

EQUATIONS FOR SPACE - TIME AND TIME CORRELATION
FUNCTIONS AND PROOF OF THE EQUIVALENCE OF
RESULTS OF THE CHAPMAN - ENSKOG AND TIME
CORRELATION METHODS*

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A study is made of the problem of determining the space-time or time correlation functions in a many-body classical system. The general correlation function of dynamical variables of a binary type (it is precisely these functions that are encountered in applications) is expressed in terms of the first two terms of a sequence of functions that depend on an increasing number of arguments and satisfy Bogolyubov's chain of equations with known initial data. In the lowest order in the density the correlation function can be expressed solely in terms of the first function of the sequence. This function is the solution of the initial-value problem for the linearized Boltzmann equation. An investigation is made of the initial-value problems for the correlation functions that determine the transport coefficients of simple and multicomponent gases. This investigation renders it possible to give a simple, complete, and rigorous proof of the results of the Chapman-Enskog and correlation function methods. The proof is based on the well-known properties of the linearized collision operator and it is possible to avoid the divergences encountered in other investigations.

In recent years the methods of nonequilibrium statistical mechanics have been widely used in the theory of irreversible processes. These methods enable one to obtain the transport laws and express a number of important characteristics, in particular, the transport coefficients of dense gases and liquids, in terms of integrals over the time of time correlation functions.

One of the most important ways of verifying the new theory is to compare its results with those of some special case, which has already been confirmed in practice. A good example of such a special case is a Boltzmann gas, since its theory is well known [1-3]. A number of papers [4-6] have been devoted to proving the equivalence of the method of correlation functions and the Chapman-Enskog theory for the case of single-component gases. However, Ernst et al. [4, 5] considered correlation functions with dynamical variables integrated over the time and they were forced to work with integrals that do not converge absolutely. Zwanzig [6] also arrived at diverging series and adopted an artificial summation of these series. Thus, the rigor and elegance of the kinetic theory of gases would appear to be wasted. In addition, the equivalence of the expressions for the transport coefficients of gaseous mixtures was not investigated at all.

In the present paper, we propose a general method of investigation of space-time and time correlation functions of both simple and multicomponent media. (Similar ideas have also been developed by Tolmachev [11], who has investigated conditional time distributions; it is, however, preferable to investigate the correlation functions themselves for a number of reasons. For the different correlation functions one obtains different initial-value problems, and each have their own specific features. The initial data enter the approximate formulas for the calculation of the correlation functions and it is precisely the form of the initial data that determines the form of the correlation functions [12].) In the Boltzmann limit, i.e., in the

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lowest order in the density, this method enables one to give a rigorous proof of the complete equivalence of the method of time correlation functions and Chapman–Enskog theory for all the transport coefficients. The space–time and time correlation functions can be expressed in terms of new g_s functions, which satisfy Bogolyubov's chain of equations [10] with known initial data. In the lowest order in the density, the correlation functions can be expressed entirely in terms of the g_1 functions, for which a closed equation (the linearized Boltzmann equation) is obtained on the basis of ideas developed by Bogolyubov [10]. The subsequent investigation is based on the use of the known properties of the linearized collision operator and does not entail an analysis of diverging series or integrals.

It should be emphasized that the rigorous proof of the equivalence is merely an illustration. In our opinion, it is most natural in the theory of fluctuations to start from the corresponding initial-value problems for Bogolyubov's chain of equations; these problems are formulated in §1.

In the present paper, we consider the correlation functions for structureless molecules that obey the laws of classical mechanics. However, the treatment can be carried through for correlation functions of multiatomic molecules that satisfy quantum mechanical laws.

1. Consider space–time correlation functions of the form

$$\psi(\mathbf{r}, \mathbf{r}', t) = \lim_{V \rightarrow \infty} \langle \hat{a}(\mathbf{r}) \hat{b}(\mathbf{r}', t) \rangle. \quad (1.1)$$

