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Generalized Enskog Theory for Homogeneous Systems

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We propose a generalization of the Enskog equation for homogeneous dense systems including the complete three-particle dynamics. To this end the time derivative of the one-particle distribution is represented in the thermodynamic limit as the sum of three terms describing the effect of the initial s-particle correlations, collisions within s-particle clusters, and coupling of s-particle clusters to the surrounding gaseous medium, respectively. The analysis of cases $s = 2$ and $s = 3$ is performed both for hard spheres and for a smooth, repulsive interaction. On assuming the equilibrium structure and spatial dependence of terms reflecting the effect of the medium, we obtain for $s = 2$ the Enskog equation, and for $s = 3$ a new equation, going beyond the Enskog theory. Apart from the Enskog collision term it contains additional contributions, and can be shown to reduce to the Choh-Uhlenbeck equation in the long-time, low-density limit.

KEY WORDS: Liouville equation; kinetic theory; thermodynamic limit; hard spheres; Enskog equation; Choh–Uhlenbeck equation; binary collision expansion; reduced distributions; thermal equilibrium.

1. INTRODUCTION

This paper is devoted to the study of the form of the kinetic equation describing the approach to equilibrium of a dense, homogeneous system. We use and further elucidate the ideas formulated in our previous work[1] (this reference is hereafter referred to as I) in which the Enskog equation has been obtained by approximately estimating the influence of the gaseous medium on the occurrence of binary collisions. Here we take a step further by considering an analogous problem at the level of three-particle dynamics. We

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thus go beyond the Enskog theory and arrive at a new kinetic equation, which includes in particular the complete effect of ternary collisions. The corresponding collision term depends on equilibrium correlations and can be shown to reduce to the Choh–Uhlenbeck form in the low-density, long-time regime. It is suggested (Section 6) that it could be used to study numerically the deviation of the self-diffusion coefficient from its value as predicted by the Enskog theory. Also, the kinetic parts of other transport coefficients could be investigated along the same lines.

We found it interesting and illuminating to develop the theory simultaneously for a gas with repulsive, short-range forces derivable from a regular (differentiable) potential, and for the hard-sphere system. The differences between these cases are discussed, supplying at the same time a new derivation of the basic equations of I, which makes the present paper self-contained.

In Section 2 we discuss the evolution equation for the one-particle velocity distribution in the case of a finite system, and in Section 3 its form in the thermodynamic limit is established. This last point has been rarely systematically studied in the papers on the kinetic theory. We then recall (Section 4) the main ideas of I, and a simplified method of obtaining the Enskog equation for a hard-sphere system is presented. Section 5 contains a detailed discussion of the next step in our approach, going beyond the Enskog theory. It leads to a new kinetic equation, which is the most important result of the present work. Its relationship with the Choh–Uhlenbeck theory for moderately dense gases is analyzed. Finally, Section 6 is devoted to the discussion of the results and their possible applications. The details of more complicated calculations are given in appendices.

2. EVOLUTION OF THE ONE-PARTICLE VELOCITY DISTRIBUTION. THE CASE OF A FINITE SYSTEM

We consider a classical gas composed of N identical particles enclosed in a cube of volume Ω. In the case of a smooth pair interaction the Liouville equation has the form

$$\frac{\partial}{\partial t}\rho_N(x,t) = -\mathscr{L}^{1\cdots N}\rho_N(x,t) \tag{1}$$

Here $\rho_N(x, t)$ represents the probability density for finding the system at time t in the microscopic state $x = (x_1,..., x_N)$, in which particles have phases $x_i = (\mathbf{r}_i, \mathbf{v}_i)$, $i = 1,..., N$. Their position and velocity vectors are denoted by $\mathbf{r}_i$ and $\mathbf{v}_i$, respectively. Here $\mathscr{L}^{1\cdots N}$ is the Liouville operator. Defining

$$\mathscr{L}_0^i = \mathbf{v}_i\frac{\partial}{\partial \mathbf{r}_i} \qquad \text{and} \qquad \delta\mathscr{L}^{ij} = \frac{\partial V(r_{ij})}{\partial \mathbf{r}_{ij}}\left(\frac{\partial}{\partial \mathbf{v}_j} - \frac{\partial}{\partial \mathbf{v}_i}\right) \tag{2}$$

we have

$$\mathscr{L}^{1\cdots N} = \mathscr{L}_0^{1\cdots N} + \delta\mathscr{L}^{1\cdots N} \tag{3}$$

where

$$\mathscr{L}_0^{1\cdots N} = \sum_{i=1}^{N} \mathscr{L}_0^i \qquad \text{and} \qquad \delta\mathscr{L}^{1\cdots N} = \sum_{(ij)}^{N} \delta\mathscr{L}^{ij}$$

$V(r_{ij})$ is the central repulsive pair potential of finite range σ, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and $\sum_{(ij)}^{N} \equiv \sum_{i=1}^{N} \sum_{j=i+1}^{N}$.

In the case of a hard-sphere system the analog of Eq. (1) takes the form[2]

$$(\partial/\partial t)\rho_N(x, t) = -\bar{\mathscr{L}}^{1\cdots N}\rho_N(x, t) \tag{4}$$

$\bar{\mathscr{L}}^{1\cdots N}$ is called a pseudo-Liouville operator and is given by

$$\bar{\mathscr{L}}^{1\cdots N} = \mathscr{L}_0^{1\cdots N} - \bar{T}^{1\cdots N}, \qquad \bar{T}^{1\cdots N} = \sum_{(ij)}^{N} \bar{T}(ij) \tag{5}$$

where

$$\bar{T}(ij) = \lim_{\tau\searrow 0} \sigma^2 \int_{\mathbf{v}_{ij}\hat{\boldsymbol{\sigma}} > 0} d\hat{\boldsymbol{\sigma}}\, (\mathbf{v}_{ij}\hat{\boldsymbol{\sigma}})\{\delta(\mathbf{r}_{ij} - \boldsymbol{\sigma})b_{\boldsymbol{\sigma}}^{ij} - \delta(\mathbf{r}_{ij} + \boldsymbol{\sigma})\} \exp(-\mathscr{L}_0^{1\cdots N}\tau) \tag{6}$$

In Eq. (6), $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\hat{\boldsymbol{\sigma}} = \boldsymbol{\sigma}/\sigma$, σ is the hard-sphere diameter, and the integration is carried over the solid angle with restriction to the hemisphere $\mathbf{v}_{ij}\hat{\boldsymbol{\sigma}} > 0$. Operator $b_{\boldsymbol{\sigma}}^{ij}$ acts on the velocity variables $\mathbf{v}_1,\ldots, \mathbf{v}_N$, changing them according to the hard-sphere binary collision law

$$\begin{aligned} b_{\boldsymbol{\sigma}}^{ij}\mathbf{v}_i &= \mathbf{v}_i' = \mathbf{v}_i - (\mathbf{v}_{ij}\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{\sigma}} \\ b_{\boldsymbol{\sigma}}^{ij}\mathbf{v}_j &= \mathbf{v}_j' = \mathbf{v}_j + (\mathbf{v}_{ij}\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{\sigma}} \\ b_{\boldsymbol{\sigma}}^{ij}\mathbf{v}_a &= \mathbf{v}_a' = \mathbf{v}_a \qquad \text{for} \quad a \neq i, j \end{aligned} \tag{7}$$

