Journal of Statistical Physics, Vol. 12, No. 2, 1975

Microscopic Approach to the Enskog Theory of a Homogeneous Gas

B. Cichocki[1] and J. Piasecki[1]

Received May 6, 1974; revised September 13, 1974

We consider the approach to thermal equilibrium of a classical homogeneous dense gas with pair interaction corresponding to strongly repulsive forces of range σ. A series of systematic approximations to the equation determining the rate of change of the one-particle reduced distribution is proposed. Attempting to formulate Enskog's ideas in microscopic language, we construct a description within which the effect of s-particle dynamics ($s = 2, 3, \ldots$) is treated exactly, and the approximation affects only the influence of the medium on the distribution of s-particle states. It is argued that for a system close to equilibrium the effect of the medium is primarily due to the equilibrium component of correlations. This leads to a series of equations for the one-particle reduced distribution. In the case of $s = 2$, after taking the thermodynamic limit and passing to the long-time regime, the Enskog equation is obtained.

KEY WORDS: Liouville equation; kinetic theory; Enskog equation; thermal equilibrium; reduced distributions; correlations.

1. INTRODUCTION

The first important contribution to the kinetic theory of dense gases dates from 1921 and is due to Enskog,$^{(1)}$ who studied the rigid sphere model. Attempting to take into account the influence of the finite size of the molecules on the probability of binary collisions together with the fact that the

---

[1] Institute of Theoretical Physics, Warsaw University, Warsaw, Poland.

centers of two colliding spheres are at a finite distance at the moment of impact, he suitably modified the Boltzmann collision term and arrived at the equation[(2,3)]

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1}\right) f_1(\mathbf{r}_1, \mathbf{v}_1; t)$$
$$= \int d\mathbf{v}_2 \int_{\mathbf{g}\cdot\mathbf{k}>0} d\mathbf{k}\, \sigma^2 \mathbf{g}\cdot\mathbf{k}$$
$$\times \{\chi(\mathbf{r}_1 + \tfrac{1}{2}\sigma\mathbf{k}) f_1(\mathbf{r}_1 + \sigma\mathbf{k}, \mathbf{v}_2'; t) f_1(\mathbf{r}_1, \mathbf{v}_1'; t)$$
$$- \chi(\mathbf{r}_1 - \tfrac{1}{2}\sigma\mathbf{k}) f_1(\mathbf{r}_1 - \sigma\mathbf{k}, \mathbf{v}_2; t) f_1(\mathbf{r}_1, \mathbf{v}_1; t)\} \tag{1}$$

Equation (1) determines (in the absence of external fields) the rate of change of the reduced one-particle distribution $f_1(\mathbf{r}, \mathbf{v}; t)$, representing at time t the density of particles with velocity $\mathbf{v}$ at point $\mathbf{r}$; σ denotes the rigid sphere diameter; and $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$. The velocities $\mathbf{v}_1, \mathbf{v}_2 \to \mathbf{v}_1', \mathbf{v}_2'$ refer to a binary collision in which the positions $\mathbf{r}_1$ and $\mathbf{r}_2$ of spheres 1 and 2 at the moment of impact are related by the equation $\mathbf{r}_2 = \mathbf{r}_1 - \sigma\mathbf{k}$, $|\mathbf{k}| = 1$. The function χ appearing in Eq. (1) is usually identified with the local equilibrium radial distribution function.

Although based on intuitive arguments, Enskog's theory agreed so well with experiment (see, e.g., Ref. 4) that it became an important theoretical problem to understand under what assumptions it could be derived from first principles. The research in this field went essentially in two directions: (a) formulation and analysis of approximations which permit one to deduce Eq. (1) from the Liouville equation; and (b) derivation of the Enskog expressions for the transport coefficients from the Green–Kubo formulas [within the Enskog theory, transport coefficients are calculated by applying the Chapman–Enskog procedure to Eq. (1)].

The elucidation of point (a) is still far from being satisfactory and an attempt to understand this problem is at the origin of the present work. In fact, the content of various papers concerned with point (a)[(5–9)] does not go beyond taking the following two steps: (i) derivation of the exact equation for the reduced distribution f_1 in the case of a rigid sphere gas:

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1}\right) f_1(\mathbf{r}_1, \mathbf{v}_1; t)$$
$$= \int d\mathbf{v}_2 \int_{\mathbf{g}\cdot\mathbf{k}>0} d\mathbf{k}\sigma^2 \mathbf{g}\cdot\mathbf{k} \{f_2(\mathbf{r}_1, \mathbf{r}_1 + \sigma\mathbf{k}, \mathbf{v}_1', \mathbf{v}_2'; t)$$
$$- f_2(\mathbf{r}_1, \mathbf{r}_1 - \sigma\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2; t)\} \tag{2}$$

where the notation is the same as in Eq. (1), and f_2 is the reduced two-particle distribution; and (ii) making the assumption, nowhere clearly justified or explained, that one can put

$$
\begin{aligned}
&f_2(\mathbf{r}_1, \mathbf{r}_1 \pm \sigma\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2; t) \\
&\qquad = g_2^{l,\text{eq.}}(\mathbf{r}_{12} = \sigma; \mathbf{r}_1 \pm \tfrac{1}{2}\sigma\mathbf{k}) f_1(\mathbf{r}_1, \mathbf{v}_1; t) f_1(\mathbf{r}_1 \pm \sigma\mathbf{k}; \mathbf{v}_2; t)
\end{aligned}
\tag{3}
$$

where $g_2^{l,\text{eq.}}$ is the local equilibrium radial distribution function.

This certainly does not give the desired understanding of Enskog's theory on the ground of statistical mechanics.

As far as point (b) is concerned, we should mention here a series of papers by Sengers *et al.*(10–12) in which a rigorous analysis of the first density corrections to the rigid sphere transport coefficients has been performed. Using the binary collision expansion technique, the authors studied systematically the three-particle contributions in the Green–Kubo theory. They showed that only the so-called "double overlap" collisions are taken into account by the Enskog theory. However, according to Sengers' estimates, all the other three-particle collision processes introduce only a small correction to the Enskog transport coefficients.

The most exhaustive study of point (b) has been performed by Ernst.(13) He investigated the reduced time correlation functions of a rigid sphere gas relevant for the Green–Kubo theory by using the cluster expansion of the evolution operator. Neglecting systematically all the terms that involved the dynamics of more than two particles, he reproduced Ono's(14) result for two-particle correlation functions and arrived at the Enskog expressions for the transport coefficients. The effect of the medium on the two-particle dynamics has been taken into account in the equilibrium averaging inherent in the Green–Kubo formulas.

Although in the present work we are concerned with point (a) only, our main ideas are close to the Ernst interpretation of the Enskog theory. In Section 2 we define the model of the gas (not confined to the rigid sphere system), and discuss its initial state. Section 3 contains the formulation, based on the Liouville equation, of a general approximation scheme for the description of the time evolution of distribution f_1. In Section 4 we specify our approach to the case corresponding to the Enskog theory and complete the derivation of Eq. (1) for a homogeneous system. Section 5 contains the discussion of our results together with indications for further investigation.

