical ensemble, (2.3), extends over systems with $\mathbf{P}\neq 0$ arising as fluctuations about the average value $\langle \mathbf{P}\rangle = 0$ due to the interaction with the heat reservoir. For such systems, Eq. (3.21) should be modified, with the aid of (3.33), as

$$\exp(-t\Lambda)\,F_{\mathrm{p}} = P_xP_y/mN + (F_{\mathrm{p}} - P_xP_y/mN)\exp(-t\lambda_v). \tag{3.39}$$

However, with the aid of (3.36), we have, corresponding to (3.37),

$$\Psi_{F,F}(t) = \langle F_{\mathrm{p}}^2\rangle\{1/N + (1-1/N)\exp(-t\lambda_v)\} \tag{3.40}$$

$$= \langle F_{\mathrm{p}}^2\rangle \exp(-t\lambda_v), \quad \text{as} \quad N\rightarrow\infty, \tag{3.41}$$

which means that the contributions of the above systems to the time-dependence of the correlation function can be neglected in the limit of $N\rightarrow\infty$. Comparison of (3.41) with (2.16) leads to the fact that $\mu(t)$ is exactly zero in the case of the Maxwell molecules and the classical limit, since in this case the only assumption necessary to derive (3.41), i.e., the assumption introduced just before (3.18) is exactly satisfied. In other cases, the magnitude of $\mu(t)$, namely, the accuracy of the approximation (2.20) depends upon the magnitude of the dispersion of $\lambda_{ij}^{(2)}$ about its average value. The magnitude of this dispersion can be determined by the momentum dependence of the scattering cross section and of the momentum distribution function. Therefore, the accuracy of the approximation (2.20) depends upon the type of intermolecular forces and the temperature of the system. A typical example of the temperature dependence is given by the fact that, when the temperature becomes low so that the peak of the distribution moves to be at low energy requiring the quantum-mechanical treatment of the scattering cross section, we cannot expect the zero dispersion even for the Maxwell molecules.

The spectrum of the master collision operator describes the relaxation processes in momentum space.[12,15] The eigenvalues are the decay constants of the different modes of relaxation. To see the physical significance of the eigenvalues λ_v and λ_T in this aspect, we consider a nonequilibrium isotropic gas of one component whose attainment of uniformity in coordinate space can be described by the hydrodynamical equations. Take a uniform small portion of macroscopic size in the gas, and cut off the interaction with the neighboring small portions. Then this uniform portion approaches complete internal thermal equilibrium rapidly by relaxation in momentum space. The spectrum of this relaxation consists of the lowest few eigenvalues of the master collision operator, which did not die out due to the influence of the neighboring portions, namely due to the coupling with the hydrodynamical process of attaining equilibrium between small portions. What eigenvalues or what modes of relaxation are excited depends upon the detailed behavior of the above coupling between the relaxation in momentum space and the hydrodynamical process. In our case, these eigenvalues turn out to be λ_v and λ_T. This is a consequence of the fact, as will be shown in a forthcoming paper,[6] that the coupling is characterized, in a certain manner, by the fluxes of viscosity and thermal conduction. We thus arrive at the fact that there exist two modes of the relaxation in momentum space in the previously-mentioned gas, and these modes can be given by the autocorrelation functions of the equilibrium fluctuations of the fluxes of viscosity and thermal conduction.

4. COMPARISON WITH ENSKOG AND CHAPMAN'S THEORY

The calculation of the eigenvalues of the master collision operator, (3.19) and (3.30), leads to explicit expressions for the coefficients of viscosity and thermal conductivity with the aid of (1.2) and (3.24). In this section, this is shown and the results are compared with Enskog and Chapman's theory of transport in dilute gases.

The straightforward calculation of (3.38) leads to

$$\lambda_v = (1/30)(N/V)(\mu/kT)^2\langle\langle g^5 Q^{(2)}(g)\rangle\rangle, \tag{4.1}$$

with the notations

$$Q^{(l)}(g) = 2\pi\int_0^\pi d\theta\,\sin\theta\,\sigma(p,\theta)\{1 - P_l(\cos\theta)\}, \tag{4.2}$$

$$\langle\langle B\rangle\rangle = 4\left[\frac{1}{\pi}\left(\frac{\mu}{2kT}\right)^3\right]^{\frac{1}{2}}\int_0^\infty B\exp\left(-\frac{\mu g^2}{2kT}\right)g^2 dg, \tag{4.3}$$

where $\langle\langle B\rangle\rangle$ means the average over the relative speed $g = p/\mu$. Equation (4.2) is related to the eigenvalues of the binary collision operator as

$$\lambda_{ij}^{(l)} = (1/V)gQ^{(l)}(g). \tag{4.4}$$

The $Q^{(2)}(g)$ in (4.1) is $\frac{3}{2}$ times the $Q^{(2)}(g)$ of Hirschfelder *et al.*,[21] which is sometimes called the transport cross section. It is interesting to note that the average value $((\lambda_{ij}^{(2)}))$ in (3.19) can be determined alternatively from (4.1) to be

$$((\lambda_{ij}^{(2)})) = \langle\lambda_{ij}^{(2)}(\psi_{ij})^2\rangle / \langle(\psi_{ij})^2\rangle, \tag{4.5}$$

which has a form similar to (3.38).