Equation (4) can be formally obtained from Eq. (1) by replacing $\delta\mathscr{L}^{1\cdots N}$ by $(-\bar{T}^{1\cdots N})$. Operators $\delta\mathscr{L}^{ij}$ and $\bar{T}(ij)$ have the following important common property:

$$\int d\mathbf{v}_i \int d\mathbf{v}_j\, \delta\mathscr{L}^{ij} = 0 \tag{8}$$

$$\int d\mathbf{v}_i \int d\mathbf{v}_j\, \bar{T}(ij) = 0 \tag{9}$$

Equations (8) and (9) should be understood in the operator sense. Equation (8) is an immediate consequence of the fact that $\delta\mathscr{L}^{ij}$ is the first-order differential operator in velocities [see Eq. (2)]. The proof of Eq. (9) follows directly from the observation that the Jacobian of transformation (7) equals 1, and that $\mathbf{v}_{ij}\hat{\boldsymbol{\sigma}} = -\mathbf{v}_{ij}'\hat{\boldsymbol{\sigma}}$. In what follows we shall deduce the evolution equation for the one-particle velocity distribution from Eq. (1), using only Eq. (8) as far as the properties of operator $\delta\mathscr{L}^{ij}$ are concerned. Equation (9) permits us then to write the corresponding equation for the hard-sphere system by simply replacing everywhere $\delta\mathscr{L}^{ij}$ by $-\bar{T}(ij)$.

The formal solution of Eq. (1) can be written as

$$\rho_N(x, t) = S_{-t}^{1\cdots N}\rho_N(x, 0) \tag{10}$$

where

$$S_{-t}^{1\cdots N} = \exp(-\mathscr{L}^{1\cdots N}t) \tag{11}$$

is the N-particle streaming operator. We are interested in the evolution of the velocity distribution

$$\varphi(\mathbf{v}_1, t) = \Omega^N \int d\mathbf{v}^{N-1}\, P\rho_N(x, t) \tag{12}$$

Here $\int d\mathbf{v}^{N-1} = \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_N$ and

$$P = \Omega^{-N} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N = P^2 \tag{13}$$

Defining

$$Q = I - P \tag{14}$$

we have

$$Q = Q^2, \qquad QP = PQ = 0 \tag{15}$$

and from Eq. (1) we get

$$\begin{aligned}(\partial/\partial t)\varphi(\mathbf{v}_1, t) = \Omega^N \int d\mathbf{v}^{N-1}\{&P(-\mathscr{L}^{1\cdots N})P\rho_N(x, t) \\ &+ P(-\mathscr{L}^{1\cdots N})QS_{-t}^{1\cdots N}\rho_N(x, 0)\}\end{aligned} \tag{16}$$

For a smooth potential the relations

$$P\mathscr{L}_0^i = \mathscr{L}_0^i P = 0 \tag{17}$$

$$P\,\delta\mathscr{L}^{ij}P = 0 \tag{18}$$

imply that $P\mathscr{L}^{1\cdots N}P = 0$, so that the first term in the rhs of Eq. (16) vanishes. For a hard-sphere system, however, $P\bar{T}(ij)P \neq 0$. Using Eq. (9) and the symmetry in variables $x_2, \ldots, x_N$, we get

$$\begin{aligned}&\Omega^N \int d\mathbf{v}^{N-1}\, P(-\bar{\mathscr{L}}^{1\cdots N})P\rho_N(x, t) \\ &\quad = (N-1)\Omega^{-1} \int dx_2\, \bar{T}(12)\varphi_2(\mathbf{v}_1, \mathbf{v}_2, t)\end{aligned} \tag{19}$$

where φ_2 is the two-particle velocity distribution.

In order to separate in Eq. (16) the evolution of the velocity distribution from that of correlations (for the general ideas of the kinetic theory followed here see Refs. 3 and 4) we introduce the so-called irreducible propagator

$$\mathscr{P}_{-t}^{1\cdots N} = Q\exp(-\mathscr{L}^{1\cdots N}Qt)Q \tag{20}$$

related to the streaming operator (11) by the equation

$$QS_{-t}^{1\cdots N} = \mathscr{P}_{-t}^{1\cdots N} - \mathscr{P}_{-t}^{1\cdots N}\mathscr{L}^{1\cdots N} * PS_{-t}^{1\cdots N} \tag{21}$$

The symbol $*$ denotes here the time convolution defined for any two operators (functions) A_t and B_t as

$$A_t * B_t = \int_0^t d\tau\, A_{t-\tau}B_\tau \tag{22}$$

Equation (21) results directly from the operator relation

$$\exp(-\mathscr{M}t) - \exp(-\mathscr{N}t) = \exp(-\mathscr{N}t)\,[\mathscr{N} - \mathscr{M}] * \exp(-\mathscr{M}t) \tag{23}$$

by putting $\mathscr{M} = \mathscr{L}^{1\cdots N}$ and $\mathscr{N} = \mathscr{L}^{1\cdots N}Q$. Identity (23) will be frequently used in the text.

In Appendix A we prove the following important relation:

$$\begin{aligned} N\int d\mathbf{v}^{N-1}\, P(-\mathscr{L}^{1\cdots N})\mathscr{P}_{-t}^{1\cdots N} &= \int d\mathbf{v}^{N-1}\Big\{\sum_{a=2}^{s}\frac{N!}{(N-a)!}\mathscr{D}_{-t}^{1\cdots a} \\ &\quad + \frac{N!}{(N-s-1)!}\mathscr{D}_{-t}^{1\cdots s} * (\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots s+1})\mathscr{P}_{-t}^{1\cdots N}\Big\} \end{aligned} \tag{24}$$

where

$$\mathscr{D}_{-t}^{1\cdots a} = P(\mathscr{L}^{1} - \mathscr{L}^{12})\mathscr{P}_{-t}^{12} * (\mathscr{L}^{12} - \mathscr{L}^{123})\mathscr{P}_{-t}^{123} * \cdots * (\mathscr{L}^{1\cdots a-1} - \mathscr{L}^{1\cdots a})\mathscr{P}_{-t}^{1\cdots a} \tag{25}$$

Equation (24) is valid in the space of functions symmetric in variables $x_1,\ldots, x_N$, for any $s = 2, 3,\ldots, s < N$. In particular, when $s = N - 1$ it takes the form

$$N\int d\mathbf{v}^{N-1}\, P(-\mathscr{L}^{1\cdots N})\mathscr{P}_{-t}^{1\cdots N} = \int d\mathbf{v}^{N-1}\sum_{a=2}^{N}\frac{N!}{(N-a)!}\mathscr{D}_{-t}^{1\cdots a} \tag{26}$$

We now multiply both sides of Eq. (16) by $n = N/\Omega$, insert in the second term in its rhs relation (21), and use Eq. (24). A simple calculation based on Eqs. (8) and (21) yields

$$n \frac{\partial}{\partial t} \varphi(\mathbf{v}_1, t)$$
$$= \sum_{a=2}^{s} \Omega^{a-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a \{\mathscr{D}_{-t}^{1\cdots a} f_a(x_1 \cdots x_a, 0)$$
$$+ \mathscr{G}_{-t}^{1\cdots a} * f_a(x_1 \cdots x_a, t)\} + \Omega^s \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_{s+1}$$
$$\times \mathscr{D}_{-t}^{1\cdots s}(\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots s+1}) * f_{s+1}(x_1 \cdots x_{s+1}, t) \tag{27}$$