2. DESCRIPTION OF THE SYSTEM AND ITS INITIAL STATE

Consider a classical dense gas composed of N identical particles enclosed in a cube of volume Ω. Its Hamiltonian is supposed to have the form

$$
\mathscr{H}(x) = \sum_{i=1}^{N} \tfrac{1}{2} v_i^2 + \sum_{j>i=1}^{N}\sum^{N} V(r_{ij})
\tag{4}
$$

where $x \equiv (x_1,..., x_N) \in \Gamma$ is a point in the phase space Γ of the gas, $x_i \equiv (\mathbf{r}_i, \mathbf{v}_i)$ represents the position $\mathbf{r}_i$ and velocity $\mathbf{v}_i$ of the ith particle, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and we formally set the particle mass $m = 1$. The pair interaction between the particles is assumed here to be represented by a continuously differentiable function $V(r)$ defined for $r > 0$, and well approximating the potential of rigid spheres of diameter σ (see, e.g., Ref. 8). We thus admit in our analysis only strongly repulsive short-range forces, vanishing over distances large with respect to some microscopic length σ. The Liouville operator in this case has the form

$$\mathscr{L} = \mathscr{L}_0 + \delta\mathscr{L} \tag{5}$$

where

$$\mathscr{L}_0 = \sum_{a=1}^{N} \mathbf{v}_a(\partial/\partial\mathbf{r}_a)$$

and

$$\delta\mathscr{L} = \sum_{b>a=1}^{N}\sum^{N} \delta\mathscr{L}^{ab} = -\sum_{b>a=1}^{N}\sum^{N} \frac{\partial V(r_{ab})}{\partial\mathbf{r}_{ab}}\left(\frac{\partial}{\partial\mathbf{v}_a} - \frac{\partial}{\partial\mathbf{v}_b}\right)$$

The N-particle distribution function $f_N(x; t)$ describing the state of the gas at time t satisfies the Liouville equation

$$(\partial/\partial t)f_N(x; t) = -\mathscr{L}f_N(x; t) \tag{6}$$

Equation (6) is to be supplemented with some boundary conditions specifying the behavior of the distribution $f_N(x; t)$ on the walls of the cubic box containing the gas. Let $\mathbf{e}_\alpha$, $\alpha = 1, 2, 3$, be three mutually orthogonal unit vectors parallel to the edges of the cube. We adopt here (for the sake of convenience) periodic boundary conditions by putting (see, e.g., Ref. 15, p. 10)

$$\begin{aligned} &f_N(x_1, ..., x_N; t) \\ &\underset{x\in\Gamma}{\equiv} f_N(x_1, ..., x_{i-1}, (\mathbf{r}_i + \Omega^{1/3}\mathbf{e}_\alpha, \mathbf{v}_i), x_{i+1}, ..., x_N; t) \\ &\qquad i = 1, ..., N, \qquad \alpha = 1, 2, 3 \end{aligned} \tag{7}$$

Equation (7) corresponds to identifying the opposite walls of the cube and considering the distribution $f_N(x; t)$ as defined on the resulting tore.

Our aim is to study the long-time behavior of the reduced one-particle distribution

$$f_1(x_1; t) = N\int dx_2 \cdots \int dx_N f_N(x_1, ..., x_N; t) \tag{8}$$

in the thermodynamic limit

$$\lim_{\infty} \equiv \lim_{N\to\infty, \Omega\to\infty, N/\Omega = n = \mathrm{const}} \tag{9}$$

Thus the particular choice (7) of the boundary conditions should be of no relevance for our final results. All the functions calculated in the thermodynamic limit (9) will be denoted in the text by capital letters, e.g., we write

$$F_1(x_1; t) = \lim_{\infty} f_1(x_1; t) \tag{10}$$

To begin with, let us formulate our assumptions about the initial state of the system.

(i) *Homogeneity condition:* At $t = 0$ the properties of the gas are the same at all points of the container.

Taking into account Eq. (7), we can give this assumption a simple analytical formulation: For all vectors $\mathbf{a} \in R^3$

$$\begin{aligned} f_N[(\mathbf{r}_1 + \mathbf{a}, \mathbf{v}_1), \ldots, (\mathbf{r}_N + \mathbf{a}, \mathbf{v}_N); 0] \\ \equiv f_N[(\mathbf{r}_1, \mathbf{v}_1), \ldots, (\mathbf{r}_N, \mathbf{v}_N); 0] \end{aligned} \tag{11}$$

Equation (11) expresses the translational invariance of the initial distribution. Since the Liouville operator (5) commutes with translations, this homogeneity condition is conserved in time. In particular, for any $t > 0$, function (8) does not depend on $\mathbf{r}_1$ and has the form

$$f_1(\mathbf{r}_1, \mathbf{v}_1; t) = n\varphi(\mathbf{v}_1; t) \tag{12}$$

where $\varphi(\mathbf{v}_1; t)$ is the normalized one-particle velocity distribution. An analogous equation holds in the thermodynamic limit

$$F_1(\mathbf{r}_1, \mathbf{v}_1; t) = n\Phi(\mathbf{v}_1; t) \tag{13}$$

where $\Phi(\mathbf{v}_1; t) = \lim_{\infty} \varphi(\mathbf{v}_1; t)$.

The number density of the particles remains constant, equal to $N/\Omega = n$.

(ii) *Factorization condition* (see Ref. 15, p. 17): At $t = 0$, in the thermodynamic limit the reduced distribution

$$\begin{aligned} & f_{i,j}(x_1, \ldots, x_i, \mathbf{v}_{i+1}, \ldots, \mathbf{v}_j; t) \\ & = \frac{N!}{(N-i)!} \int d\mathbf{r}_{i+1} \cdots \int d\mathbf{r}_j \int dx_{j+1} \cdots \int dx_N f_N(x_1, \ldots, x_N; t) \end{aligned} \tag{14}$$

$$0 \leqslant i < j \leqslant N$$

factorizes into product of the form

$$\lim_{\infty} f_{i,j}(x_1, \ldots, x_i, \mathbf{v}_{i+1}, \ldots, \mathbf{v}_j; 0) = F_i(x_1, \ldots, x_i; 0) \prod_{a=i+1}^{j} \Phi(\mathbf{v}_a; 0) \tag{15}$$

where

$$\begin{aligned} F_i(x_1, \ldots, x_i; t) &\equiv \lim_{\infty} f_i(x_1, \ldots, x_i; t) \\ &\equiv \lim_{\infty} \frac{N!}{(N-i)!} \int dx_{i+1} \cdots \int dx_N f_N(x_1, \ldots, x_N; t) \end{aligned} \tag{16}$$

and Φ is given by Eq. (13).