Since the density-dependent symmetry effects due to Bose-Einstein and Fermi-Dirac statistics can be neglected, we obtain from (2.1)

$$\langle F_{\mathrm{p}}^2\rangle = (N/m^2)\langle p_{ix}^2\rangle\langle p_{iy}^2\rangle = N(kT)^2. \tag{4.6}$$

Therefore, Eq. (2.21), resulting from (3.41) and (1.2), leads to

$$\eta = P/\lambda_v, \tag{4.7}$$

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[21] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), p. 675.

where $P=(N/V)kT$ is the pressure. This relation between the viscosity and the relaxation time has been derived a long time ago by Maxwell on the basis of a phenomenological consideration.[20] Equation (4.1) is inserted into Maxwell's relation (4.7) to yield the quantum-mechanical equation for the viscosity coefficient. This expression differs from the classical one only in the fact that the classical cross section has been replaced by the quantum-mechanical counterpart.[1,21]

In the same way as for (4.6), we have from (3.23)

$$\langle G_{\mathrm{p}}^2\rangle=5N(kT)^3/2m, \tag{4.8}$$

where use has been made of the relation $h=5kT/2$ for nondegenerate gases. It is interesting to note that although the second term of (3.23) is invariant to collisions between molecules so that it gives no contribution to the eigenvalue λ_T, (3.30), this term gives an important contribution to (4.8) as a result of its fluctuations due to the interaction with the heat reservoir; if we neglect that, then $\langle G_{\mathrm{p}}^2\rangle$ becomes $\frac{7}{2}$ times as large as (4.8).[6] The thermal conductivity is obtained by inserting the equation,

$$\Psi_{G,G}(t)=\langle G_{\mathrm{p}}^2\rangle\exp(-t\lambda_T), \tag{4.9}$$

into Eq. (3.24). Thus we have

$$\kappa=\frac{(\langle G_{\mathrm{p}}^2\rangle/VkT^2)}{\lambda_T} \tag{4.10}$$

$$=5C_vP/3\lambda_T, \tag{4.11}$$

where $C_v=3k/2m$ is the heat capacity per unit mass. Equation (4.11) gives the relation between the thermal conductivity and the corresponding relaxation time in momentum space. The relation between the two relaxation times, (3.32), leads to

$$\kappa=(5/2)C_v\eta, \tag{4.12}$$

which agrees with Chapman's relation between the coefficients of viscosity and thermal conductivity.[1]

The mean time between collisions, i.e., the mean free time, is well defined only for the hard-core molecules. To obtain the physical picture of the transport processes in gases, it is convenient, however, to define the corresponding quantity for other short-range forces. It may be defined as[1]

$$\tau_f=1/2^{\frac{1}{2}}(N/V)Q(T)\bar{v}, \tag{4.13}$$

where $\bar{v}$ is the mean speed of molecules and $Q(T)$ is the "effective" total cross section defined by

$$Q(T)=\pi a^2\Omega^{(2,2)\star}, \tag{4.14}$$

where $\Omega^{(2,2)\star}$ is the quantity defined by Eq. (8.2-8) of reference 21 and becomes unity for the hard-core model with the diameter a. Then, we obtain from (4.1)

$$\tau_v=1/\lambda_v=(5/4)\tau_f. \tag{4.15}$$

Thus it turns out that the relaxation times of the fluxes of viscosity and thermal conduction are of the same order of magnitude as the mean free time.

So far we have neglected the density-dependent symmetry effects which come from the overlapping of the wave packets of more than three molecules. This leads to remarkable modifications of the average value of the square of fluxes and the relaxation times. The influence of Bose-Einstein or Fermi-Dirac statistics on the average value of the square of the fluxes can be evaluated straightforwardly and yields a qualitative analysis of the recent experiments of the viscosity of He^3.[22] The results of the consideration of both effects for extremely degenerate Fermi gases can be shown to agree with Tomonaga's work.[23] Details of these studies will be presented in a subsequent article.

Our investigation of the transport properties of gases, as Maxwell and Boltzmann's theory,[15,20] was based on the detailed analysis of the relaxation processes in momentum space. The macroscopic transport coefficients were connected with the corresponding relaxation times by simple relations, such as Maxwell's relation and Eq. (4.11), which were derived from the relations (1.2) and (3.24). Thus, our theory may be regarded as a generalization of Maxwell and Boltzmann's theory.

5. TEMPORAL DEVELOPMENT OF THE HEISENBERG OPERATOR

In order to proceed to the problem (II) stated in the end of Sec. 2, we investigate some important properties of the canonical transformation governing the temporal development of the Heisenberg operator.