For $s = N - 1$, using Eq. (26) we get in a similar way

$$n \frac{\partial}{\partial t} \varphi(\mathbf{v}_1, t)$$
$$= \sum_{a=2}^{N} \Omega^{a-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}^a \{\mathscr{D}_{-t}^{1\cdots a} f_a(x_1 \cdots x_a, 0)$$
$$+ \mathscr{G}_{-t}^{1\cdots a} * f_a(x_1 \cdots x_a, t)\} \tag{28}$$

In Eqs. (27) and (28) there appear the reduced distributions

$$f_a(x_1 \cdots x_a, t) = \frac{N!}{(N-a)!} \int dx_{a+1} \cdots \int dx_N \, \rho_N(x_1 \cdots x_N, t) \tag{29}$$

and collision operators $\mathscr{G}_{-t}^{1\cdots a}$ defined by

$$\mathscr{G}_{-t}^{1\cdots a} = \mathscr{D}_{-t}^{1\cdots a}(-\mathscr{L}^{1\cdots a})P \tag{30}$$

By replacing in Eqs. (20), (25), and (30) the Liouville operators by the pseudo-Liouville operators [see Eq. (5)] we obtain the hard-sphere kinetic operators $\overline{\mathscr{P}}_{-t}^{1\cdots N}$, $\overline{\mathscr{D}}_{-t}^{1\cdots a}$, and $\overline{\mathscr{G}}_{-t}^{1\cdots a}$, respectively. Then, taking into account Eqs. (19) and (29), we write the analog of Eqs. (27) and (28) for the hard-sphere gas in the form

$$n \frac{\partial}{\partial t} \varphi(\mathbf{v}_1, t)$$
$$= \Omega \int d\mathbf{v}_2 \, P\overline{T}(12) P f_2(x_1, x_2, t)$$
$$+ \sum_{a=2}^{s} \Omega^{a-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a \{\overline{\mathscr{D}}_{-t}^{1\cdots a} f_a(x_1 \cdots x_a, 0)$$
$$+ \overline{\mathscr{G}}_{-t}^{1\cdots a} * f_a(x_1 \cdots x_a, t)\} + \Omega^s \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_{s+1}$$
$$\times \overline{\mathscr{D}}_{-t}^{1\cdots s}(\overline{\mathscr{L}}^{1\cdots s} - \overline{\mathscr{L}}^{1\cdots s+1}) * f_{s+1}(x_1 \cdots x_{s+1}, t) \tag{31}$$

$$
\begin{aligned}
n \frac{\partial}{\partial t} \varphi(\mathbf{v}_1, t)
&= \Omega \int d\mathbf{v}_2\, P\bar{T}(12) P f_2(x_1, x_2, t) \\
&\quad + \sum_{a=2}^{N} \Omega^{a-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a \{ \bar{\mathscr{D}}_{-t}^{1\cdots a} f_a(x_1 \cdots x_a, 0) \\
&\quad + \bar{\mathscr{G}}_{-t}^{1\cdots a} * f_a(x_1 \cdots x_a, t) \}
\end{aligned} \tag{32}
$$

It is important to notice that the last term in the rhs of Eq. (27) can be transformed by using the BBGKY hierarchy equation

$$\left(\frac{\partial}{\partial t} + \mathscr{L}^{1\cdots s} \right) f_s(x_1 \cdots x_s, t) = \sum_{j=1}^{s} \int dx_{s+1} (-\delta \mathscr{L}^{js+1}) f_{s+1}(x_1 \cdots x_{s+1}, t) \tag{33}$$

to the form

$$\Omega^{s-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_s\, \mathscr{D}_{-t}^{1\cdots s} * \left(\frac{\partial}{\partial t} + \mathscr{L}^{1\cdots s} \right) f_s(x_1 \cdots x_s, t) \tag{34}$$

The same can be done for Eq. (31), since Eq. (33) with $(-\delta\mathscr{L}^{ij})$ replaced by $\bar{T}(ij)$ holds for the hard-sphere gas. The structure of Eqs. (27) and (31) emerged from the separation in the irreducible propagator $\mathscr{P}_{-t}^{1\cdots N}$ (or $\bar{\mathscr{P}}_{-t}^{1\cdots N}$) of the part depending only on s-particle dynamics. The effects of collisions between more than s particles are described by the last term in both equations. Equations (27), (28), (31), and (32), which are valid for a finite system, are usually supplemented with periodic boundary conditions. In the next section we discuss their form in the thermodynamic limit.

3. EVOLUTION OF THE ONE-PARTICLE VELOCITY DISTRIBUTION. THE CASE OF AN INFINITE SYSTEM

We denote the thermodynamic limit by

$$\lim_{\infty} = \lim_{N\to\infty, \Omega\to\infty, N/\Omega = n = \text{const}} \tag{35}$$

For all distributions calculated in this limit capital letters will be used. E.g., we write

$$
\begin{aligned}
\lim_{\infty} \varphi(\mathbf{v}_j, t) &= \Phi(\mathbf{v}_j, t) \\
\lim_{\infty} f_a(x_1 \cdots x_a, t) &= F_a(x_1 \cdots x_a, t)
\end{aligned} \tag{36}
$$

The limits (36) are supposed to exist for all times t.

Consider next correlation functions $g_a(x_1 \cdots x_a, t)$, $a = 2, 3,\ldots,$ defined by the cluster decomposition of the reduced distributions, which for a homogeneous gas can be written as

$$\begin{aligned} f_1(x_1, t) &= f_1(\mathbf{v}_1, t) \\ f_2(x_1, x_2, t) &= [1 + g_2(x_1, x_2, t)] \prod_{j=1}^{2} f_1(\mathbf{v}_j, t) \\ f_3(x_1, x_2, x_3, t) &= \left[1 + \sum_{(ab)}^{3} g_2(x_a, x_b, t) + g_3(x_1, x_2, x_3, t)\right] \prod_{j=1}^{3} f_1(\mathbf{v}_j, t) \end{aligned} \tag{37}$$

etc.

We shall assume that for all times t, functions $g_a(x_1 \cdots x_a, t)$ go to zero when the distance between any pair of particles $1 \cdots a$ tends to infinity. This cluster property of correlations implies that

$$\lim_{\infty} \Omega^{-s} \int d\mathbf{r}_{i_1} \cdots \int d\mathbf{r}_{i_s}\, g_a(x_1 \cdots x_a, t) = 0, \qquad 1 \leqslant i_1 < i_2 \cdots < i_s \leqslant a \tag{38}$$

and in particular leads to the relation

$$\lim_{\infty} \varphi_a(\mathbf{v}_1 \cdots \mathbf{v}_a, t) = \prod_{j=1}^{a} \Phi(\mathbf{v}_j, t) \tag{39}$$

where φ_a is the a-particle velocity distribution (see I, Section 2). Using definitions (13) and (29), we thus obtain

$$\lim_{\infty} Pf_a(x_1 \cdots x_a, t) = \prod_{j=1}^{a} F_1(\mathbf{v}_j, t) \tag{40}$$

where $F_1(\mathbf{v}_j, t) = n\Phi(\mathbf{v}_j, t)$. In particular,

$$\lim_{\infty} \Omega \int d\mathbf{v}_2\, P\overline{T}(12) Pf_2(x_1, x_2, t) = \int dx_2\, \overline{T}(12) \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \tag{41}$$

which establishes the form of the first term in the rhs of Eqs. (31) and (32) in the thermodynamic limit.