Here, the limit sign stands for the thermodynamic limit when $N, V \rightarrow \infty$ with $N/V = n = \text{const}$ and the angular brackets stand for averaging over the equilibrium (or, possibly, locally equilibrium) ensemble $\rho_N(x_1, \dots, x_N)$; $x_i = (\mathbf{r}_i, \mathbf{p}_i)$ are the coordinates and momenta of the i -th particle. The dynamical variables $a(\mathbf{r})$, $b(\mathbf{r})$, ... have the form

$$\hat{a}(\mathbf{r}) = \sum_{i=1}^N \left[a_i + \frac{1}{2} \sum_{j=1}^N a_{ij} \right] \delta(\mathbf{r} - \mathbf{r}_i),$$

$$a_i = a(\mathbf{p}_i), \quad a_{ij} = a_{ji} = a(\mathbf{p}_i, \mathbf{p}_j, \mathbf{r}_{ij}), \quad \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \quad \hat{a}(\mathbf{r}, t) = \exp(-tH_N) \hat{a}(\mathbf{r}),$$

where $\exp(-tH_N)$ is the evolution operator of a system of N particles. We assume that the potential of the interaction Φ_{ij} and the functions a_{ij} are short-range functions, i.e., they vanish for $r_{ij} \geq \sigma$, where σ is the range of the forces.

Using the symmetry properties of the functions \hat{a} , \hat{b} , and ρ_N under permutations of the particles, we can express (1.1) in the form

$$\psi(\mathbf{r}, \mathbf{r}', t) = n \int dx_1 a_1 \delta(\mathbf{r} - \mathbf{r}_1) g_1(x_1 | \mathbf{r}', t) + \frac{n^2}{2} \int dx_1 dx_2 a_{12} \delta(\mathbf{r} - \mathbf{r}_1) g_2(x_1, x_2 | \mathbf{r}', t), \quad (1.2)$$

where we have introduced g_s functions in accordance with the formulas

$$n^s g_s(x_1, \dots, x_s | \mathbf{r}', t) = \lim_{V \rightarrow \infty} \frac{N!}{(N-s)!} \int dx^{N-s} \hat{b}(\mathbf{r}', t) \rho_N. \quad (1.3)$$

The g_s functions satisfy Bogolyubov's well-known chain of equations [10]:

$$\frac{\partial g_s}{\partial t} + H_s g_s = n \sum_{i=1}^s \int dx_{s+1} [\Phi_{i,s+1} g_{s+1}] \quad (1.4)$$

and, in addition, initial data that can be obtained from (1.3):

$$\begin{aligned} g_s(x_1, \dots, x_s | \mathbf{r}', t=0) &= \sum_{i=1}^s \left[b_i + \frac{1}{2} \sum_{j=1}^s b_{ij} \right] \delta(\mathbf{r}' - \mathbf{r}_i) F_s \\ &+ n \int dx_{s+1} b_{s+1} \delta(\mathbf{r}' - \mathbf{r}_{s+1}) F_{s+1} + \frac{n}{2} \sum_{i=1}^s \int dx_{s+1} b_{i,s+1} [\delta(\mathbf{r}' - \mathbf{r}_{s+1}) \\ &+ \delta(\mathbf{r}' - \mathbf{r}_i)] F_{s+1} + \frac{n^2}{2} \int dx_{s+1} dx_{s+2} b_{s+1,s+2} \delta(\mathbf{r}' - \mathbf{r}_{s+1}) F_{s+2}, \end{aligned} \quad (1.5)$$

where we have introduced the equilibrium s -particle distribution functions F_s :

$$n^s F_s(x_1, \dots, x_s) = \lim_{V \rightarrow \infty} \frac{N!}{(N-s)!} \int dx^{N-s} \rho_N. \quad (1.6)$$

Thus, the determination of the g_s functions, in terms of which the correlation functions (1.1) can be expressed, reduces to the initial-value problem (1.4)–(1.5) for Bogolyubov's chain of equations.

2. In the Boltzmann limit, i.e., in the lowest order in the density n , Eq. (1.2) yields

$$\psi(\mathbf{r}, \mathbf{r}', t) = n \int d\mathbf{p} a(\mathbf{p}) g_1(x | \mathbf{r}', t), \quad x = (\mathbf{r}, \mathbf{p}). \quad (2.1)$$

For small n one can readily obtain a closed equation for g_1 . Indeed, we shall seek the solution of the chain (1.4) as an expansion

$$g_s = g_s^{(0)} + n g_s^{(1)} + \dots \quad (2.2)$$

The equations for the functions of the zeroth approximation have the solution

$$g_s^{(0)}(t) = \exp(-tH_s) g_s^{(0)}(t=0). \quad (2.3)$$

We now combine Eqs. (2.2) and (1.5) with $s = 1$ and 2 for $r_{12} \leq \sigma$, $t \gg \tau_{st} \sim \sigma (m/kT)^{1/2}$. In the lowest order in n , we then obtain

$$g_2^{(0)}(x_1, x_2 | \mathbf{r}', t) = I_2(x_1, x_2) [g_1^{(0)}(x_1 | \mathbf{r}', t) F_1(p_2) + F_1(p_1) g_1^{(0)}(x_2 | \mathbf{r}', t)], \quad (2.4)$$

$$I_2(x_1, x_2) = \lim_{\tau \rightarrow \infty} \exp\{-\tau H_2(x_1, x_2)\} \exp\{\tau [H_1(x_1) + H_1(x_2)]\}.$$

In deriving (2.4) we have also used an expansion of the functions F_s with respect to n [10].