Equation (2.4) may be written as

$$F(t)=T(t,t_0)F(t_0), \tag{5.1}$$

with

$$T(t,t_0)=\exp[(t-t_0)L], \tag{5.2}$$

where L is the commutator operator generated from the Hamiltonian as[2]

$$LF=\{F,H\}\equiv(FH-HF)/i\hbar. \tag{5.3}$$

This is seen from the fact that Eq. (5.1) satisfies the Heisenberg equation of motion. In the classical limit, L becomes the Poisson bracket,

$$\lim_{\hbar\to 0}L=\sum_{i=1}^{N}[(\nabla_{\mathrm{p}_i}H)\cdot\nabla_{\mathrm{r}_i}-(\nabla_{\mathrm{r}_i}H)\cdot\nabla_{\mathrm{p}_i}]. \tag{5.4}$$

The algebraic properties of the L operator are parallel to those of the commutator bracket.[11] In Eq. (5.3), replace H by observables H_1 and H_2, and denote the L operators thus obtained by L_1 and L_2, respectively. If $\{H_1,H_2\}=0$, then we obtain

$$\begin{gathered}L_1L_2=L_2L_1,\\ \exp(L_1)\exp(L_2)=\exp(L_1+L_2).\end{gathered} \tag{5.5}$$

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[22] R. Dean Taylor and J. G. Dash, Phys. Rev. **106**, 398 (1957).

[23] S. Tomonaga, Z. Physik **110**, 573 (1938).

$T(t,t_0)$ gives the Heisenberg operator at time t from that at time t_0, so that it should satisfy

$$T(t,t_0)=T(t,t')T(t',t_0). \tag{5.6}$$

The motion of the system consists of the free motion of molecules and the interaction between molecules. Let us denote the interaction part of the Hamiltonian by H_1:

$$H=H_0(t)+H_1(t). \tag{5.7}$$

The total Hamiltonian is a constant of the motion, but its parts change in time according to Eq. (5.1). Let us now define

$$L_0(t)G\equiv\{G,H_0(t)\}, \tag{5.8}$$

and, in order to separate the free motion from the effect due to the molecular interaction which is responsible for irreversible processes, let us introduce a new operator,

$$K(t,t_0)\equiv\exp[-tL_0(t)]T(t,t_0)\exp[t_0L_0(t_0)], \tag{5.9}$$

which satisfies

$$\begin{aligned}&K(t,t)=1,\\&K(t,t_0)=K(t,t')K(t',t_0).\end{aligned} \tag{5.10}$$

The physical picture of the K operator can be made clear by the following argument for its classical analog. Consider a classical system and denote its phase point at time t by $X(t)$. There is a unique phase X_t which goes over into the phase $X(t)$ after time t by a free motion of the system obtained by cutting off the molecular interaction. This point is called a hypothetical initial phase in contrast with the initial phase $X(0)$. The $K(t,t_0)$ operates on a hypothetical initial phase X_{t_0} and expresses a free motion from X_{t_0} to $X(t_0)$, a subsequent actual motion from $X(t_0)$ to $X(t)$ and then a free backward motion from $X(t)$ to X_t.

If there is no interaction between molecules in a time interval t_0 to t_1, then we have

$$K(t,t_0)=1,\quad (t_0<t<t_1). \tag{5.11}$$

Therefore, the deviation of K from unity expresses effects due to the molecular interaction.

Now we divide the system into two groups of molecules, A and B;

$$H=H_A(t)+H_B(t)+H_{AB}(t), \tag{5.12}$$

where H_A is the Hamiltonian of the subgroup A separated from the subgroup B, and H_{AB} the interaction energy between the subgroups. With the aid of the operator

$$L_A(t)G\equiv\{G,H_A(t)\}, \tag{5.13}$$

we define

$$T_A(t,t_0)\equiv\exp[(t-t_0)L_A(t_0)]. \tag{5.14}$$

If we cut off the interaction between A and B at time t_0, then we have a hypothetical motion of the subgroup A governed by the Hamiltonian H_A. Equation (5.14) is the T operator for this motion. The K operator for this isolated motion of the subgroup A is denoted by $K_A(t,t_0)$. If there is no interaction between A and B in a time interval t_0 to t_1, then we obtain

$$T(t,t_0)=T_A(t,t_0)T_B(t,t_0),\quad (t_0<t<t_1), \tag{5.15}$$

corresponding to the fact that the temporal development of the system can be described by the Hamiltonian $H'\equiv H_A+H_B$, $\{H_A,H_B\}=0$, in that time interval. Substitution of (5.15) into (5.9) yields

$$K(t,t_0)=K_A(t,t_0)K_B(t,t_0),\quad (t_0<t<t_1). \tag{5.16}$$

Equation (5.16) is an operator form of the decomposition condition of the phase-space transformation function which has been used in a quantum-mechanical derivation of the Maxwell-Boltzmann equation by Mori and Ross.[24]

By making use of Eqs. (5.11) and (5.16), we derive a simple expansion formula of $K(t,0)$ for dilute gases whose molecular motion can be analyzed in terms of binary collisions. For this purpose, let us suppose, for a while, a dilute gas in which, on the average, one pair of molecules at most makes a collision in a short time interval τ. If, in a time interval t to $t+\tau$, there is a collision between molecules i and j, then Eqs. (5.16) and (5.11) lead to

$$K(t+\tau,\,t)=1+\delta W_{ij}(t), \tag{5.17}$$

where we have defined

$$\delta W_{ij}(t)\equiv K_{ij}(t+\tau,\,t)-1 \tag{5.18}$$

with the K operator of the subgroup of molecules i and j. Therefore, by taking into consideration all possible encounters, we obtain

$$K(t+\tau,\,t)=1+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\delta W_{ij}(t). \tag{5.19}$$