It follows from Eqs. (30) and (34) that in order to calculate the rhs of Eq. (27) for an infinite system it is sufficient to find in this case the action of the operator

$$\Omega^{a-1} \int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a\, \mathscr{D}_{-t}^{1\cdots a} \tag{42}$$

on functions $f_a(x_1 \cdots x_a, 0)$,

$$(-\mathscr{L}^{1\cdots a}) Pf_a(x_1 \cdots x_a, t), \qquad \left(\frac{\partial}{\partial t} + \mathscr{L}^{1\cdots a}\right) f_a(x_1 \cdots x_a, t) \tag{43}$$

[An analogous statement can be formulated for Eq. (31).] Due to the homogeneity of the state of the gas (translational invariance of the reduced distributions) functions (43) depend only on vectors $\mathbf{r}_i - \mathbf{r}_j$, $1 \leqslant i < j \leqslant a$, as far as their position dependence is concerned. The analysis of operator (42) will be based on the following remark:

Let us denote the free a-particle streaming operator by

$$S_{0,-t}^{1\cdots a} = \exp(-\mathscr{L}_0^{1\cdots a}t) \tag{44}$$

From the equation

$$S_{-t}^{1\cdots a} = S_{0,-t}^{1\cdots a} + S_{0,-t}^{1\cdots a} * (-\delta\mathscr{L}^{1\cdots a})S_{-t}^{1\cdots a} \tag{45}$$

[see identity (23)] and Eqs. (14) and (17) we get

$$PS_{-t}^{1\cdots a}Q = 1 * P(-\delta\mathscr{L}^{1\cdots a})S_{-t}^{1\cdots a}Q \tag{46}$$

Definition (13) of projector P and the fact that each interaction $\delta\mathscr{L}^{ij}$ restricts the domain of integration over positions $\mathbf{r}_i$, $\mathbf{r}_j$ to the region $|\mathbf{r}_i - \mathbf{r}_j| \leqslant \sigma$ (= range of the pair potential) show that in the thermodynamic limit operator $PS_{-t}^{1\cdots a}Q$ is of order Ω^{-1}. Equation (21) thus implies that we can replace in this limit the irreducible propagator $\mathscr{P}_{-t}^{1\cdots a}$ by $QS_{-t}^{1\cdots a}Q$, and even by $S_{-t}^{1\cdots a}Q$, since the last two operators differ precisely by $PS_{-t}^{1\cdots a}Q$. In this way we arrive at an important result [compare with Eq. (25)]

$$\begin{aligned}\lim_{\infty} \Omega^{a-1}\int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a\, \mathscr{D}_{-t}^{1\cdots a} &= \lim_{\infty} \Omega^{a-1}\int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a\, P(-\delta\mathscr{L}^{12})S_{-t}^{12} \\ &\quad * Q\left(-\sum_{b=1}^{2} \delta\mathscr{L}^{b3}\right)S_{-t}^{123} * \cdots * Q\left(-\sum_{r=1}^{a-1} \delta\mathscr{L}^{ra}\right)S_{-t}^{1\cdots a}Q\end{aligned} \tag{47}$$

Within the theory of homogeneous systems the above operator can be further transformed. The translational invariance of the integrand together with the fact that sequences

$$(\delta\mathscr{L}^{12}, \delta\mathscr{L}^{b3}, \ldots, \delta\mathscr{L}^{ra}) \tag{48}$$

introduce consecutively phase variables $x_2, x_3, \ldots, x_a$ permit us to write

$$\begin{aligned}\lim_{\infty} \Omega^{a-1}\int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a\, \mathscr{D}_{-t}^{1\cdots a} &= \lim_{\infty} \int dx_2(-\delta\mathscr{L}^{12})S_{-t}^{12} \\ &\quad * Q_2\int dx_3\left(-\sum_{b=1}^{2} \delta\mathscr{L}^{b3}\right)S_{-t}^{123} * \cdots * Q_{a-1}\int dx_a\left(-\sum_{r=1}^{a-1} \delta\mathscr{L}^{ra}\right)S_{-t}^{1\cdots a}Q_a\end{aligned} \tag{49}$$

where

$$Q_j = I - P_j = I - \Omega^{-j}\int d\mathbf{r}_1 \cdots \int d\mathbf{r}_j$$

It is clear from Eq. (49) that all the $(a - 1)$ volume integrations inherent in the integrals over phases $x_2 \cdots x_a$ are restricted by operators (48) to bounded regions whose linear dimensions are of the order of the range of the potential. This ensures the existence of the limit. The detailed analysis of the structure of operator (49) is given in Appendix B. Here we are interested only in two cases: $a = 2$ and $a = 3$. For $a = 2$ from Eq. (49) we get

$$\lim_{\infty} \Omega \int d\mathbf{v}_2\, \mathscr{D}^{12}_{-t} = \lim_{\infty} \int dx_2\,(-\delta\mathscr{L}^{12})S^{12}_{-t}Q_2 \tag{50}$$

For $a = 3$, Eq. (49) and the results of Appendix B yield

$$\begin{aligned}
&\lim_{\infty} \Omega^2 \int d\mathbf{v}_2 \int d\mathbf{v}_3\, \mathscr{D}^{123}_{-t} \\
&\quad = \lim_{\infty} \sum_{b=1}^{2} \int dx_2(-\delta\mathscr{L}^{12})S^{12}_{-t} * Q_2 \int dx_3\,(-\delta\mathscr{L}^{b3})S^{123}_{-t}Q_3 \qquad (51)\\
&\quad = \lim_{\infty} \int dx_2 \int dx_3\,(-\delta\mathscr{L}^{12})S^{12}_{-t} * \sum_{b=1}^{2} (-\delta\mathscr{L}^{b3})\left[S^{123}_{-t} - S^{b3}_{-t}\Omega^{-1}\int d\mathbf{r}_{3-b}\right]Q_3
\end{aligned}$$

Equations (50) and (51) reduce the problem of writing Eq. (27) with $s = 2$ or $s = 3$ for an infinite system to the calculation in this case of the action of projectors Q_2 and Q_3, $\Omega^{-1}\int d\mathbf{r}_i\, Q_3$, $i = 1, 2$, on functions (43) with $s = 2$ and $s = 3$, respectively. Using Eqs. (38) and (39), we get

$$\lim_{\infty} Q_a f_a(x_1 \cdots x_a, 0) = F_a(x_1 \cdots x_a, 0) - \prod_{j=1}^{a} F_1(\mathbf{v}_j, 0) \tag{52}$$

$$\lim_{\infty} Q_a(-\mathscr{L}^{1\cdots a})Pf_a(x_1 \cdots x_a, t) = (-\delta\mathscr{L}^{1\cdots a})\prod_{j=1}^{a} F_1(\mathbf{v}_j, t) \tag{53}$$

$$\begin{aligned}
&\lim_{\infty} Q_a\left(\frac{\partial}{\partial t} + \mathscr{L}^{1\cdots a}\right)f_a(x_1 \cdots x_a, t) \\
&\quad = \left(\frac{\partial}{\partial t} + \mathscr{L}^{1\cdots a}\right)F_a(x_1 \cdots x_a, t) - \frac{\partial}{\partial t}\prod_{j=1}^{a} F_1(\mathbf{v}_j, t) \qquad (54)
\end{aligned}$$