In particular, the j-particle velocity distribution

$$\varphi_j(\mathbf{v}_1, \ldots, \mathbf{v}_j; 0) = f_{0,j}(\mathbf{v}_1, \ldots, \mathbf{v}_j; 0) \tag{17}$$

satisfies the equation

$$\lim_{\infty} \varphi_j(\mathbf{v}_1, \ldots, \mathbf{v}_j; 0) \equiv \Phi_j(\mathbf{v}_1, \ldots, \mathbf{v}_j; 0) = \prod_{a=1}^{j} \Phi(\mathbf{v}_a; 0) \tag{18}$$

$$j = 1, 2, \ldots$$

Equation (15) is intimately connected with cluster properties of correlations. In order to show this, let us study, e.g., the case of the two-particle function

$$\varphi_2(\mathbf{v}_1, \mathbf{v}_2; 0) = \frac{1}{N(N-1)} \int d\mathbf{r}_1 \int d\mathbf{r}_2 f_2(x_1, x_2; 0) \tag{19}$$

In view of the assumed translational invariance (11), the cluster decomposition of f_2 has the form

$$\begin{aligned} f_2(x_1, x_2; 0) = {} & n^2 \varphi(\mathbf{v}_1; 0)\varphi(\mathbf{v}_2; 0) \\ & \times [1 + g_2(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2; 0)] \end{aligned} \tag{20}$$

where g_2 is the initial two-particle correlation function. Hence

$$\varphi_2(\mathbf{v}_1, \mathbf{v}_2; 0) = \frac{N}{N-1} \varphi(\mathbf{v}_1; 0)\varphi(\mathbf{v}_2; 0)\left[1 + \frac{1}{\Omega}\int d\mathbf{r}\, g_2(\mathbf{r}, \mathbf{v}_1, \mathbf{v}_2; 0)\right] \tag{21}$$

Now, if $g_2(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2; 0)$ vanishes for $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$, the second term in square brackets in Eq. (21) tends in the thermodynamic limit to zero, and we get

$$\lim_{\infty} \varphi_2(\mathbf{v}_1, \mathbf{v}_2; 0) = \Phi(\mathbf{v}_1; 0)\Phi(\mathbf{v}_2; 0)$$

which is the desired result (compare with Ref. 15, pp. 15, 16). In a similar way all the other equations in condition (15) can be shown to be implied by cluster properties of correlations.

The fundamental question still remains whether the property (15) is conserved in time. Various arguments have been given in favor of this conjecture, but to our knowledge a satisfactory proof is still lacking. An elegant discussion of some aspects of this problem can be found in Ref. 16. We shall assume here that Eq. (15) remains valid for all $t > 0$. We thus suppose that in the course of the evolution of the gas the correlation functions at each moment have the cluster properties, i.e., they tend to zero when the spatial separation between the particles tends to infinity. A proof of this important dynamic property, which seems to us highly probable on physical grounds, would be welcomed. In order to avoid any confusion, it should be stressed that Eq. (15) does not impose factorization conditions on the reduced distribution (16), a property physically unrealistic and obviously not conserved in time (see Ref. 19, p. 242).

We shall now show that the homogeneity and factorization conditions (i) and (ii) admit the existence of a time-independent idempotent operator $P = P^2$ extracting in the thermodynamic limit from the distribution $f_N(x; t)$ its uncorrelated part $\prod_i f_1(x_i; t)$ at any $t > 0$. In order to make this statement precise, let us define this operator by the equation

$$(Pf_N)(x_1, \ldots, x_N; t) = \Omega^{-N}\varphi_N(\mathbf{v}_1, \ldots, \mathbf{v}_N; t) \tag{22}$$

[see Eq. (17)]. The calculation of the thermodynamic limit for the reduced distributions associated with Pf_N gives

$$\lim_{\infty} \frac{N!}{(N-s)!}\int dx_{s+1}\cdots\int dx_N\,(Pf_N)(x_1, \ldots, x_N; t)$$
$$= \prod_{i=1}^{s}[n\Phi(\mathbf{v}_i; t)] = \prod_{i=1}^{s} F_1(\mathbf{v}_i; t) \tag{23}$$

where our assumptions (i) and (ii) have been taken into account. Defining the operator $Q = I - P$, we can thus say that the decomposition

$$f_N(x; t) = Pf_N(x; t) + Qf_N(x; t) \tag{24}$$

corresponds to the division of the distribution $f_N(x; t)$ into the uncorrelated and correlated parts. This interpretation of P and Q, valid for any $t \geqslant 0$, will turn out to be very useful for the derivation of the equations of the next section.

3. TIME EVOLUTION OF THE REDUCED ONE-PARTICLE DISTRIBUTION. IDEA OF APPROXIMATION

The Liouville equation (6) can be formally written as

$$\frac{\partial}{\partial t}f_N(x; t) = -\mathscr{L}f_N(x; t) = -\mathscr{L}f_N[\tilde{x}(x; -t); 0]$$
$$= -\mathscr{L}[\exp(-\mathscr{L}t)]f_N(x; 0) \tag{25}$$

where $\exp(-\mathscr{L}t)$ is the N-particle streaming operator, transforming the phase x of the system at time zero into the phase $\tilde{x}(x; -t)$ which it had a time t earlier. In order to make evident in the right-hand side of Eq. (25) the dynamical evolution of correlations in the gas, we shall introduce the operators P and Q defined by Eqs. (22) and (24). We follow here the ideas of the theory of kinetic equations as developed by the Brussels school (Refs. 15, 17;

see also Ref. 18). The physical interpretation of decomposition (24) given at the end of Section 2 is to be constantly kept in mind.

Applying operator P to Eq. (25) and using the identity

$$\exp(-\mathscr{L}t) = \exp(-\mathscr{L}Qt) - \int_0^t d\tau\, [\exp(-\mathscr{L}Q\tau)]\mathscr{L}P \exp[-\mathscr{L}(t-\tau)] \quad (26)$$

we get

$$\frac{\partial}{\partial t} Pf_N(x;t) = \mathscr{D}(t)Qf_N(x;0) + \int_0^t d\tau\, \mathscr{G}(\tau)Pf_N(x;t-\tau) \quad (27)$$

where

$$\mathscr{D}(t) = -P\delta\mathscr{L}Q[\exp(-\mathscr{L}Qt)]Q \quad (28)$$

$$\mathscr{G}(t) = P\delta\mathscr{L}Q[\exp(-\mathscr{L}Qt)]/Q\delta\mathscr{L}P \quad (29)$$

In writing Eqs. (28) and (29), the relations

$$P\mathscr{L}_0 = \mathscr{L}_0P = P\mathscr{L}_0P = 0 \quad (30)$$

have been taken into account. The structure of Eq. (27) is well known from the general theory of kinetic equations, and will not be discussed here. Let us only notice the appearance in Eqs. (28) and (29) of a modified evolution operator

$$Q[\exp(-\mathscr{L}Qt)]Q = \mathscr{P}(t) \quad (31)$$

The role of the generator of time translations is played here by $Q\mathscr{L}Q$, which corresponds to constantly subtracting from the propagated distribution its uncorrelated part. In this sense operator (31) is said to describe an irreducible dynamics of correlations.