Restricting ourselves to the lowest order in n , we substitute (2.4), in which we now omit the superscript (0), into the first equation of the chain. After the usual simple transformations of the collision integral [10], the resulting equation reduces to the linearized Boltzmann equation

$$\frac{\partial g_1}{\partial t} + \frac{\mathbf{p}}{m} \frac{\partial g_1}{\partial \mathbf{r}} = nJ(g_1), \quad (2.5)$$

$$J(g_1) = \int [F_1(p') g_1(\mathbf{p}', \mathbf{r} | \mathbf{r}', t) + F_1(p_1') g_1(\mathbf{p}', \mathbf{r} | \mathbf{r}', t) - F_1(p) g_1(\mathbf{p}_1, \mathbf{r} | \mathbf{r}', t) - F_1(p_1) g_1(\mathbf{p}, \mathbf{r} | \mathbf{r}', t)] g b db d\epsilon d\mathbf{p}_1,$$

where \mathbf{p}' and \mathbf{p}_1' are the momenta of the two particles after a collision characterized by the initial momenta \mathbf{p} and \mathbf{p}_1 , the impact b , and the azimuth ϵ ; $g = |\mathbf{p} - \mathbf{p}_1|/m$.

Equation (2.5) must be solved with the initial condition

$$g_1(\mathbf{p}, \mathbf{r} | \mathbf{r}', t=0) = b(\mathbf{p}) \delta(\mathbf{r} - \mathbf{r}') F_1(p). \quad (2.6)$$

For the time correlation functions

$$\Psi(t) = \lim_{V \rightarrow \infty} \frac{1}{V} \langle \hat{a} \hat{b}(t) \rangle, \quad (2.7)$$

$$\hat{a} = \sum_{i=1}^N \left[a_i + \frac{1}{2} \sum_{j=1}^N a_{ij} \right],$$

we obtain an analogous equation in the Boltzmann limit:

$$\Psi(t) = n \int d\mathbf{p} a(\mathbf{p}) G_1(\mathbf{p}, t), \quad (2.8)$$

where the function $G_1(\mathbf{p}, t)$ is the solution of the initial-value problem for the spatially homogeneous linearized Boltzmann equation

$$\frac{\partial G_1}{\partial t} = nJ(G_1), \quad G_1(\mathbf{p}, t=0) = b(\mathbf{p}) F_1(p). \quad (2.9)$$

In the case of a gaseous mixture consisting of L components the time correlation functions

$$\Psi(t) = \lim_{V \rightarrow \infty} \frac{1}{V} \langle \hat{a} \hat{b}(t) \rangle, \quad (2.10)$$

$$\hat{a} = \sum_{k=1}^L \sum_{i=1}^{N_k} \left[a_i^{(k)} + \frac{1}{2} \sum_{i=1}^L \sum_{j=1}^{N_j} a_{ij}^{(kl)} \right]$$

are determined by a similar equation:

$$\Psi(t) = n \sum_{k=1}^L \int d\mathbf{p} a^{(k)}(\mathbf{p}) G^{(k)}(\mathbf{p}, t), \quad (2.11)$$

where functions $G_1^{(k)}(\mathbf{p}, t)$ are the solution of the initial-value problem for the system of linearized Boltzmann equations

$$\frac{\partial G_1^{(k)}}{\partial t} = n \sum_{l=1}^L J_{lk}(G_1), \quad G_1^{(k)}(\mathbf{p}, t=0) = b_1^{(k)} F_1^{(k)}, \quad (2.12)$$

$$J_{lk}(G_1) = \int [F_1^{(k)}(\mathbf{p}') G_1^{(l)}(\mathbf{p}_1', t) + F_1^{(l)}(\mathbf{p}_1') G_1^{(k)}(\mathbf{p}', t) - F_1^{(k)}(\mathbf{p}) G_1^{(l)}(\mathbf{p}_1, t) - F_1^{(l)}(\mathbf{p}_1) G_1^{(k)}(\mathbf{p}, t)] g_{kl} b b b d s d \mathbf{p}_1,$$

$$g_{kl} = |\mathbf{p}/m_k - \mathbf{p}_1/m_l|, \quad n F_1^{(k)}(\mathbf{p}) = \frac{n_k}{(2\pi m_k K T)^{3/2}} \exp \frac{-p^2}{2m_k K T}.$$