$a = 2, 3,\ldots$. The action of projector $\Omega^{-1}\int d\mathbf{r}_1\, Q_3$ gives

$$\lim_{\infty} \Omega^{-1}\int d\mathbf{r}_1\, Q_3 f_3(x_1, x_2, x_3, 0) = G_2(x_2, x_3, 0)\prod_{j=1}^{3} F_1(\mathbf{v}_j, 0) \tag{55}$$

$$\lim_{\infty} \Omega^{-1}\int d\mathbf{r}_1\, Q_3(-\mathscr{L}^{123})Pf_3(x_1, x_2, x_3, t) = (-\delta\mathscr{L}^{23})\prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{56}$$

$$\lim_{\infty} \Omega^{-1} \int d\mathbf{r}_1 \, Q_3 \left(\frac{\partial}{\partial t} + \mathscr{L}^{123} \right) f_3(x_1, x_2, x_3, t)$$
$$= \left(\frac{\partial}{\partial t} + \mathscr{L}^{23} \right) F_2(x_2, x_3, t) F_1(\mathbf{v}_1, t) - \frac{\partial}{\partial t} \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{57}$$

where $G_2(x_1, x_2, t) = \lim_\infty g_2(x_1, x_2, t)$. The corresponding results for projector $\Omega^{-1} \int d\mathbf{r}_2 \, Q_3$ are obtained from Eqs. (55)–(57) by interchanging indices $1 \leftrightarrow 2$.

Combining Eqs. (50) and (51) with Eqs. (52)–(57), we find the evolution equation (27) for $s = 2$ and $s = 3$ for an infinite system. In both cases it has the following structure:

$$\frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) = \Lambda^{(s)}_{\mathrm{corr}}(\mathbf{v}_1, t) + \Lambda^{(s)}_{\mathrm{coll}}(\mathbf{v}_1, t) + \Lambda^{(s)}_{\mathrm{med}}(\mathbf{v}_1, t) \tag{58}$$

where $\Lambda^{(s)}_{\mathrm{corr}}$ describes the effect of the initial s-particle correlations, $\Lambda^{(s)}_{\mathrm{coll}}$ represents the influence of s-particle collisions (as if they were taking place in vacuum), and $\Lambda^{(s)}_{\mathrm{med}}$ gives the necessary correction to the s-particle collision term coming from the infinite surrounding medium. When $s = 2$ we get

$$\begin{aligned}
\Lambda^{(2)}_{\mathrm{corr}}(\mathbf{v}_1, t) &= \int dx_2 \, (-\delta\mathscr{L}^{12}) S^{12}_{-t} G_2(x_1, x_2, 0) \prod_{j=1}^{2} F_1(\mathbf{v}_j, 0) \\
\Lambda^{(2)}_{\mathrm{coll}}(\mathbf{v}_1, t) &= \int dx_2 \, (-\delta\mathscr{L}^{12}) S^{12}_{-t} (-\delta\mathscr{L}^{12}) * \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \\
\Lambda^{(2)}_{\mathrm{med}}(\mathbf{v}_1, t) &= \int dx_2 \, (-\delta\mathscr{L}^{12}) S^{12}_{-t} \\
&\quad * \left\{ \left(\frac{\partial}{\partial t} + \mathscr{L}^{12} \right) F_2(x_1, x_2, t) - \frac{\partial}{\partial t} \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \right\}
\end{aligned} \tag{59}$$

We can write at once the corresponding formulas for the hard-sphere system by adding term (41) and replacing everywhere $(-\delta\mathscr{L}^{ij})$ by $\overline{T}(ij)$. An important simplification occurs because of the relation

$$\overline{T}(ij) S^{ij}_{0,-t} \overline{T}(ij) = 0 \qquad \text{for all times } t \tag{60}$$

(see Ref. 2; various properties of hard spheres are collected in Ref. 5). Equation (60) in particular implies that

$$\overline{T}(ij) \bar{S}^{ij}_{-t} = \overline{T}(ij) S^{ij}_{0,-t} \tag{61}$$

Taking this into account, we obtain the following analog of Eq. (59) for hard spheres:

$$
\begin{aligned}
\bar{\Lambda}^{(2)}_{\mathrm{corr}}(\mathbf{v}_1, t) &= \int dx_2\, \bar{T}(12) S^{12}_{0,-t} G_2(x_1, x_2, 0) \prod_{j=1}^{2} F_1(\mathbf{v}_j, 0) \\
\bar{\Lambda}^{(2)}_{\mathrm{coll}}(\mathbf{v}_1, t) &= \int dx_2\, \bar{T}(12) \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \\
\bar{\Lambda}^{(2)}_{\mathrm{med}}(\mathbf{v}_1, t) &= \int dx_2\, \bar{T}(12) S^{12}_{0,-t} * \left\{ \left(\frac{\partial}{\partial t} + \mathscr{L}^{12} \right) F_2(x_1, x_2, t) \right. \\
&\quad \left. - \frac{\partial}{\partial t} \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \right\}
\end{aligned}
\tag{62}
$$

When $s = 3$ the rhs of Eq. (58) is the sum of the terms

$$
\begin{aligned}
\Lambda^{(3)}_{\mathrm{corr}}(\mathbf{v}_1, t) &= \Lambda^{(2)}_{\mathrm{corr}}(\mathbf{v}_1, t) \\
&\quad + \sum_{b=1}^{2} \int dx_2 \int dx_3\, (-\delta\mathscr{L}^{12}) S^{12}_{-t} * (-\delta\mathscr{L}^{b3}) \\
&\quad \times \left\{ S^{123}_{-t} \left[F_3(x_1, x_2, x_3, 0) - \prod_{j=1}^{3} F_1(\mathbf{v}_j, 0) \right] \right. \\
&\quad \left. - S^{b3}_{-t} G_2(x_b, x_3, 0) \prod_{j=1}^{3} F_1(\mathbf{v}_j, 0) \right\} \\
\Lambda^{(3)}_{\mathrm{coll}}(\mathbf{v}_1, t) &= \Lambda^{(2)}_{\mathrm{coll}}(\mathbf{v}_1, t) + \sum_{b=1}^{2} \int dx_2 \int dx_3\, (-\delta\mathscr{L}^{12}) S^{12}_{-t} \\
&\quad * (-\delta\mathscr{L}^{b3}) \{ S^{123}_{-t} (-\delta\mathscr{L}^{123}) - S^{b3}_{-t} (-\delta\mathscr{L}^{b3}) \} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \\
\Lambda^{(3)}_{\mathrm{med}}(\mathbf{v}_1, t) &= \sum_{b=1}^{2} \int dx_2 \int dx_3\, (-\delta\mathscr{L}^{12}) S^{12}_{-t} * (-\delta\mathscr{L}^{b3}) \left\{ S^{123}_{-t} \right. \\
&\quad * \left[\left(\frac{\partial}{\partial t} + \mathscr{L}^{123} \right) F_3(x_1, x_2, x_3, t) - \frac{\partial}{\partial t} \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \right] \\
&\quad - S^{b3}_{-t} * \left[\left(\frac{\partial}{\partial t} + \mathscr{L}^{b3} \right) F_2(x_b, x_3, t) F_1(\mathbf{v}_{3-b}, t) \right. \\
&\quad \left. \left. - \frac{\partial}{\partial t} \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \right] \right\}
\end{aligned}
\tag{63}
$$