Integrating Eq. (27) over the velocities of particles 2, ..., N and multiplying by Ω^N, we obtain

$$(\partial/\partial t)\varphi(\mathbf{v}_1;t) = \Omega^N \int (d\mathbf{v})^{N-1} \Big\{ -P\delta\mathscr{L}\mathscr{P}(t)f_N(x;0) + \int_0^t d\tau\, P\delta\mathscr{L}\mathscr{P}(t)\delta\mathscr{L}Pf_N(x;t-\tau) \Big\} \quad (32)$$

where $\int (d\mathbf{v})^{N-1} \equiv \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_N$. The kinetic operators (28) and (29) have been expressed here in terms of the irreducible operator (31).

Equation (32) is exact and can serve as the basis for the microscopic analysis of the time evolution of a dense gas. In order to go a step further, we shall now separate out the class of contributions depending on the dynamics of no more than s particles. To this end, we notice that, due to the symmetric role played by all the particles, we can transform Eq. (32) to the form

$$\begin{aligned} &n(\partial/\partial t)\varphi(\mathbf{v}_1;t) \\ &\quad = \sum_{a=2}^{s} \Omega^{a-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a \biggl\{ \mathscr{D}^{1\cdots a}(t) Q f_a(x_1, \ldots, x_a; 0) \\ &\qquad + \int_0^t d\tau\, \mathscr{G}^{1,\ldots,a}(\tau) P f_a(x_1, \ldots, x_a; t-\tau) \biggr\} \\ &\qquad + \Omega^s \int_0^t d\tau \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_{s+1}\, \mathscr{D}^{1\cdots s}(\tau)[-\mathscr{L}^{1\cdots(s+1)} + \mathscr{L}^{1\cdots s}] \\ &\qquad \times f_{s+1}(x_1, \ldots, x_{s+1}; t-\tau) \end{aligned} \tag{33}$$

In the terms in curly brackets in Eq. (33) the correlated and uncorrelated parts of the a-particle reduced distributions are acted upon by the kinetic operators

$$\begin{aligned} \mathscr{D}^{12}(t) &= P(-\mathscr{L}^{12} + \mathscr{L}^{1})\mathscr{P}^{12}(t) \\ \mathscr{D}^{1\cdots a}(t) &= \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_4 \cdots \int_0^{\tau_{a-1}} d\tau_a\, P\{(-\mathscr{L}^{12} + \mathscr{L}^{1})\mathscr{P}^{12}(t-\tau_3) \\ &\quad \times (-\mathscr{L}^{123} + \mathscr{L}^{12})\mathscr{P}^{123}(\tau_3 - \tau_4) \cdots \mathscr{P}^{1\cdots a-1}(\tau_{a-1} - \tau_a) \\ &\quad \times (-\mathscr{L}^{1\cdots a} + \mathscr{L}^{1\cdots a-1})\mathscr{P}^{1\cdots a}(\tau_a)\}, \qquad a \geqslant 3 \end{aligned} \tag{34}$$

and

$$\mathscr{G}^{1\cdots a}(\tau) = -\mathscr{D}^{1\cdots a}(\tau)\mathscr{L}^{1\cdots a}P \tag{35}$$

respectively. Here $\mathscr{L}^{1\cdots b}$ denotes the b-particle Liouville operator, and $\mathscr{P}^{1\cdots b}(t)$ is given by Eq. (31) with $\mathscr{L}$ replaced by $\mathscr{L}^{1\cdots b}$. A simple method of proving Eq. (33) is presented in the appendix.

It is clear that both operators (34) and (35) are determined by the a-particle dynamics. On the contrary, the last term in Eq. (33), containing the operator $(-\mathscr{L}^{1\cdots s+1} + \mathscr{L}^{1\cdots s})$, describes the effects due to collisions between $s+1$ or more particles. For the purpose of further discussion we rewrite it in the form

$$\begin{aligned} &\Omega^{s-1} \int_0^t d\tau \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_s\, \mathscr{D}^{1\cdots s}(\tau) \\ &\qquad \times [(\partial/\partial t) + \mathscr{L}^{1\cdots s}] f_s(x_1, \ldots, x_s; t-\tau) \end{aligned} \tag{36}$$

where the BBGKY hierarchy has been used (see, e.g., Ref. 3, p. 37).

Approximations consisting in neglecting term (36) in Eq. (33) are well known and correspond to the expansion in powers of density of the kinetic operators. For $s = 2$ and $s = 3$ they lead to the Boltzmann and Choh–Uhlenbeck theories, respectively. However, for $s > 3$ the nonanalyticity in density shows up and one is faced with the divergence problems extensively discussed in the literature (see, e.g., Ref. 19 and references given there).

We shall now propose another type of approximation to Eq. (33), which in the case of $s = 2$ will lead to the Enskog theory. The physical ideas underlying our approach refer to a dense gas at the late stage of its evolution toward thermal equilibrium. This is conveniently taken into account by introducing the reduced s-particle distributions of the form

$$f_s^{\mathrm{eq}}(x_1, \ldots, x_s)\varphi(\mathbf{v}_1, \ldots, \mathbf{v}_s; t)/\varphi^{\mathrm{eq}}(\mathbf{v}_1, \ldots, \mathbf{v}_s) \tag{37}$$

which correspond to approximating the correlations in the gas at time t by their equilibrium values. The exact distribution can be then written as

$$\begin{aligned} f_s(x_1, \ldots, x_s; t) &= f_s^{\mathrm{eq}}(x_1, \ldots, x_s)\varphi_s(\mathbf{v}_1, \ldots, \mathbf{v}_s; t)/\varphi_s^{\mathrm{eq}}(\mathbf{v}_1, \ldots, \mathbf{v}_s) \\ &\quad + \delta f_s(x_1, \ldots, x_s; t) \end{aligned} \tag{38}$$

where the additional term δf_s describes the nonequilibrium deviations of correlations, Keeping decomposition (38) in mind, let us now analyze contribution (36) on the rhs of Eq. (33). Its role consists in modifying the influence of s-particle dynamics on the rate of change of the distribution $f_1(x_1; t)$ by taking into account the presence of the surrounding medium through collisions involving more than s particles. Indeed, the s-particle kinetic operator $\mathscr{D}^{1\cdots s}(\tau)$ in Eq. (36) is followed by the expression

$$[(\partial/\partial t) + \mathscr{L}^{1\cdots s})]f_s(x_1, \ldots, x_s; t - \tau) \tag{39}$$

which, as is known from the BBGKY hierarchy, determines (in the thermodynamic limit) the effect of collisions with $N - s$ particles of the medium on the phase space and the time dependence of the distribution $f_s(x_1, \ldots, x_s; t - \tau)$. It is precisely the term (39) that we want to approximate. The s-particle dynamics will be treated exactly within our theory.