3. In nonequilibrium statistical mechanics the transport coefficients are expressed in terms of integrals over the time of the time correlation functions. Thus, the coefficients of shear η and dilatational ζ viscosity and the thermal conductivity λ of a simple medium can be expressed in the form

$$\eta = \int_0^\infty dt \lim_{V \rightarrow \infty} \frac{1}{10VKT} \langle \hat{P}_{\alpha\beta} \hat{\Pi}_{\alpha\beta}(t) \rangle,$$

$$\zeta = \int_0^\infty dt \lim_{V \rightarrow \infty} \frac{1}{9VKT} \langle \hat{P}_{\alpha\alpha} \hat{\Pi}'_{\beta\beta}(t) \rangle,$$

$$\lambda = \int_0^\infty dt \lim_{V \rightarrow \infty} \frac{1}{3VKT^2} \langle \hat{Q}_\alpha \hat{S}_\alpha(t) \rangle,$$

$$\hat{P}_{\alpha\beta} = \sum_{i=1}^N \left[\frac{p_{i\alpha} p_{i\beta}}{m} - \frac{1}{2} \sum_{j=1}^{N'} r_{ija} \frac{\partial \Phi_{ij}}{\partial r_{ij\beta}} \right], \quad \hat{\Pi}_{\alpha\beta} = \hat{P}_{\alpha\beta} - \frac{1}{3} \hat{P}_{\gamma\gamma} \delta_{\alpha\beta}, \quad (3.1)$$

$$\hat{\Pi}'_{\alpha\alpha} = \hat{P}_{\alpha\alpha} - 3PV - 3 \left(\frac{\partial P}{\partial E} \right)_n (\hat{E} - EV), \quad \hat{S}_\alpha = \hat{Q}_\alpha - \frac{h}{\rho} \hat{P}_\alpha,$$

$$\hat{Q}_\alpha = \sum_{i=1}^N \left[\frac{p_{i\alpha}}{m} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j=1}^{N'} \left(\frac{p_{i\alpha}}{m} \Phi_{ij} - \frac{p_{i\beta}}{m} r_{ija} \frac{\partial \Phi_{ij}}{\partial r_{ij\beta}} \right) \right],$$

$$\hat{P}_\alpha = \sum_{i=1}^N p_{i\alpha}, \quad \hat{E} = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j=1}^{N'} \Phi_{ij} \right], \quad h = E + P,$$

E is the density of the internal energy; P is the pressure; ρ is the mass density; summation from 1 and 3 is understood over repeated Greek indices.

Introducing G_1 functions instead of (3.1), we obtain the following equations in the lowest order in n :

$$\eta = \frac{n}{10KTm} \int_0^\infty dt \int d\mathbf{p} p_\alpha p_\beta G_{1\alpha\beta}(\mathbf{p}, t),$$

$$\zeta = \frac{n}{9KTm} \int_0^\infty dt \int d\mathbf{p} p^2 G_1(\mathbf{p}, t), \quad (3.2)$$

$$\lambda = \frac{n}{6KT^2 m^2} \int_0^\infty dt \int d\mathbf{p} p_\alpha p^2 G_{1\alpha}(\mathbf{p}, t).$$

*Since we are considering the canonical ensemble, the term describing the density fluctuations (see [14, 15]) does not occur here.

The functions $G_{1\alpha\beta}(\mathbf{p}, t)$, $\alpha, \beta = 1, 2, 3$, $G_1(\mathbf{p}, t)$, $G_{1\alpha}(\mathbf{p}, t)$, $\alpha = 1, 2, 3$ satisfy the spatially homogeneous Boltzmann equation (2.9) and initial data which have the following form in the lowest order in n :

$$\begin{aligned} G_{1\alpha\beta}(\mathbf{p}, t=0) &= \frac{1}{m} \left[p_\alpha p_\beta - \frac{1}{3} p^2 \delta_{\alpha\beta} \right] F_1(\mathbf{p}), \\ G_{1\alpha}(\mathbf{p}, t=0) &= \frac{p_\alpha}{m} \left(\frac{p^2}{2m} - \frac{5}{2} KT \right) F_1(\mathbf{p}), \\ G_1(\mathbf{p}, t=0) &= \left[\left(\frac{p^2}{m} - 3KT \right) - 3 \left(\frac{\partial P}{\partial E} \right)_n \left(\frac{p^2}{2m} - \frac{3}{2} KT \right) \right] F_1(\mathbf{p}) = 0, \end{aligned} \quad (3.3)$$

since $P = nKT = 2E/3$. From the last condition of (3.3) it follows that $G_1(\mathbf{p}, t) \equiv 0$ and, hence, the coefficient of dilatational viscosity vanishes, $\xi = 0$.