Let us write

$$\delta K(t,0)\equiv K(t+\tau,\,0)-K(t,0). \tag{5.20}$$

Then, with the aid of (5.10), Eq. (5.19) leads to

$$\delta K(t,0)=\Big[\sum_{i<j}\delta W_{ij}(t)\Big]K(t,0). \tag{5.21}$$

We let τ become infinitesimally small (but $\tau\gg\tau_0$, τ_0= mean collision time)[25] so that the δW's and δK may be regarded as differentials. Thus, by integrating (5.21), we obtain

$$K(t,0)=1+\sum_{i<j}\int_0^t\delta W_{ij}(t')\,K(t',0), \tag{5.22}$$

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[24] H. Mori and J. Ross, Phys. Rev. **109**, 1877 (1958).

[25] It has been assumed, as in Sec. 2, that the duration of a collision is instantaneous relative to the mean free time. Thus, the τ may be treated as an ordinary differential as far as, for example, time intervals comparable to the mean free time are concerned.

which can be solved, by iteration, to yield

$$K(t,0)=1+\sum_{n=1}^{\infty}\sum_{i_1<j_1}\cdots\sum_{i_n<j_n}\int_0^t \delta W_{i_1j_1}(t_1)\cdots \times\int_0^{t_{n-1}}\delta W_{i_nj_n}(t_n), \quad (5.23)$$

$$\equiv\exp_{(+)}\left[\sum_{i<j}\int_0^t \delta W_{ij}(t')\right]. \quad (5.24)$$

The notation of Eq. (5.24) is a kind of ordered exponential.[26] It should be noted, however, that $t_1>t_2>\cdots>t_n$ in Eq. (5.23).[27] Namely, Equation (5.23) does not include those products which contain more than two δW factors defined at the same time, such as $\delta W_{ij}(t')\delta W_{kl}(t')$, and $\delta W_{i_1j_1}(t_1)\delta W_{i_2j_2}(t')\delta W_{i_3j_3}(t')$, etc. This is a consequence of the fact that more than two collisions do not occur simultaneously in the above hypothetical gas.

To generalize Eq. (5.23) for the description of an actual dilute gas, we require, however, that Eq. (5.23) includes these products except those in which two δW factors defined at the same time have the subscripts of the same molecule, such as $[\delta W_{ij}(t')]^n$, $n\geqq 2$, and $\delta W_{ij}(t')\delta W_{kl}(t')\delta W_{jm}(t')$, etc. Then, it can be shown, with this requirement, that Eqs. (5.23) and (5.24) hold for the dilute gas, in which any molecule collides with at most one other molecule in a short time interval (namely, the binary collision approximation is valid), but the simultaneous occurrence of any number of disjoint binary collisions is possible. We prove this in the following. The binary collision approximation leads to[24]

$$K(t+\tau,t)=\prod_{(ij)}K_{ij}(t+\tau,t), \quad (5.25)$$

for time intervals $\tau\ll\tau_r$, where $\prod_{(ij)}$ means the product over all pairs of molecules which interact with each other in the time intervals. Therefore, by taking into consideration all possible combinations of disjoint pairs, we obtain, with the use of (5.18),

$$K(t+\tau,t)=1+\sum_{n=1}^{\frac{1}{2}N\geqq}\frac{1}{n!}\sum_{i_1<j_1}{}'\cdots\sum_{i_n<j_n}{}' \times\delta W_{i_1j_1}(t)\cdots\delta W_{i_nj_n}(t), \quad (5.26)$$

where $\sum'_{i_1<j_1}$ means the summation over all pairs under the condition that i_1, j_1, i_2, $\cdots$, and j_n represent molecules different from each other corresponding to n disjoint binary collisions. The factor $1/n!$ removes the repetition arising from the $n!$ permutations of the pairs $(i_1j_1)\cdots(i_nj_n)$. Equation (5.26) is an extension of Eq. (5.19). With the aid of the assumption of instantaneous collisions, it is shown in the Appendix that Eq. (5.23) with previously-mentioned requirement yields Eq. (5.26) for short time intervals in which no succession of binary collisions occurs. This guarantees, according to Eq. (5.10), that Eq. (5.23) can be obtained alternatively from Eq. (5.26) as an infinite product of the K operators for time intervals infinitesimally small (but larger than the mean collision time[25]) (see reference 27). Thus it turns out that Eq. (5.23) with the requirement stated before Eq. (5.25) is valid for the description of collisions in a dilute gas. It is interesting to note that the above expansion has some resemblance to Mayer's expansion of the Boltzmann factor in the equilibrium theory of gases.[28]

We designate a binary collision between i and j as (ij). The nth order term of Eq. (5.23), $\delta W_{i_1j_1}(t_1)\cdots\times\delta W_{i_nj_n}(t_n)$, $(t_1\geqq t_2\geqq\cdots\geqq t_n)$, arises from all successive and disjoint binary collisions which contain (i_nj_n) at time t_n, $\cdots$, (i_2j_2) at t_2, and (i_1j_1) at t_1, and which will be called, for convenience, the associated successive and disjoint collisions, respectively. Furthermore, it should be noticed that the ordered exponential (5.24) cannot be reduced to the exponential even in the classical limit.