To being with, let us notice that at equilibrium expression (39) takes the form

$$\begin{aligned} &[(\partial/\partial t) + \mathscr{L}^{1\cdots s}]f_s^{\mathrm{eq}}(x_1, \ldots, x_s) \\ &= \mathscr{L}^{1\cdots s}f_s^{\mathrm{eq}}(x_1, \ldots, x_s) \\ &= n^s\varphi^{\mathrm{eq}}(v_1, \ldots, v_s)W_s(\mathbf{r}_1, \ldots, \mathbf{r}_s)\mathscr{L}^{1\cdots s}y_s(\mathbf{r}_1, \ldots, \mathbf{r}_s) \end{aligned} \tag{40}$$

where we put

$$f_s^{\mathrm{eq}}(x_1, \ldots, x_s) = n^s\varphi_s^{\mathrm{eq}}(v_1, \ldots, v_s)W_s(\mathbf{r}_1, \ldots, \mathbf{r}_s)y_s(\mathbf{r}_1, \ldots, \mathbf{r}_s) \tag{41}$$

with

$$W_s(\mathbf{r}_1, \ldots, \mathbf{r}_s) = \exp\left[-\beta \sum_{i>j=1}^{s}\sum^{s} V(\mathbf{r}_{ij})\right]; \qquad \beta = 1/kT$$

where T is the temperature and k is the Boltzmann constant.

On inserting decomposition (38) into Eq. (39), we recover an analogous term

$$n^s \varphi_s(\mathbf{v}_1, \ldots, \mathbf{v}_s; t - \tau) W_s(\mathbf{r}_1, \ldots, \mathbf{r}_s) \mathscr{L}^{1\cdots s} y_s(\mathbf{r}_1, \ldots, \mathbf{r}_s) \tag{42}$$

in which the time-dependent velocity distribution has replaced φ^{eq}. Besides this, we shall find additionally two contributions

$$f_s^{\text{eq}}[(\partial/\partial t) + \mathscr{L}^{1\cdots s}](\varphi_s/\varphi_s^{\text{eq}}) + [(\partial/\partial t) + \mathscr{L}^{1\cdots s}]\, \delta f_s \tag{43}$$

Expression (42) represents a nonequilibrium generalization of the rhs of Eq. (40), in which the dependence on the position variables is kept unchanged. Therefore, in contradistinction to contributions (43), it refers to the equilibrium component of the correlations in the gas, and can thus be supposed, for a system close to thermal equilibrium, to give a very good approximation to the influence of the medium on the evolution of the distribution f_s. Adopting this point of view, we can now construct a theory in which the calculation of the rate of change of the one-particle reduced distribution is based on the following principles: (a) The influence of s-particle dynamics is rigorously taken into account, and (b) the influence of the medium on the distribution of s-particle states [Eq. (39)] is approximated by expression (42).

Let us stress once more that point (b) implies that the role of the equilibrium component in the actual time-dependent correlations is properly taken into account. This in fact is necessary to get the correct equilibrium properties at the final stage of the evolution of a dense system, which was one of the problems Enskog was concerned with. It is clear that point (b) makes our approach fundamentally different from theories based on the density expansion of the kinetic operators.

Applying principles (a) and (b) to Eq. (33), we get

$$\begin{aligned}
&(\partial/\partial t) n\varphi(\mathbf{v}_1; t) \\
&\quad = \sum_{a=2}^{s} \Omega^{a-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a \biggl\{ \mathscr{D}^{1\cdots a}(t) f_a(x_1, \ldots, x_a; 0) \\
&\qquad + \int_0^t d\tau\, \mathscr{G}^{1\cdots a}(\tau) f_a(x_1, \ldots, x_a; t - \tau) \biggr\} \\
&\qquad + \Omega^{s-1} \int_0^t d\tau \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_s\, \mathscr{D}^{1\cdots s}(\tau) n^s \varphi_s(\mathbf{v}_1, \ldots, \mathbf{v}_s; t - \tau) \\
&\qquad \times W_s(\mathbf{r}_1, \ldots, \mathbf{r}_s) \mathscr{L}^{1\cdots s} y_s(\mathbf{r}_1, \ldots, \mathbf{r}_s)
\end{aligned} \tag{44}$$

In the next section the case of $s = 2$ is shown to correspond to the Enskog theory.

4. DERIVATION OF THE ENSKOG EQUATION

In this section we study Eq. (44) for $s = 2$. Using Eqs. (12), (22), (34), and (35), we write it in the form

$$\begin{aligned}(\partial/\partial t)f_1(\mathbf{v}_1; t) = &-\int dx_2\, \delta\mathscr{L}^{12} \exp(-\mathscr{L}^{12}Qt) \\ &\times Qf_2(x_1, x_2; 0) + \int_0^t d\tau \int dx_2\, \delta\mathscr{L}^{12} \exp(-\mathscr{L}^{12}Q\tau) \\ &\times Q\{\mathscr{L}^{12}Pf_2(x_1, x_2; t-\tau) - \exp[-\beta V(r_{12})] \\ &\times \mathscr{L}_0^{12} y(r_{12}) n^2 \varphi_2(\mathbf{v}_1, \mathbf{v}_2; t-\tau)\}\end{aligned} \tag{45}$$

where $y(r_{12}) = y_2(\mathbf{r}_1, \mathbf{r}_2)$.

The term in the curly brackets in Eq. (45) contains the expression

$$\begin{aligned}&\{\exp[-\beta V(r_{12})]\}\mathscr{L}_0^{12} y(r_{12}) \\ &\quad = \mathscr{L}^{12}\{\exp[-\beta V(r_{12})]\}y(r_{12}) - y(r_{12})\mathscr{L}_0^{12}\{\exp[-\beta V(r_{12})]\} \\ &\quad - \delta\mathscr{L}^{12}\{\exp[-\beta V(r_{12})]\}y(r_{12})\end{aligned} \tag{46}$$

where the terms

$$\begin{aligned}&y(r_{12})\mathscr{L}_0^{12} \exp[-\beta V(r_{12})] \\ &\quad = y(r_{12})\mathbf{v}_{12}\{(\partial/\partial \mathbf{r}_{12}) \exp[-\beta V(r_{12})]\}\end{aligned} \tag{47}$$

and

$$\begin{aligned}&\delta\mathscr{L}^{12}\{\exp[-\beta V(r_{12})]\}y(r_{12}) \\ &\quad = \beta^{-1} y(r_{12})\left\{\frac{\partial}{\partial \mathbf{r}_{12}} \exp[-\beta V(r_{12})]\right\}\left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_2}\right)\end{aligned} \tag{48}$$

appear. In both of them the function $y(r_{12})$ multiplies the derivative

$$(\partial/\partial \mathbf{r}_{12}) \exp[-\beta V(r_{12})] \tag{49}$$

According to our assumption (see Section 2) the interaction $V(r_{12})$, although continuously differentiable, is close to the rigid sphere potential

$$V(r_{12}) = \begin{cases}\infty, & r_{12} < \sigma \\ 0, & r_{12} > \sigma\end{cases} \tag{50}$$

Thus the presence of the derivative (49) in terms (47) and (48) reduces the space integration in the corresponding contributions to the rhs of Eq. (45) to a small neighborhood of the sphere $r_{12} = \sigma$. It is therefore justified to replace in both of them the continuous [even for potential (50)] function $y(r_{12})$ by its value $y(r_{12})|_{r_{12}=\sigma} = y(\sigma)$. Although this procedure is rigorous only for the rigid sphere interaction, it is certainly a very good approximation for strongly repulsive forces of range σ.