The corresponding formulas for the hard-sphere gas read

$$\begin{aligned}
\bar{\Lambda}^{(3)}_{\text{corr}}(\mathbf{v}_1, t) &= \bar{\Lambda}^{(2)}_{\text{corr}}(\mathbf{v}_1, t) \\
&\quad + \sum_{b=1}^{2} \int dx_2 \int dx_3\, \bar{T}(12) S^{12}_{0,-t} * \bar{T}(b3) \\
&\quad \times \left\{ \bar{S}^{123}_{-t} \left[F_3(x_1, x_2, x_3, 0) - \prod_{j=1}^{3} F_1(\mathbf{v}_j, 0) \right] \right. \\
&\quad \left. - S^{b3}_{0,-t} G_2(x_b, x_3, 0) \prod_{j=1}^{3} F_1(\mathbf{v}_j, 0) \right\} \\
\bar{\Lambda}^{(3)}_{\text{coll}}(\mathbf{v}_1, t) &= \bar{\Lambda}^{(2)}_{\text{coll}}(\mathbf{v}_1, t) \\
&\quad + \sum_{b=1}^{2} \int dx_2 \int dx_3\, \bar{T}(12) S^{12}_{0,-t} * \bar{T}(b3) \bar{S}^{123}_{-t} \bar{T}^{123} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \\
\bar{\Lambda}^{(3)}_{\text{med}}(\mathbf{v}_1, t) &= \sum_{b=1}^{2} \int dx_2 \int dx_3\, \bar{T}(12) S^{12}_{0,-t} * \bar{T}(b3) \left\{ S^{123}_{-t} \right. \\
&\quad * \left[\left(\frac{\partial}{\partial t} + \mathscr{L}^{123} \right) F_3(x_1, x_2, x_3, t) - \frac{\partial}{\partial t} \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \right] \\
&\quad - S^{b3}_{0,-t} * \left[\left(\frac{\partial}{\partial t} + \mathscr{L}^{b3} \right) F_2(x_b, x_3, t) F_1(\mathbf{v}_{3-b}, t) \right. \\
&\quad \left. \left. - \frac{\partial}{\partial t} \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \right] \right\}
\end{aligned} \tag{64}$$

We have thus established the form of the evolution equation for the velocity distribution of an infinite system both for a smooth pair potential and for the hard-sphere interaction. The cases of $s = 2$ and $s = 3$ will be further analyzed in the next sections on assuming the existence of the long-time regime in which the term $\Lambda^{(s)}_{\text{corr}}$ ($\bar{\Lambda}^{(s)}_{\text{corr}}$) representing in Eq. (58) the effect of the initial correlations can be neglected. The justification of this assumption requires, especially for $s = 3$, a subtle analysis which can be found in Ref. 6.

4. ENSKOG EQUATION FOR HOMOGENEOUS SYSTEMS

We begin by recalling the main ideas of paper I. In Section 3 it has been indicated that term $\Lambda^{(s)}_{\text{med}}$ in Eq. (58) reflects the fact that s-particle collisions take place not in a vacuum but in an infinite gaseous medium. In the theory of dense gases this term should thus play a fundamental role. Clearly the presence of the medium shows in the structure of $\Lambda^{(s)}_{\text{med}}$ via the appearance of terms

$$\left(\frac{\partial}{\partial t} + \mathscr{L}^{1\cdots s} \right) F_s(x_1 \cdots x_s, t) - \frac{\partial}{\partial t} \prod_{j=1}^{s} F_1(\mathbf{v}_j, t) \tag{65}$$

[see Eqs. (59) and (63)]. In I we have developed the idea of approximating $\Lambda^{(s)}_{\text{med}}$ for systems close to equilibrium by taking into account only the equilibrium component of spatial correlations in Eq. (65). By this we mean the following: At complete equilibrium, where the reduced distributions have the form

$$F_s^{\text{eq}}(x_1 \cdots x_s) = W_s(\mathbf{r}_1 \cdots \mathbf{r}_s) Y_s(\mathbf{r}_1 \cdots \mathbf{r}_s) \prod_{j=1}^{s} F_1^{\text{eq}}(v_j) \tag{66}$$

with

$$F_1^{\text{eq}}(v_j) = n(2\pi k_B T)^{-3/2} \exp(-v_j^2/2k_B T)$$
$$W_s(\mathbf{r}_1 \cdots \mathbf{r}_s) = \exp\left[-\sum_{(ij)}^{s} V(r_{ij})/k_B T\right]$$

(k_B is the Boltzmann constant, T is the temperature), term (65) reduces to

$$\mathscr{L}^{1\cdots s} F_s^{\text{eq}}(x_1 \cdots x_s) = W_s(\mathbf{r}_1 \cdots \mathbf{r}_s) \mathscr{L}_0^{1\cdots s} Y_s(\mathbf{r}_1 \cdots \mathbf{r}_s) \prod_{j=1}^{s} F_1^{\text{eq}}(v_j) \tag{67}$$

We thus proposed to replace in $\Lambda_{med}^{(s)}$ the exact expressions (65) involving the dynamics of the entire system by terms

$$W_s(\mathbf{r}_1 \cdots \mathbf{r}_s) \mathscr{L}_0^{1\cdots s} Y_s(\mathbf{r}_1 \cdots \mathbf{r}_s) \prod_{j=1}^{s} F_1(\mathbf{v}_j, t) \tag{68}$$

in which purely equilibrium spatial dependence has been retained. The non-equilibrium character of expression (68) is due uniquely to the deviation from equilibrium of distributions $F_1(\mathbf{v}_j, t)$ [compare with Eq. (67)]. Recently we have found that within the theory of the hard-sphere gas such an approximation can be given a clear microscopic interpretation. This problem, which seems to us of theoretical interest, will be the subject of a separate paper. Here we restrict ourselves to the analysis of the resulting kinetic equations. Let us first consider the case $s = 2$ for the hard-sphere system. From Eq. (62), using approximation (68) and the relation

$$\overline{T}(ij) S_{0,-t}^{ij} [W_2(r_{ij}) - 1] = 0 \tag{69}$$

(see Refs. 2 and 5) we get in the long-time regime the equation

$$\begin{aligned} \frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) &= \int dx_2\, \overline{T}(12) F_1(\mathbf{v}_1, t) F_1(\mathbf{v}_2, t) \\ &\quad + \int dx_2\, \overline{T}(12) S_{0,-t}^{12} \mathscr{L}_0^{12} Y_2(r_{12}) * F_1(\mathbf{v}_1, t) F_1(\mathbf{v}_2, t) \end{aligned} \tag{70}$$

The second term in the rhs of Eq. (70) can be written as

$$-\int dx_2 \frac{\partial}{\partial t} \{\overline{T}(12) S_{0,-t}^{12} [Y_2(r_{12}) - 1]\} * \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \tag{71}$$

It is important to notice that the expression

$$\bar{T}(12)S^{12}_{0,-t}[Y_2(r_{12}) - 1] \tag{72}$$

vanishes for times $t \gg \tau$, where τ is the average time that two colliding spheres need to separate beyond the range of the two-particle equilibrium correlations. In the long-time regime the variation of the velocity distribution over the time intervals of the order of τ is supposed to be negligible, so that we replace term (71) by

$$\begin{aligned} -\lim_{T\to\infty} \int dx_2 \left\{ \int_0^T d\tau \frac{\partial}{\partial\tau} \bar{T}(12)S^{12}_{0,-\tau}[Y_2(r_{12}) - 1] \right\} \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \\ = \int dx_2\, \bar{T}(12)[Y_2(r_{12}) - 1] \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \end{aligned} \tag{73}$$

But

$$\bar{T}(12)Y_2(r_{12}) = Y_2(\sigma)\bar{T}(12) \tag{74}$$

Hence, within the above approximation Eq. (70) takes the familiar form of the Enskog equation for homogeneous gases

$$\frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) = Y_2(\sigma) \int dx_2\, \bar{T}(12)F_1(\mathbf{v}_1, t)F_1(\mathbf{v}_2, t) \tag{75}$$

In I it has been shown that the Enskog equation is also well justified for smooth, strongly repulsive, finite-range potentials if the effect of the medium $\Lambda^{(2)}_{\text{med}}$ is estimated in accordance with Eq. (68).