6. KINETIC EQUATION FOR THE DIAGONAL ELEMENTS

The Heisenberg operator for the dynamical variable F can be written as

$$F(t)=\exp[tL_0(t)]K(t,0)F. \quad (6.1)$$

In accordance with the relaxation times of the viscosity and thermal conduction fluxes, our main interest is in the temporal behavior of Eq. (6.1) for time intervals of the order of magnitude of the mean free time. With the aid of the assumption of instantaneous collisions, therefore, we may neglect effects due to pairs of molecules in collision at instants 0 and t. Since, therefore, $H_0(t)=H_0(0)$, the diagonal elements of the Heisenberg operator can be written, with the aid of the relation $\langle\mathbf{p}|\{G,H_0\}|\mathbf{p}\rangle=0$ for an arbitrary quantity G, as

$$\langle\mathbf{p}|F(t)|\mathbf{p}\rangle=\langle\mathbf{p}|K(t,0)F|\mathbf{p}\rangle \quad (6.2)$$

$$=\sum_{n=0}^{\infty}\sum_{i_1<j_1}\cdots\sum_{i_n<j_n}\int_0^t\cdots\int_0^{t_{n-1}} \times\langle\mathbf{p}|\delta W_{i_1j_1}(t_1)\cdots\delta W_{i_nj_n}(t_n)F|\mathbf{p}\rangle, \quad (6.3)$$

where Eq. (5.23) has been inserted. We discuss in this section how we can derive the kinetic equation (2.13) from Eq. (6.3), to clarify the problem of the use of the random phase assumption.

As has been pointed out in Sec. 2, the random phase

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[26] M. L. Goldberger and E. N. Adams II, J. Chem. Phys. 20, 240 (1952).

[27] This can be seen clearly from the fact that the above procedure is a mathematical technique of inserting Eq. (5.19) into the equation $K(t,0)=K(t,t-\tau)K(t-\tau,t-2\tau)\cdots K(\tau,0)$, and arranging the terms thus obtained in the form of (5.23).

[28] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), Chaps. 12, 13.

assumption introduced before Eq. (2.5) is related to successions of the binary collisions, which appear in the higher order terms of Eq. (6.3). To analyze the higher order terms, it is convenient to classify the terms into the following three types; the type A, in which both of two molecules of a δW_{ij} are not contained in any other δW factor appearing to the right of the δW_{ij}, and the other type B, in which one of two molecules of each δW_{ij} is contained in at least one other δW factor appearing to the right of the δW_{ij}. The type B is divided into BI, in which one of two molecules of each δW_{ij} is not contained in any δW factor to the right, and BII, in which both of two molecules of a δW_{ij} are contained to the right.

As an example of the type BI, we consider

$$\langle \mathbf{p} | \delta W_{24}(t_3) \delta W_{13}(t_2) \delta W_{12}(t_1) F \,|\mathbf{p}\rangle, \tag{6.4}$$

where $t_3 > t_2 > t_1$. Let us write down F as

$$F = \textstyle\sum_{\mathbf{p}} |\mathbf{p}\rangle F_{\mathbf{p}} \langle \mathbf{p}|$$

with the use of Dirac's ket and bra vectors $|\mathbf{p}\rangle$ and $\langle \mathbf{p}|$,[29] representing the eigenvectors of the total momentum of the system. The products $|\mathbf{p}\rangle\langle\mathbf{p}|$ are the projection operators of the set of eigenvectors. Denoting the eigenvector of the momentum of molecule i by $|\mathbf{p}_i\rangle$, we have

$$|\mathbf{p}\rangle = |\mathbf{p}_1\rangle\, |\mathbf{p}_2\rangle \cdots |\mathbf{p}_N\rangle. \tag{6.5}$$

If k is different from i and j, then we obtain

$$\delta W_{ij} [\,|\mathbf{p}_k\rangle\, A \,\langle \mathbf{p}_k|\,] = |\mathbf{p}_k\rangle [\delta W_{ij} A] \langle \mathbf{p}_k|. \tag{6.6}$$