Using this fact, we write the rhs of Eq. (46) in a simplified form:

$$\mathscr{L}^{12}[y(r_{12}) - y(\sigma)] \exp[-\beta V(r_{12})] \tag{51}$$

and by inserting it into Eq. (45) we obtain

$$\begin{aligned}(\partial/\partial t)f_1(\mathbf{v}_1; t) = \int dx_2 \Big\{ & -\delta\mathscr{L}^{12}\, [\exp(-\mathscr{L}^{12}Qt)]Qf_2(x_1; x_2; 0) \\ & - \int_0^t d\tau\, \delta\mathscr{L}^{12}\, [\exp(-\mathscr{L}^{12}Q\tau)]Q\mathscr{L}^{12}Q \exp[-\beta V(r_{12})] \\ & \times [y(r_{12}) - y(\sigma)]n^2\varphi_2(\mathbf{v}_1, \mathbf{v}_2; t - \tau) \\ & + \int_0^t d\tau\, \delta\mathscr{L}^{12}\, [\exp(-\mathscr{L}^{12}Q\tau)]Q\, \delta\mathscr{L}^{12}P \exp[-\beta V(r_{12})] \\ & \times y(\sigma)n^2\varphi_2(\mathbf{v}_1, \mathbf{v}_2; t - \tau)\Big\} \end{aligned} \tag{52}$$

where the relation

$$\begin{aligned} Pf_2(x_1, x_2; t - \tau) &= [N(N - 1)/\Omega^2]\varphi_2(\mathbf{v}_1, \mathbf{v}_2; t - \tau) \\ &= P\{\exp[-\beta V(r_{12})]\}y(r_{12})n^2\, \varphi_2(\mathbf{v}_1, \mathbf{v}_2; t - \tau) \end{aligned}$$

has been taken into account [see also Eq. (41)].

In order to pass in Eq. (52) to the thermodynamic limit, we notice that due to our assumptions about the initial state (see Section 2) the following equation holds:

$$\begin{aligned} &\lim_{\infty} Qf_2(x_1, x_2; 0) \\ &\quad = \lim_{\infty}[f_2(x_1, x_2; 0) - N(N - 1)\Omega^{-2}\varphi_2(\mathbf{v}_1, \mathbf{v}_2; 0)] \\ &\quad = F_2(x_1, x_2; 0) - n^2\Phi(\mathbf{v}_1, \mathbf{v}_2; 0) = F_2(x_1, x_2; 0) - F_1(x_1; 0)F_2(x_2; 0) \end{aligned}$$

By introducing the two-particle correlation function

$$G_2(x_1, x_2; 0) = [F_2(x_1, x_2; 0)/F_1(x_1; 0)F_1(x_2; 0) - 1]$$

we get

$$\lim_{\infty} Qf_2(x_1, x_2; 0) = G_2(x_1, x_2; 0)F_1(x_1; 0)F_1(x_2; 0) \tag{53}$$

Similar calculations lead to the equation

$$\lim_{\infty} Q \exp[-\beta V(r_{12})]\{y(r_{12}) - y(\sigma)\} = G_2^{\mathrm{eq}}(r_{12}) - Y(\sigma)G_{2,0}^{\mathrm{eq}}(r_{12}) \tag{54}$$

where $Y(\sigma) = \lim_{\infty} y(\sigma)$ and $G_{2,0}^{\mathrm{eq}}(r_{12}) = \exp[-\beta(V(r_{12})] - 1$ is the zeroth-order term in the expansion in powers of density of the equilibrium pair correlation function $G_2^{\mathrm{eq}}(r_{12})$.

Finally we have

$$\lim_{\infty} P \exp[-\beta V(r_{12})] = 1 \tag{55}$$

Apart from Eqs. (53)–(55) it can be shown that when $\Omega \to \infty$ the difference between the operators $[\exp(-\mathscr{L}^{12}Qt)]Q$ and $[\exp(-\mathscr{L}^{12}t)]Q$ behaves like Ω^{-1}. Indeed, from Eq. (26) we get

$$\begin{aligned}&[\exp(-\mathscr{L}^{12}Qt)]Q - [\exp(-\mathscr{L}^{12}t)]Q\\ &\quad = \int_0^t d\tau \,\{\exp[-\mathscr{L}^{12}Q(t-\tau)]\}\delta\mathscr{L}^{12}P[\exp(-\mathscr{L}^{12}\tau)]Q\end{aligned} \tag{56}$$

Since for the short-range forces considered here,

$$\begin{aligned}&P[\exp(-\mathscr{L}^{12}\tau)]Q\\ &\quad = P\int_0^\tau d\tau'\,(\partial/\partial\tau')\,[\exp(-\mathscr{L}^{12}\tau')]Q\\ &\quad = -\int_0^\tau d\tau'\,P\,\delta\mathscr{L}^{12}\,[\exp(-\mathscr{L}^{12}\tau')]Q\\ &\quad = -\Omega^{-1}\int_0^\tau d\tau'\int d\mathbf{r}_2\,\delta\mathscr{L}^{12}\,[\exp(-\mathscr{L}^{12}\tau')]Q \sim \Omega^{-1}\end{aligned} \tag{57}$$

the rhs of Eq. (56) can be neglected in the thermodynamic limit (see also Ref. 20). Consequently Eq. (52) for an infinite volume of a homogeneous gas takes the form

$$\begin{aligned}&(\partial/\partial t)F_1(\mathbf{v}_1;t)\\ &\quad = \int dx_2\Big\{-\delta\mathscr{L}^{12}\,[\exp(-\mathscr{L}^{12}t)]G_2(x_1,x_2;0)\\ &\qquad \times F_1(\mathbf{v}_1;0)F_1(\mathbf{v}_2;0) - \int_0^t d\tau\,\delta\mathscr{L}^{12}\,[\exp(-\mathscr{L}^{12}\tau)]\mathscr{L}^{12}\\ &\qquad \times [G_2^{\text{eq}}(r_{12}) - Y(\sigma)G_{2,0}^{\text{eq}}(r_{12})]F_1(\mathbf{v}_1;t-\tau)F_1(\mathbf{v}_2;t-\tau)\\ &\qquad + \int_0^t d\tau\,\delta\mathscr{L}^{12}\,[\exp(-\mathscr{L}^{12}\tau)]\,\delta\mathscr{L}^{12}\,F_1(\mathbf{v}_1;t-\tau)F_1(\mathbf{v}_2;t-\tau)\,Y(\sigma)\Big\}\end{aligned} \tag{58}$$

In writing Eq. (58), the factorization property of the velocity distribution (see Section 2) has been used.