Let us investigate the initial-value problem (2.9) with the initial data (3.3). We recall the basic properties of the collision operator J . On the Hilbert space $L^2_{F_1^{-1}}$, where F_1^{-1} is the weight,* J is a symmetric dissipative operator. There is a fivefold degenerate vanishing eigenvalue to which there correspond the eigenfunctions F_1 ; $p_\alpha F_1$, $\alpha = 1, 2, 3$, $(p^2/2m)F_1$. For a large class of potentials that Grad [13] has called "hard," there exists a constant $\rho > 0$ such that

$$(Jf, f) \leq -\rho(f, f) \quad ((f, g) = \int F_1^{-1}(p) f(\mathbf{p}) g(\mathbf{p}) d\mathbf{p}), \quad (3.4)$$

if the function f is orthogonal to the null space $Z(J)$ of J , i.e., to the eigenfunctions that belong to the vanishing eigenvalue. For "hard" potentials, the solution of the initial-value problem exists and is unique. If the initial function $\varphi(\mathbf{p})$ is orthogonal to $Z(J)$, then the norm of the solution is bounded in time by the function $\|\varphi\| \exp(-\rho t)$.

We now note that the initial conditions (3.3) are orthogonal to $Z(J)$ and, hence, all the functions $G_1(\mathbf{p}, t)$ (the subscripts $\alpha\beta$ or α are omitted temporarily) are majorized by the functions $\|G_1(t=0)\| \exp(-\rho t)$. Thus, the integrals over the time in (3.2) converge absolutely. Introducing the new functions

$$G(\mathbf{p}) = \int_0^\infty G_1(\mathbf{p}, t) dt / F_1(\mathbf{p}), \quad f(\mathbf{p}) = n F_1(\mathbf{p}) \quad (3.5)$$

[the function $f(\mathbf{p})$ is a Maxwellian distribution normalized to the number of particles in unit volume n], we obtain

$$\begin{aligned} \eta &= \frac{1}{10mKT} \int d\mathbf{p} f(\mathbf{p}) p_\alpha p_\beta G_{\alpha\beta}(\mathbf{p}), \\ \lambda &= \frac{1}{6m^2KT^2} \int d\mathbf{p} f(\mathbf{p}) p_\alpha p^2 G_\alpha(\mathbf{p}). \end{aligned} \quad (3.6)$$

Integrating both sides of Eq. (2.9) over the time from 0 to ∞ and allowing for (3.3), we obtain equations for the functions $G(\mathbf{p})$

$$\begin{aligned} -\frac{1}{m} \left(p_\alpha p_\beta - \frac{1}{3} p^2 \delta_{\alpha\beta} \right) &= I(G_{\alpha\beta}), \\ -\frac{p_\alpha}{m} \left(\frac{p^2}{2m} - \frac{5}{2} KT \right) &= I(G_\alpha), \\ I(G) &= \int f(\mathbf{p}_1) [G(\mathbf{p}_1') + G(\mathbf{p}') - G(\mathbf{p}_1) - G(\mathbf{p})] g^1 b^1 d\mathbf{b}^1 d\mathbf{p}_1. \end{aligned} \quad (3.7)$$

The results (3.6) and (3.7) are identical with the corresponding results of the Chapman-Enskog theory [1-3]. In the Chapman-Enskog theory a further additional condition ensures unique solvability of the second equation of (3.7). In the method of correlation functions this condition can be obtained from the auxiliary conditions imposed on the nonequilibrium distribution when the latter is found in the linear approximation in the gradients of the macroscopic parameters [14, 15], namely, from the condition that the correction to the locally equilibrium distribution makes no contribution to the total momentum. This condition

*Generally speaking, one should introduce dimensionless variables and functions. In order to keep the exposition as simple as possible, we shall assume that dimensionless variables are introduced without actually doing so.

can be represented in the form

$$\int_0^\infty dt \lim_{V \rightarrow \infty} \frac{1}{V} \langle \hat{P}_\alpha \hat{S}_\alpha(t) \rangle = 0, \quad (3.8)$$

or, introducing G_α functions in the lowest order in n , in the form

$$\int d\mathbf{p} f(\mathbf{p}) p_\alpha G_\alpha(\mathbf{p}) = 0. \quad (3.9)$$