Therefore, since the subscript 4 is not contained in any δW factor to the right of δW_{24}, Eq. (6.4) may be written as

$$\langle \mathbf{p}_1\mathbf{p}_3 | f | \mathbf{p}_1\mathbf{p}_3\rangle, \tag{6.7}$$

where

$$f = \sum_{\mathbf{p}_4'} \langle \mathbf{p}_2\mathbf{p}_4|\, \delta W_{24} [\,|\mathbf{p}_4'\rangle G_{\mathbf{p}_4'} \langle \mathbf{p}_4'|\,]\, |\mathbf{p}_2\mathbf{p}_4\rangle, \tag{6.8}$$

$$G_{\mathbf{p}_4'} = \sum_{\mathbf{p}_1'} \sum_{\mathbf{p}_2'} \sum_{\mathbf{p}_3'} \delta W_{13} [\,|\mathbf{p}_3'\rangle (\delta W_{12} | \mathbf{p}_1'\mathbf{p}_2'\rangle \times F_{\mathbf{p}_1'\mathbf{p}_2'\mathbf{p}_3'\mathbf{p}_4'} \langle \mathbf{p}_1'\mathbf{p}_2'|) \langle \mathbf{p}_3'|\,], \tag{6.9}$$

$$F_{\mathbf{p}_1'\mathbf{p}_2'\mathbf{p}_3'\mathbf{p}_4'} = F_{\mathbf{p}_1'\mathbf{p}_2'\mathbf{p}_3'\mathbf{p}_4'\mathbf{p}_5\cdots\mathbf{p}_N}. \tag{6.10}$$

Denoting the eigenvectors of the relative and center-of-mass momenta of molecules i and j by $|\mathbf{p}_{ij}\rangle$ and $|\mathbf{p}_{cij}\rangle$, we obtain

$$\begin{aligned} |\mathbf{p}_i\mathbf{p}_j\rangle &= |\mathbf{p}_{cij}\rangle\, |\mathbf{p}_{ij}\rangle, \\ |\mathbf{p}_j\rangle &= |\mathbf{p}_{cij}\rangle\, |\mathbf{p}_{ij}\rangle\, \langle \mathbf{p}_i|. \end{aligned} \tag{6.11}$$

Therefore, Eq. (6.8) becomes

$$f = \sum_{\mathbf{p}_{24}'} \langle \mathbf{p}_{24}|\, \delta W_{24} [\,|\mathbf{p}_{24}'\rangle \langle \mathbf{p}_2' | G_{\mathbf{p}_4'} | \mathbf{p}_2'\rangle \langle \mathbf{p}_{24}'|\,]\, |\mathbf{p}_{24}\rangle, \tag{6.12}$$

where $\mathbf{p}_{c24}' = \mathbf{p}_{c24}$. Here use has been made of the fact that δW_{ij} is independent of the center-of-mass motion; namely, denoting the K operator for the relative motion by K_r, we have

$$\delta W_{ij}(t) = K_r(t+\tau, t) - 1. \tag{6.13}$$

Equation (6.12) can be expressed in terms of the binary collision operator defined by Eq. (2.12) with the aid of the equation,

$$\sum_{\mathbf{p}_{ij}'} \langle \mathbf{p}_{ij} | \delta W_{ij}(t) [\,|\mathbf{p}_{ij}'\rangle\, g(\mathbf{p}_{ij}')\, \langle \mathbf{p}_{ij}'|\,]\, |\mathbf{p}_{ij}\rangle = -\tau \Lambda_{ij} g(\mathbf{p}_{ij}), \tag{6.14}$$

where $\tau \gg \tau_0$, and $g(\mathbf{p}_{ij})$ is an arbitrary function of $\mathbf{p}_{ij}$. Equation (6.14) can be shown as follows. The $\delta W_{ij}(t)$ is nonvanishing only when the collision (ij) occurs in the time interval t to $t+\tau$. And in that case the molecules i and j are isolated from other molecules in that time interval τ $(\tau_r \gg \tau \gg \tau_0)$. Accordingly, we may consider a two-particle system which makes a collision in the time interval t to $t+\tau$ in the same way as the molecules i and j. Denoting the U operator for the relative motion of that system by $U_r(t)$, the left-hand side of (6.14) becomes, with the aid of (6.13).

$$\sum_{\mathbf{p}_{ij}'} w(\mathbf{p}_{ij}', \mathbf{p}_{ij}; \tau) g(\mathbf{p}_{ij}') - g(\mathbf{p}_{ij}), \tag{6.15}$$

where we have defined

$$w(\mathbf{p}_{ij}', \mathbf{p}_{ij}; t) = |\langle \mathbf{p}_{ij}' | U_r(t) | \mathbf{p}_{ij}\rangle|^2. \tag{6.16}$$

With the aid of the equation for $w(\mathbf{p}_{ij}', \mathbf{p}_{ij}; t)$ corresponding to Eq. (2.7), Eq. (6.15) can be written as

$$\sum_{\mathbf{p}_{ij}' (\neq \mathbf{p}_{ij})} w(\mathbf{p}_{ij}', \mathbf{p}_{ij}; \tau) \{ g(\mathbf{p}_{ij}') - g(\mathbf{p}_{ij}) \}. \tag{6.17}$$

According to the Lippmann-Schwinger theory of scattering,[30] Eq. (6.16) can be expressed in terms of the scattering cross section with the aid of the adiabatic approximation, and can be shown to satisfy the second equation of (2.10).[24] Thus we arrive at Eq. (6.14). It should be noted here that the adiabatic approximation is responsible for the inequality of the direction of time axis of Eq. (2.13).[13]