We shall now analyze the rhs of Eq. (58) for long times, i.e., for

$$t \gg \tau_{\text{micr}} \sim \sigma v^{-1}$$

where σ is the range of the interparticle forces and v is the mean particle velocity. The standard arguments used in deriving the Boltzmann equation can be applied here. We thus notice that because of the presence of the operator $\delta\mathscr{L}^{12}$ in the term

$$\int dx_2\, \delta\mathscr{L}^{12}\, [\exp(-\mathscr{L}^{12}t)]G_2(x_1, x_2; 0)F_1(\mathbf{v}_1; 0)F_2(\mathbf{v}_2; 0) \tag{59}$$

the phases x_1 and x_2 of particles 1 and 2 appearing in the initial correlation function $G_2(x_1, x_2; 0)$ are constrained to configurations for which $|\mathbf{r}_1 - \mathbf{r}_2| \sim \sigma$. Therefore at $t = 0$ particles 1 and 2 interact via strongly repulsive forces. The exact two-body streaming operator $\exp(-\mathscr{L}^{12}t)$ then changes (x_1, x_2) into phases which particles 1 and 2 had a time t earlier. Thus for $t \gg \tau_{\text{micr}}$ both particles will be moving freely and their distance will be large with respect to σ. But for a system close to equilibrium the range of the initial pair correlation function can be supposed to be of the same order as the range of equilibrium correlations $G_2^{\text{eq}}(r_{12})$, vanishing for $r_{12} \gg \sigma$. Hence for times $t \gg \tau_{\text{micr}}$ the term (59) can be neglected.

The next two terms in Eq. (58), which can be written as

$$\int_0^t d\tau \int dx_2 \left\{\frac{\partial}{\partial\tau}\, \delta\mathscr{L}^{12}\, [\exp(-\mathscr{L}^{12}\tau)][G_2^{\text{eq}}(r_{12}) - Y(\sigma)G_{2,0}^{\text{eq}}(r_{12})]\right\}$$
$$\times\, F_1(\mathbf{v}_1; t - \tau)F_1(\mathbf{v}_2; t - \tau) \tag{60}$$

and

$$-\,Y(\sigma)\int_0^t d\tau \int dx_2 \left\{\frac{\partial}{\partial\tau}\, \delta\mathscr{L}^{12} \exp(-\mathscr{L}^{12}\tau) \exp(\mathscr{L}_0^{12}\tau)\right\}$$
$$\times\, F_1(\mathbf{v}_1; t - \tau)F_1(\mathbf{v}_2; t - \tau) \tag{61}$$

also contain the operator $\delta\mathscr{L}^{12}$. By the same kind of argument as above, the integrand in Eq. (60) can be shown to vanish when $\tau \gg \tau_{\text{micr}}$. For quite a different reason this also turns out to be true in the case of expression (61): The time derivative is applied there to the operator

$$\delta\mathscr{L}^{12} \exp(-\mathscr{L}^{12}\tau) \exp(\mathscr{L}_0^{12}\tau) \tag{62}$$

which, as shown, e.g., in Ref. 3, p. 51, is time independent for $\tau \gg \tau_{\text{micr}}$.

Assuming that the distribution F_1 changes slowly on the microscopic time scale and that $t \gg \tau_{\text{micr}}$, we can thus approximate the product $F_1(\mathbf{v}_1; t - \tau)F_1(\mathbf{v}_2; t - \tau)$ in both terms (60) and (61) by its value at $\tau = 0$. After integrating over τ we rewrite expressions (60) and (61) in the form

$$\int dx_2\, \delta\mathscr{L}^{12}\, [\exp(-\mathscr{L}^{12}t)][G_2^{\text{eq}}(r_{12}) - Y(\sigma)G_{2,0}^{\text{eq}}(r_{12})]$$
$$\times\, F_1(\mathbf{v}_1; t)F_2(\mathbf{v}_2; t) \tag{63}$$

and

$$-\,Y(\sigma)\int dx_2\, \{\delta\mathscr{L}^{12} \exp(-\mathscr{L}^{12}t) \exp(\mathscr{L}_0^{12}t)\}F_1(\mathbf{v}_1; t)F_1(\mathbf{v}_2; t) \tag{64}$$

respectively. For $t \gg \tau_{\text{micr}}$ expression (63) vanishes [compare with expression (59)] whereas in term (64) the operator in curly brackets [expression (62)] can be replaced by its limit when $t \to \infty$. As has been shown by various authors (see, e.g., Ref. 3 and references given there) we then get, up to the factor $Y(\sigma)$, the Boltzmann collision term.

Our analysis has thus shown that on the basis of much the same arguments that are used in deriving the Boltzmann equation, Eq. (58) for long times takes the form

$$\begin{aligned}\frac{\partial}{\partial t} F_1(\mathbf{v}_1; t) &= Y(\sigma) \times \text{Boltzmann collision term}\\ &= Y(\sigma) \int d\mathbf{v}_2 \int b\, db \int d\epsilon\\ &\quad \times g_{12}\{F_1(\mathbf{v}_1'; t)F_1(\mathbf{v}_2'; t) - F_1(\mathbf{v}_1; t)F_1(\mathbf{v}_2; t)\} \qquad (65)\end{aligned}$$

(for the notation see Ref. 3).

In the case of rigid sphere interaction Eq. (65) is identical with the Enskog equation (1) written for a homogeneous gas. Our basic approximation (42) to the term (39) has introduced the effect of the medium on the binary collisions between the particles by multiplying the Boltzmann collision term by a factor

$$Y(\sigma) = \lim_{r \to \sigma} \{\exp[\beta V(r)]\}\{G_2^{\text{eq}}(r) + 1\}$$

5. DISCUSSION

In this paper we have studied the approach to thermal equilibrium of a homogeneous dense gas. Our ideas originated from an attempt to understand the Enskog theory at the microscopic level. In order to gain an insight into this problem, we have calculated the rate of change of the reduced one-particle distribution [Eq. (33)], making evident (i) the contribution from pure s-particle dynamics, and (ii) the contribution corresponding to collisions between more than s particles.

On the basis of formula (36), we could interpret term (ii) as representing the modification of the effect of s-particle dynamics caused by the influence of the medium composed of $N - s$ particles on the phase space and time dependence of the distribution of s-particle states. Our main object then became to find a realistic approximation to this influence, analytically described by expression (39).

The gas was assumed to be at a late stage of its evolution, when the correlations are already close to their final equilibrium values. In this situation it seemed reasonable to relate the dominant effect of the medium on the distribution of s-particle states to the equilibrium component [see Eq. (38)] in the actual time-dependent correlations. This is why our approximation to quantity (39) consisted in taking the same spatial dependence as at equilibrium [Eq. (40)]. As a result, we obtained Eq. (44), or rather a series of equations corresponding to various values of s.