4. Consider the transport coefficients of a multicomponent mixture. The coefficients of diffusion $D_{kk'}$ and thermal diffusion D_k^T can be represented in the form

$$D_{kk'} = \int_0^\infty dt \lim_{V \rightarrow \infty} \frac{1}{3V} \langle \hat{J}_{k\alpha} \hat{I}_{k'\alpha}(t) \rangle, \\ D_k^T = \int_0^\infty dt \lim_{V \rightarrow \infty} \frac{1}{3V} \langle \hat{J}_{k\alpha} \hat{S}_\alpha(t) \rangle = \int_0^\infty dt \lim_{V \rightarrow \infty} \frac{1}{3V} \langle \hat{Q}_\alpha \hat{I}_{k\alpha}(t) \rangle. \quad (4.1)$$

The formulas for the coefficients η , ζ , and λ have the same form (3.1) as for a simple medium but the dynamical variables $\hat{P}_{\alpha\beta}$, $\hat{\Pi}_{\alpha\beta}$, \hat{Q}_α , \hat{S}_α , and \hat{P}_α in these coefficients must be replaced by the corresponding expressions for an L-component mixture. For example,

$$\hat{P}_{\alpha\beta} = \sum_{k=1}^L \sum_{i=1}^{N_k} \left[\frac{p_{i\alpha}^{(k)} p_{i\beta}^{(k)}}{m_k} - \frac{1}{2} \sum_{i=1}^L \sum_{j=1}^{N_l} r_{ij\alpha}^{(kl)} \frac{\partial \Phi_{ij}^{(kl)}}{\partial r_{ij\beta}^{(kl)}} \right], \\ \hat{Q}_\alpha = \sum_{k=1}^L \sum_{i=1}^{N_k} \left[\frac{p_{i\alpha}^{(k)}}{m_k} \frac{p_i^{(k)^2}}{2m_k} + \frac{1}{2} \sum_{i=1}^L \sum_{j=1}^{N_l} \left(\frac{p_{i\alpha}^{(k)}}{m_k} \Phi_{ij}^{(kl)} - \frac{p_{i\beta}^{(k)}}{m_k} r_{ij\alpha} \frac{\partial \Phi_{ij}^{(kl)}}{\partial r_{ij\beta}} \right) \right]$$

etc. In formulas (4.1)

$$\hat{J}_{k\alpha} = \sum_{i=1}^{N_k} \frac{p_{i\alpha}^{(k)}}{m_k}, \quad \hat{I}_{k\alpha} = \hat{J}_{k\alpha} - \frac{n_k}{\rho} \hat{P}_\alpha,$$

n_k is the density of the number of particles of the k -th species; $\mathbf{x}_i^{(k)} = (\mathbf{r}_i^{(k)}, \mathbf{p}_i^{(k)})$ are the coordinates and the momenta of the i -th particle of the k -th species, $i = 1, \dots, N_k$, $k = 1, \dots, L$. The coefficients $D_{kk'}$ appear as factors of the gradients $\nabla \nu_{k'}$ ($\nu_k = \mu_k/KT$; μ_k is the chemical potential of the k -th component of the mixture and K is Boltzmann's constant) in the expression for the vector flux \mathbf{J}_k of the number of particles of the k -th species and the coefficients D_k^T appear as factors of the gradients $\nabla(KT)^{-1}$ in the expression for \mathbf{J}_k and of the gradients $\nabla \nu_k$ in the expression for the heat flux vector [14]. The coefficients D_k^T are written down in (4.1) in two equivalent forms (see [15]), of which we shall restrict ourselves in what follows to the first, for example. Introducing $G_i^{(k)}$ functions, we obtain from (2.10)–(2.12) the following equations in the lowest order in n :