Applying Eq. (6.14) to Eq. (6.12), Eq. (6.8) becomes

$$f = -\tau \Lambda_{24} \langle \mathbf{p}_2 | G_{\mathbf{p}_4} | \mathbf{p}_2\rangle. \tag{6.18}$$

In the same way, we obtain

$$\begin{aligned} &\langle \mathbf{p}_1\mathbf{p}_2\mathbf{p}_3 | G_{\mathbf{p}_4} | \mathbf{p}_1\mathbf{p}_2\mathbf{p}_3\rangle \\ &\quad = -\tau \Lambda_{13} \langle \mathbf{p}_1\mathbf{p}_2 | \delta W_{12} [\sum_{\mathbf{p}_1'} \sum_{\mathbf{p}_2'} |\mathbf{p}_1'\mathbf{p}_2'\rangle F_{\mathbf{p}_1'\mathbf{p}_2'} \langle \mathbf{p}_1'\mathbf{p}_2'|\,] | \mathbf{p}_1\mathbf{p}_2\rangle \\ &\quad = -\tau \Lambda_{13} (-\tau \Lambda_{12} F_{\mathbf{p}_1\mathbf{p}_2\cdots\mathbf{p}_N}). \end{aligned}$$

Thus, Eq. (6.7) or Eq. (6.4) becomes

$$(-\tau\Lambda_{24})(-\tau\Lambda_{13})(-\tau\Lambda_{12}) F_{\mathbf{p}}. \tag{6.19}$$

Terms of the type BI can be calculated by the iterative

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[29] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, 1947).

[30] B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950).

use of the procedure from Eqs. (6.4) to (6.18) so that the collision operators Λ_{ij} appear instead of δW_{ij}'s.

On the contrary, terms of the type BII cannot be expressed in terms only of the collision operator. Any term of BII is such that the every associated successive collision has the closed collision cycles. For brevity, consider $\delta W_{13}\,\delta W_{14}\,\delta W_{23}\,\delta W_{12}$ and its associated successive collision of the smallest size (12) (23) (14) (13). For example, the two δW factors corresponding to the first and last binary collisions of the closed collision cycle cannot be replaced by the collision operator, because the term cannot be reduced to the form of (6.8) nor $\langle \mathbf{p}_1 | \delta W_{12} [\sum_{\mathbf{p}_1'} \sum_{\mathbf{p}_2'} | \mathbf{p}_1' \mathbf{p}_2' \rangle G \langle \mathbf{p}_1' \mathbf{p}_2' |] | \mathbf{p}_1 \rangle$.

Terms of the type A and the equation obtained by replacing their δW's by Λ_{ij}'s become zero for any observable F which is a simple sum of quantities of molecules like Eq. (2.1).

According to the requirement stated before Eq. (5.25), Eq. (6.3) does not include those products in which two δW factors defined at the same time have the same molecule. However, we may include these products except those which contain the same $\delta W_{ij}(t)$ more than two times, because the added terms arising from multiple collisions vanish automatically due to the binary collision approximation. The excluded products belong to the type BII. If the δW factors of those of the added terms which belong to the type BI are replaced by the collision operators, then the equations thus obtained do not vanish as a consequence of the separate integration of each factor over all its configuration; (the separate integration is incompatible with the configuration of multiple collisions). However, the contributions of these equations to the time integral of Eq. (6.3) can be neglected compared to those of other terms.

Thus, if the terms of the type BII and the equations obtained by replacing their δW's by the collision operators are negligible compared to the contributions due to the terms of the type BI, then Eq. (6.3) becomes

$$\langle \mathbf{p} | F(t) | \mathbf{p} \rangle = \exp\Big(-t \sum_{i<j} \Lambda_{ij}\Big) F_{\mathbf{p}}. \tag{6.20}$$

As has been pointed out by Brout,[18] the number of terms of the type BII is, in a given finite order, negligible compared to that of terms of the type BI in the limit of large numbers of molecules. Accordingly, Eq. (6.20) can be considered to be a good approximation in the thermodynamic system. Thus, the kinetic equation for the diagonal elements has been derived with the assumptions of binary and instantaneous collisions and with the adiabatic approximation for binary collisions.

The successive collisions associated with the terms of the type BII propagate correlations in the sense that the occurrence of the last binary collision of any closed collision cycle depends upon the detailed behavior of the previous collisions, whereas any collision of the successive collisions of the type BI can occur, by adjusting the path of the new partner, even if any change in the behavior of the previous collisions has been made. Equation (6.20) was derived without the use of the usual formulation of the random phase assumption by recognizing the negligible influence of closed collision cycles explicitly. This shows that the physical significance of the random phase assumption may be considered to be the discarding of correlations introduced by collisions by severing closed collision cycles, and this assumption can be justified in the limit of an infinite system.

It is interesting to note that, as can be seen from Eq. (2.2), the classical counterpart of the diagonal elements of the Heisenberg operator is the average over configuration space,

$$\langle \mathbf{p} | F(t) | \mathbf{p} \rangle = \frac{1}{V^N} \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N\, F(t), \tag{6.21}$$

where $(\mathbf{p},\mathbf{r})$ is the phase point at the initial time. On the basis of this equation, the classical formulation parallel to the above follows.