5. THREE-PARTICLE COLLISION OPERATOR FOR A DENSE HOMOGENEOUS GAS

We now come to the main point of the present paper, which is the analysis of the kinetic equation (58) when $s = 3$. The theory will be developed first for the hard-sphere system, and the results for smooth potentials will be given at the end of the section. In accordance with our previous considerations, which led to Eq. (68), we replace the exact term $\bar{\Lambda}^{(3)}_{\text{med}}$ [Eq. (64)], representing the influence of the medium on ternary collisions, by

$$\begin{aligned} \sum_{b=1}^{2} \int dx_2 \int dx_3\, \bar{T}(12)S^{12}_{0,-t} * \bar{T}(b3)\{\bar{S}^{123}_{-t} W_3(123)\mathscr{L}^{123}_0 Y_3(123) \\ - S^{b3}_{0,-t} W_2(b3)\mathscr{L}^{b3}_0 Y_2(b3)\} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \end{aligned} \tag{76}$$

Here $W_3(123) \equiv W_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, $W_2(b3) \equiv W_2(r_{b3})$, and the same abbreviated notation has been used for the arguments of functions Y_3, Y_2 [see Eq. (66)].

Moreover, in the long-time regime we neglect the effect of the initial correlations represented in Eq. (64) by $\overline{\Lambda}^{(3)}_{\text{corr}}$. Then kinetic equation (58) takes the form

$$\begin{aligned}\frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) &= \int dx_2\, \overline{T}(12) \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) \\ &\quad + \sum_{b=1}^{2} \int dx_2 \int dx_3\, \overline{T}(12) S^{12}_{0,-t} * \overline{T}(b3) \\ &\quad \times \{\overline{S}^{123}_{-t}[\overline{T}^{123} + W_3(123)\mathscr{L}^{123}_0 Y_3(123)] \\ &\quad - S^{b3}_{0,-t}\mathscr{L}^{b3}_0 Y_2(b3)\} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \end{aligned} \tag{77}$$

where in writing the last term we have used relation (69) to omit the Boltzmann factor $W_2(b3)$ [compare with Eq. (76)].

The equation

$$\begin{aligned} W_3(123)\mathscr{L}^{123}_0 Y_3(123) &+ \overline{T}^{123} \\ &= \overline{\mathscr{L}}^{123}(W_3(123) Y_3(123) - 1) - Y_3(123)\overline{\mathscr{L}}^{123} W_3(123) + \mathscr{L}^{123}_0 \end{aligned} \tag{78}$$

together with the fact that $\mathscr{L}^{123}_0$ vanishes on the velocity distribution permit us to put the expression in the curly brackets in Eq. (77) in the form

$$\begin{aligned}&\frac{\partial}{\partial t}\{-\overline{S}^{123}_{-t}[W_3(123) Y_3(123) - 1] + S^{b3}_{0,-t}[Y_2(b3) - 1]\} \\ &\quad - \overline{S}^{123}_{-t} Y_3(123)\overline{\mathscr{L}}^{123} W_3(123)\end{aligned} \tag{79}$$

Here the first term is a time derivative, and according to the relation

$$A_t * \frac{\partial}{\partial t} B_t = \frac{\partial}{\partial t}(A_t * B_t) - A_t B_0 \tag{80}$$

the corresponding contribution to the rhs of Eq. (77) will contain the term

$$\begin{aligned}&\frac{\partial}{\partial t}\left\{\sum_{b=1}^{2} \int dx_2 \int dx_3\, \overline{T}(12) S^{12}_{0,-t} * \overline{T}(b3)[-\overline{S}^{123}_{-t}(W_3(123) Y_3(123) - 1)\right. \\ &\quad \left. + S^{b2}_{0,-t}(Y_2(b3) - 1)]\right\} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t)\end{aligned} \tag{81}$$

which can be neglected in the long-time regime on a similar basis as $\overline{\Lambda}^{(3)}_{\text{corr}}$ [in Eq. (81) the equilibrium correlations play an analogous role to the initial correlations in Eq. (64)]. Taking this into account and using the formula

$$\begin{aligned}&\sum_{b=1}^{2} \int dx_3 \int dx_2\, \overline{T}(12) S^{12}_{0,-t} * \overline{T}(b3)\overline{S}^{123}_{-t} \\ &\quad = \int dx_2 \int dx_3\, \overline{T}(12)(\overline{S}^{123}_{-t} - S^{12}_{0,-t})\end{aligned} \tag{82}$$

we deduce from Eq. (77) the kinetic equation

$$\frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) = \int dx_2\, \bar{T}(12) \prod_{j=1}^{2} F_1(\mathbf{v}_j, t)$$
$$+ \int dx_2 \int dx_3\, \bar{T}(12)\Big\{[-\bar{S}^{123}_{-t} + S^{12}_{0,-t}] Y_3(123)\bar{\mathscr{L}}^{123} W_3(123)$$
$$+ S^{12}_{0,-t} \sum_{b=1}^{2} \bar{T}(b3)[Y_3(123) W_3(123)$$
$$- Y_2(b3) W_2(b3)]\Big\} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{83}$$

We shall separate the Enskog collision term in order to put in evidence the structure of the collision operator in Eq. (83). To this end, we use the identity

$$\int d\mathbf{r}_3 \left[Y_3(123)\bar{\mathscr{L}}^{123} W_3(123) + \sum_{b=1}^{2} \bar{T}(b3) Y_3(123) W_3(123)\right]$$
$$= n^{-1} W_2(12)\mathscr{L}_0^{12} Y_2(12) + \int d\mathbf{r}_3\, Y_3(123) W_2(13) W_2(23)\bar{\mathscr{L}}^{12} W_2(12) \tag{84}$$

(for the proof see Appendix C), which permits us to write Eq. (83) in an equivalent form

$$\frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) = \int dx_2\, \bar{T}(12) \prod_{j=1}^{2} F_1(\mathbf{v}_j, t)$$
$$+ \int dx_2\, \bar{T}(12) S^{12}_{0,-t} W_2(12)\mathscr{L}_0^{12} Y_2(12) * \prod_{j=1}^{2} F_1(\mathbf{v}_j, t)$$
$$- \int dx_2 \int dx_3\, \bar{T}(12)\Big\{\bar{S}^{123}_{-t} Y_3(123)\bar{\mathscr{L}}^{123} W_3(123)$$
$$+ S^{12}_{0,-t}\Big[\sum_{b=1}^{2} \bar{T}(b3) Y_2(b3) W_2(b3)$$
$$- Y_3(123) W_2(13) W_2(23)\bar{\mathscr{L}}^{12} W_2(12)\Big]\Big\} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{85}$$