$$D_{kk'} = \frac{n}{3m_k} \int_0^\infty dt \int d\mathbf{p} p_\alpha G_{ik\alpha}^{(k)}(\mathbf{p}, t), \\ D_k^T = \frac{n}{3} \sum_{i=1}^L \int_0^\infty dt \int d\mathbf{p} \frac{p_\alpha}{m_i} \frac{p^2}{2m_i} G_{i\alpha}^{(i)}(\mathbf{p}, t), \quad (4.2) \\ \eta = \frac{n}{10KT^2} \sum_{k=1}^L \int_0^\infty dt \int d\mathbf{p} \frac{p_\alpha p_\beta}{m_k} G_{i\alpha\beta}^{(k)}(\mathbf{p}, t), \\ \lambda = \frac{n}{3KT^2} \sum_{k=1}^L \int_0^\infty dt \int d\mathbf{p} \frac{p_\alpha}{m_k} \frac{p^2}{2m_k} G_{i\alpha}^{(k)}(\mathbf{p}, t); \\ G_{i\alpha}^{(k)}(\mathbf{p}, t=0) = \frac{p_\alpha}{m_i} \left(\delta_{ki} - \frac{m_i n_k}{\rho} \right) F_1^{(k)}, \\ G_{i\alpha}^{(k)}(\mathbf{p}, t=0) = \frac{p_\alpha}{m_k} \left(\frac{p^2}{2m_k} - \frac{5}{2} \frac{n_k KT m_k}{\rho} \right) F_1^{(k)}, \quad (4.3) \\ G_{i\alpha\beta}^{(k)}(\mathbf{p}, t=0) = \frac{1}{m_k} \left(p_\alpha p_\beta - \frac{1}{3} p^2 \delta_{\alpha\beta} \right) F_1^{(k)}.$$

The expression for the coefficient of dilatational viscosity ξ is omitted here since $\xi = 0$ in the lowest order in n , as in the case of a simple gas.

One can readily show that all functions $G_1^{(k)}$ which are a solution of the initial-value problem (2.12) with the initial data (4.3) decreases exponentially with the time. For let us consider the set of functions $G^{(k)}$, $k = 1, \dots, L$, as a column vector G with L components and define the scalar product

$$(G, H) = \sum_{k=1}^L \int (F_1^{(k)})^{-1} G^{(k)} H^{(k)} d\mathbf{p}. \quad (4.4)$$

Then the matrix of the linear collision operators $J = \{J_{kl}\}_{k,l=1}^L$, regarded as a linear operator on the Hilbert space with the scalar product (4.4), possesses the properties listed in §3 with the only difference that 0 is an $(L + 4)$ -fold degenerate eigenvalue to which there correspond the eigenfunctions

$$\psi_i^{(k)} = \delta_{ik} F_1^{(k)}, \quad i = 1, \dots, L; \quad \psi_{L+\alpha}^{(k)} = p_\alpha F_1^{(k)}, \quad \alpha = 1, 2, 3; \quad \psi_{L+4}^{(k)} = \frac{p^2}{2m_k} F_1^{(k)}. \quad (4.5)$$

It is readily shown that all the initial functions (4.3) are orthogonal to all the function (4.5) and hence, the corresponding solutions of the initial-value problems decrease exponentially with the time. The integrals over the time in formulas (4.2) exist. Introducing the new functions

$$G^{(k)}(\mathbf{p}) = \int_0^\infty G_1^{(k)}(\mathbf{p}, t) dt / F_1^{(k)}(\mathbf{p}), \quad f^{(k)}(\mathbf{p}) = n F_1(\mathbf{p}),$$

we obtain

$$\begin{aligned} D_{kk'} &= \frac{1}{3m_k} \int f^{(k)}(\mathbf{p}) p_\alpha G_{k'\alpha}^{(k)}(\mathbf{p}) d\mathbf{p}, \\ D_k^T &= \frac{1}{3} \sum_{l=1}^L \int f^{(l)}(\mathbf{p}) \frac{p_\alpha}{m_l} \frac{p^2}{2m_l} G_{k\alpha}^{(l)}(\mathbf{p}) d\mathbf{p}, \\ \eta &= \frac{1}{10KT} \sum_{k=1}^L \int f^{(k)}(\mathbf{p}) \frac{p_\alpha p_\beta}{m_k} G_{\alpha\beta}^{(k)}(\mathbf{p}) d\mathbf{p}, \\ \lambda &= \frac{1}{3KT^2} \sum_{k=1}^L \int f^{(k)}(\mathbf{p}) \frac{p_\alpha}{m_k} \frac{p^2}{2m_k} G_\alpha^{(k)}(\mathbf{p}) d\mathbf{p}. \end{aligned} \quad (4.6)$$