The above method can be applied to the density matrix $\rho(t)$ to lead to the master equation,

$$\langle \mathbf{p} | \rho(t) | \mathbf{p} \rangle = \exp\big(-t \textstyle\sum_{i<j} \Lambda_{ij}\big) \langle \mathbf{p} | \rho(0) | \mathbf{p} \rangle, \tag{6.22}$$

under the initial condition

$$\rho(0) = \textstyle\sum_{\mathbf{p}} | \mathbf{p} \rangle P(\mathbf{p}) \langle \mathbf{p} |, \tag{6.23}$$

which corresponds to the initial preparation of the ensemble for a macroscopically homogeneous gas of low density. The alteration is only to change the sign of the L operator. Then, to obtain Eq. (6.14) with the corresponding δW_{ij} function, it is necessary to use the concept of microscopic reversibility,

$$w(\mathbf{p}_{ij}, \mathbf{p}_{ij}'; s) = w(\mathbf{p}_{ij}', \mathbf{p}_{ij}; s), \tag{6.24}$$

in deriving Eq. (6.17). In this case, terms of the type A do not vanish, but their δW's can be replaced by the binary collision operators except those terms whose associated successive collisions have closed collision cycles and which can be neglected according to the above discussion. Thus, we arrive at Eq. (6.22). Since the dependence of the quantum-mechanical phase-space distribution function on configuration space coordinates comes from the off-diagonal elements of the density matrix, the random phase assumption is equivalent to the neglect of the configuration dependence of the distribution function.[24] Therefore, Eq. (6.22) is the quantum-mechanical counterpart of the master equation established by Kac[12] and Brout.[18]

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APPENDIX. DERIVATION OF EQ. (5.26) FROM EQ. (5.23)

We take a time interval t_0 to t in which no succession of binary collisions occurs. Equation (5.23) does not include those products in which two δW factors defined at the same time have the subscripts of the same molecule. And, corresponding to no succession of binary collisions, those terms in which two δW's have the subscripts of the same molecule vanish. Therefore, we obtain

$$K(t,t_0)=1+\sum_{n=1}^{\frac{1}{2}N\geqq}\sum_{i_1<j_1}{}'\cdots\sum_{i_n<j_n}{}'$$
$$\times\int_{t_0}^{t}\delta W_{i_1j_1}(t_1)\cdots\int_{t_0}^{t_{n-1}}\delta W_{i_nj_n}(t_n),\quad\text{(A.1)}$$

where $\sum'_{i_1<j_1}$ means the same summation as in Eq. (5.26). It should be noted here that such products as $\delta W_{ij}(t')\delta W_{ij}(t'')$, $t'\neq t''$, have been taken to be zero with the assumption of instantaneous collisions so that we have neglected, for example, long time orbiting in collisions.[21] With the aid of the commutativity,

$$\delta W_{ij}(t_1)\delta W_{kl}(t_2)=\delta W_{kl}(t_2)\delta W_{ij}(t_1),\quad\text{(A.2)}$$

for i, $j\neq k$, l, the nth order term of (A.1) becomes

$$\frac{1}{n!}\sum_{i_1<j_1}{}'\cdots\sum_{i_n<j_n}{}' W_{i_1j_1}(t,t_0)\cdots W_{i_nj_n}(t,t_0),\quad\text{(A.3)}$$

where we have defined

$$W_{ij}(t,t_0)=\int_{t_0}^{t}\delta W_{ij}(t').\quad\text{(A.4)}$$

This is similar to the relation

$$t^n/n!=\int_0^t dt_1\cdots\int_0^{t_{n-1}}dt_n.$$

The $W_{ij}(t,t_0)$ is identical with that defined by

$$K_{ij}(t,t_0)=1+W_{ij}(t,t_0).\quad\text{(A.5)}$$

This can be shown, with the aid of the assumption of instantaneous collisions, as follows. We recall that $K_{ij}(t,t_0)$ is a K operator for the hypothetical motion of the subgroup of molecules i and j obtained by cutting off the interaction with the other part at time t_0. However, since i and j are isolated from the other molecules in the time interval t_0 to t [as far as (A.4) does not vanish], the $K_{ij}(t,t_0)$ describes the actual motion of i and j in the gas. Therefore, with the aid of Eq. (5.10), we obtain

$$K_{ij}(t,t_0)=K_{ij}(t,t')K_{ij}(t',t_0).\quad\text{(A.6)}$$

If i and j do not interact with each other at an instant t', then

$$W_{ij}(t,t')W_{ij}(t',t_0)=0,\quad\text{(A.7)}$$

which leads to

$$W_{ij}(t,t_0)=W_{ij}(t,t')+W_{ij}(t',t_0).\quad\text{(A.8)}$$

According to the assumption of instantaneous collisions, the collision between i and j starts and ends in a short time interval t to $t+\tau$, so that (A.8) leads to (A.4). Thus, Eqs. (A.3) and (A.4) give Eq. (5.26).