At this point it should be mentioned that the problem of the influence of the medium on a two-particle cluster has been recently analyzed in a similar spirit by Mazenko$^{(21)}$ in his study of the self-diffusion in single-component fluids. Mazenko discussed the Enskog approximation for the corresponding memory function. The peculiarity of this problem, in which the equilibrium averaging appears from the very beginning and quite a different formalism is used by the author, makes a direct comparison with our approach rather difficult.

The analysis of Eq. (44) in the case of $s = 2$ [Eq. (45)] for strongly repulsive forces of range σ has been based in Section 4 on the standard arguments used in deriving the Boltzmann equation. In the thermodynamic limit and for long times Eq. (45) was shown to coincide with the Enskog equation for a homogeneous gas. According to our approach, it should provide a good description not only for the singular rigid sphere potential (50), but also for a regular potential close to it [see derivation of formula (51)].

A number of open questions remain. The systematic character of the theory permits to formulate our approximation at the level of s-particle dynamics for all $s \geqslant 2$. Whereas for $s \geqslant 4$ we encounter the well-known divergences of the kinetic theory,$^{(19)}$ the case $s = 3$ (in three dimensions) is free of these difficulties and permits us to generalize the Enskog ideas to the level of three-particle dynamics. The corresponding kinetic equation, containing a modified Choh–Uhlenbeck operator, renormalized by the equilibrium correlations, is under investigation. Since this problem is rather complicated and demands a long and subtle analysis, we plan to discuss it in a separate paper.

Another question left unanswered is the quantitative estimation of the role of the neglected terms (43) in Eq. (36), necessary for the full justification of our approximation. The agreement of the Enskog equation with experiment shows that at least for $s = 2$, terms (43) are physically negligible. This provides a kind of a posteriori argument in favor of our approach. However, the full understanding of the physical reason for the smallness of terms (43) remains an open question, which we plan to study in further work. Finally, one could also think of generalizing the present theory to the case of an inhomogeneous gas.

APPENDIX

Here we indicate the method of proving Eq. (33). Consider first the case of $s = 2$. The last term in Eq. (33) then can be written as

$$\begin{aligned}
&\Omega^2 \int_0^t d\tau \int d\mathbf{v}_2 \int d\mathbf{v}_3\, \mathscr{D}^{12}(\tau)[-\mathscr{L}^{123} + \mathscr{L}^{12}] f_3(x_1, x_2, x_3; t - \tau) \\
&\quad = \Omega \int d\mathbf{v}_2 \int_0^t d\tau\, \mathscr{D}^{12}(\tau)\left(-\frac{\partial}{\partial\tau} + \mathscr{L}^{12}\right) f_2(x_1; x_2; t - \tau) \\
&\quad = -\Omega \int d\mathbf{v}_2\, \mathscr{D}^{12}(t) f_2(x_1, x_2; 0) - \Omega P \int d\mathbf{v}_2\, \delta\mathscr{L}^{12} \\
&\qquad \times f_2(x_1, x_2; t) + \Omega \int d\mathbf{v}_2 \int_0^t d\tau \\
&\qquad \times \left(\frac{\partial}{\partial\tau} \mathscr{D}^{12}(\tau) + \mathscr{D}^{12}(\tau)\mathscr{L}^{12}\right) f_2(x_1, x_2; t - \tau)
\end{aligned} \tag{A.1}$$

where the second BBGKY hierarchy equation has been used and the integration by parts with respect to τ has been performed.

Equation (33) for $s = 2$ follows directly from Eq. (A.1) if the first BBGKY hierarchy equation

$$(\partial/\partial t) n\varphi(\mathbf{v}_1; t) = -\Omega p \int d\mathbf{v}_2\, \delta\mathscr{L}^{12} f_2(x_1, x_2; t)$$

and the relation

$$(\partial/\partial\tau)\mathscr{D}^{12}(\tau) + \mathscr{D}^{12}(\tau)\mathscr{L}^{12} Q = 0$$

[see Eq. (34)] are taken into account.

By systematically using the relations

$$(\partial/\partial t)\mathscr{D}^{1\cdots s}(t) = -\mathscr{D}^{1\cdots s}\mathscr{L}^{1\cdots s} Q + \mathscr{D}^{1\cdots s-1}(-\mathscr{L}^{1\cdots s} + \mathscr{L}^{1\cdots s-1}) Q$$

one can also apply the same method to derive Eq. (33) for $s > 2$.

REFERENCES

1. D. Enskog, *K. Svensk. Vet.-Akad. Handl.* **63** (4) (1921).
2. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, Cambridge (1970).
3. J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases*, North-Holland, Amsterdam (1972).
4. J. V. Sengers, *Intern. J. Heat Mass Transfer* **8**:1103 (1965).
5. J. T. O'Toole and J. S. Dahler, *J. Chem. Phys.* **32**:1097 (1960).
6. H. B. Hollinger and C. F. Curtiss, *J. Chem. Phys.* **33**:1386 (1960).
7. R. F. Suider and C. F. Curtiss, *Phys. Fluids* **3**:903 (1960).

8. J. V. Sengers and E. G. O. Cohen, *Physica* **27**:230 (1961).
9. P. M. Livingston and C. F. Curtiss, *Phys. Fluids* **4**:816 (1961).
10. J. V. Sengers, *Phys. Fluids* **9**:1333 (1966).
11. W. R. Hoegy and J. V. Sengers, *Phys. Rev. A* **2**:2461 (1970).
12. J. V. Sengers, M. H. Ernst, and D. T. Gillespie, *J. Chem. Phys.* **56**:5583 (1972).
13. M. H. Ernst, *Physica* **32**:272 (1966).
14. S. Ono, in *Statistical Mechanics of Equilibrium and Non-Equilibrium* (Aachen 1964), J. Meixner, Amsterdam (1965).
15. R. Balescu, *Statistical Mechanics of Charged Particles*, Wiley–Interscience, New York (1963).
16. M. Kac, *Probability and Related Topics in Physical Sciences*, Interscience, London (1959).
17. I. Prigogine, *Non-Equilibrium Statistical Mechanics*, Wiley–Interscience, New York (1962); P. Resibois, A perturbative approach to irreversible statistical mechanics, in *Physics of Many-Particle System*, ed. by E. Meeron, Gordon and Breach, New York (1966).
18. J. Rae, *Ac. Roy. Belg. Bull. Cl. Sc.* **11**:980 (1969); **11**:1040 (1969).
19. E. Cohen, in *Fundamental Problems of Statistical Mechanics*, II, North-Holland, Amsterdam (1968).
20. J. Brocas, *Adv. Chem. Phys.* **XI**:317 (1967).
21. G. F. Mazenko, *Phys. Rev. A* **7**:209 (1973).