Integrating both sides of Eq. (2.12) over the time from 0 to ∞ and taking into account (4.3), we obtain equations for the functions G :

$$\begin{aligned} -\frac{p_\alpha}{m_k} \left(\delta_{ki} - \frac{m_k n_k}{\rho} \right) &= \sum_{k'=1}^L I_{kk'}(G_{i\alpha}), \\ -\frac{1}{m_k} \left(p_\alpha p_\beta - \frac{1}{3} p^2 \delta_{\alpha\beta} \right) &= \sum_{k'=1}^L I_{kk'}(G_{\alpha\beta}), \\ -\frac{p_\alpha}{m_k} \left(\frac{p^2}{2m_k} - \frac{5m_k n_k KT}{2\rho} \right) &= \sum_{k'=1}^L I_{kk'}(G_\alpha), \end{aligned} \quad (4.7)$$

where

$$I_{kk'}(G) = \int f^{(k')}(\mathbf{p}_1) [G^{(k')}(\mathbf{p}_1') + G^{(k)}(\mathbf{p}') - G^{(k')}(\mathbf{p}_1) - G^{(k)}(\mathbf{p})] g_{kl} b db d\epsilon d\mathbf{p}_1.$$

The results (4.6) and (4.7) are identical with the corresponding results of the Chapman-Enskog theory [3]. The additional conditions imposed on the functions $G_\alpha^{(k)}(\mathbf{p})$ and $G_{i\alpha}^{(k)}(\mathbf{p})$ in order to obtain unique solvability of Eqs. (4.7) can be derived, as in the case of a simple gas, from the condition that the part of the nonequilibrium distribution that is linear in the gradients of the macroscopic parameters make no contribution to the total momentum. Using the independence of the thermodynamic forces (gradients), we obtain $L + 1$ conditions:

$$\int_0^{\infty} dt \lim_{V \rightarrow \infty} \frac{1}{V} \langle \hat{P}_a \hat{S}_a(t) \rangle = 0,$$

$$\int_0^{\infty} dt \lim_{V \rightarrow \infty} \frac{1}{V} \langle \hat{P}_a \hat{I}_{ka}(t) \rangle = 0, \quad k = 1, \dots, L. \quad (4.8)$$

Introducing $G^{(k)}$ functions, we obtain the additional conditions of the Chapman–Enskog theory in the lowest order in n from (4.8):

$$\sum_{k=1}^L \int d\mathbf{p} f^{(k)}(\mathbf{p}) G_a^{(k)}(\mathbf{p}) = 0,$$

$$\sum_{k'=1}^L \int d\mathbf{p} f^{(k')}(\mathbf{p}) G_{ka}^{(k')}(\mathbf{p}) = 0. \quad (4.9)$$

5. We have already mentioned that the transport coefficients of a simple (or multicomponent) medium can be written in the form

$$\kappa = \int_0^{\infty} \Psi(t) dt, \quad \Psi(t) = \lim_{V \rightarrow \infty} \frac{1}{V} \langle \hat{a} \hat{b}(t) \rangle \quad (5.1)$$

or, after the introduction of the G_s functions,

$$n^s G_s(x_1, \dots, x_s; t) = \lim_{V \rightarrow \infty} \frac{N!}{(N-s)!} \int dx^{N-s} \hat{b}(t) \rho_N \quad (5.2)$$

in the form

$$\kappa = \int_0^{\infty} dt \left\{ n \int d\mathbf{p} a(\mathbf{p}) G_1(\mathbf{p}, t) + \frac{n^2}{2} \int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_{12} a(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_{12}) G_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_{12}, t) \right\}. \quad (5.3)$$

Usually, one assumes that the correlation functions $\Psi(t)$ decrease exponentially with the time (this fact was proved rigorously for the case of a Boltzmann gas in §§ 3 and 4). One can then introduce the new functions

$$Q_s(x_1, \dots, x_s) = \int_0^{\infty} G_s(x_1, \dots, x_s, t) dt \quad (5.4)$$

and express κ in the form

$$\kappa = n \int d\mathbf{p} a(\mathbf{p}) Q_1(\mathbf{p}) + \frac{n^2}{2} \int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_{12} a(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_{12}) Q_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_{12}, t). \quad (5.5)$$

Integrating Bogolyubov's chain over the time from 0 to ∞ , we obtain equations for the functions $Q_s(x_1, \dots, x_s)$:

$$-G_s(x_1, \dots, x_s; t=0) + H_s Q_s = n \sum_{i=1}^s \int [\Phi_{i, s+1}, Q_{s+1}] dx_{s+1}. \quad (5.6)$$

The functions $G_s(t=0)$ can be calculated by setting $t=0$ in Eq. (5.2). The chain (5.6) does not contain the time as a variable and differs from Bogolyubov's chain for the equilibrium distribution functions by the presence of the inhomogeneous term. Evidently, the chain (5.6) can be solved by several of the methods used in the equilibrium theory of dense media.

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