According to the results of the previous section, the first two terms in the rhs of Eq. (85) correspond to the Enskog collision term. Moreover, for the hard-sphere gas

$$\bar{T}(12) S^{12}_{0,-t} Y_3(123) W_2(13) W_2(23)\bar{\mathscr{L}}^{12} W_2(12) = 0 \tag{86}$$

[see Eq. (60)], and combining this with Eqs. (69) and (74), we put the kinetic equation in the final form

$$\frac{\partial}{\partial t}F_1(\mathbf{v}_1, t) = Y_2(\sigma)\int dx_2\,\bar{T}(12)\prod_{j=1}^{2}F_1(\mathbf{v}_j, t)$$
$$-\int dx_2\int dx_3\,\bar{T}(12)\{\bar{S}_{-t}^{123}Y_3(123)\mathscr{L}^{123}W_3(123)$$
$$+\,Y_2(\sigma)[\bar{T}(13)+\bar{T}(23)]\} * \prod_{j=1}^{3}F_1(\mathbf{v}_j, t) \tag{87}$$

Equation (87) determines the evolution of the velocity distribution of a dense, hard-sphere gas. Its rhs corresponds to the action of the three-particle collision operator including the effect of the medium (functions Y_2, Y_3) on $F_1(\mathbf{v}_1, t)$. With the use of operators

$$T(ij) = \bar{T}(ij) + W_2(ij)\mathscr{L}_0^{ij} - \mathscr{L}_0^{ij}W_2(ij) \tag{88}$$

(for their interpretation see Ref. 2) we can rewrite Eq. (87), obtaining

$$\frac{\partial}{\partial t}F_1(\mathbf{v}_1, t) = Y_2(\sigma)\int dx_2\,\bar{T}(12)\prod_{j=1}^{2}F_1(\mathbf{v}_j, t)$$
$$-\int dx_2\int dx_3\,\bar{T}(12)\{-\bar{S}_{-t}^{123}Y_3(123)W_3(123)[T(12)+T(13)$$
$$+\,T(23)] + Y_2(\sigma)[T(13)+T(23)]\} * \prod_{j=1}^{3}F_1(\mathbf{v}_j, t) \tag{89}$$

which gives the collision operator a particularly transparent structure.

Let us compare this result with the Choh–Uhlenbeck equation[7] (see also Ref. 8, Chapter 13) by considering the case of a moderately dense system. We thus develop the rhs of Eq. (87) in powers of number density n, and retain only terms proportional to n^2 and n^3. Since

$$Y_2(12) = 1 + n\int d\mathbf{r}_3\,[W_2(13)-1][W_2(23)-1] + O(n^2) \tag{90}$$

the term of order n^2 reads

$$\int dx_2\,\bar{T}(12)\prod_{j=1}^{2}F_1(\mathbf{v}_j, t) \tag{91}$$

and thus corresponds to the Enskog–Boltzmann theory. Using expansion (90), we find that the next term $\sim n^3$ has the form

$$\int dx_2\int dx_3\,\bar{T}(12)\Big\{[W_2(13)-1][W_2(23)-1]\prod_{j=1}^{3}F_1(\mathbf{v}_j, t)$$
$$-\,[\bar{S}_{-t}^{123}\mathscr{L}^{123}W_3(123)+\bar{T}(13)+\bar{T}(23)] * \prod_{j=1}^{3}F_1(\mathbf{v}_j, t)\Big\} \tag{92}$$

Equations (60), (61), and (69) permit us to rewrite expression (92) in the form

$$\int dx_2 \int dx_3\, \bar{T}(12)[W_2(13) - 1][W_2(23) - 1] \prod_{j=1}^{3} F_1(\mathbf{v}_j, t)$$
$$+ \int dx_2 \int dx_3 \left\{ \frac{\partial}{\partial t} \bar{T}(12)[\bar{S}_{-t}^{123} W_3(123) - \bar{S}_{-t}^{12}[\bar{S}_{-t}^{13} W_2(13) + \bar{S}_{-t}^{23} W_2(23)]] \right\}$$
$$* \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{93}$$

In the long-time regime we replace the time convolution by

$$\lim_{T\to\infty} \int dx_2 \int dx_3 \int_0^T d\tau \frac{\partial}{\partial \tau} \bar{T}(12)[\bar{S}_{-\tau}^{123} W_3(123) - \bar{S}_{-\tau}^{12}[\bar{S}_{-\tau}^{13} W_2(13)$$
$$+ \bar{S}_{-\tau}^{23} W_2(23)]] \prod_{j=1}^{3} F_1(\mathbf{v}_j, t)$$
$$= \int dx_2 \int dx_3 \lim_{T\to\infty} \bar{T}(12)[\bar{S}_{-T}^{123} W_3(123) - \bar{S}_{-T}^{12}[\bar{S}_{-T}^{13} W_2(13) + \bar{S}_{-T}^{23} W_2(23)]$$
$$- [W_3(123) - W_2(13) - W_2(23)]] \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{94}$$

This procedure is analogous to that leading from Eq. (71) to Eq. (73), but requires a more subtle analysis. As we shall see in a moment, it leads to the Choh–Uhlenbeck theory and thus must correspond to the Bogoliubov functional hypothesis assuming F_2 to be a time-independent functional of F_1. Using Eq. (94) we write term (93) in the form

$$\lim_{T\to\infty} \int dx_2 \int dx_3\, \bar{T}(12)\{\bar{S}_{-T}^{123} W_3(123) - \bar{S}_{-T}^{12} W_2(12) \bar{S}_{-T}^{13} W_2(13)$$
$$- \bar{S}_{-T}^{12} W_2(12) \bar{S}_{-T}^{23} W_2(23) + 1\} \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{95}$$

where again Eq. (69) has been used. Defining the asymptotic operators

$$\bar{\sigma}_{-\infty}^{1\cdots a} = \lim_{T\to\infty} S_{-T}^{1\cdots a} W_a(1 \cdots a) S_{0,T}^{1\cdots a} \tag{96}$$

we thus deduce from Eq. (87) the following kinetic equation for a moderately dense, hard-sphere gas:

$$\frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) = \int dx_2\, \bar{T}(12) \prod_{j=1}^{2} F_1(\mathbf{v}_j, t)$$
$$+ \int dx_2 \int dx_3\, \bar{T}(12)\{\bar{\sigma}_{-\infty}^{123} - \bar{\sigma}_{-\infty}^{12} \bar{\sigma}_{-\infty}^{13} - \bar{\sigma}_{-\infty}^{12} \bar{\sigma}_{-\infty}^{23} + \bar{\sigma}_{-\infty}^{12}\}$$
$$\times \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \tag{97}$$

It coincides with the Choh–Uhlenbeck equation[2] (Ref. 8, Chapter 13).

Our basic result, which is Eq. (87) [or (89)], can be looked upon as the generalization of the Choh–Uhlenbeck theory to the case of dense systems much in the same spirit as the Enskog equation generalizes the Boltzmann theory. Moreover, Eq. (87) still contains the time convolution, since in its derivation we have not used the Bogoliubov functional hypothesis underlying the Choh–Uhlenbeck equation.

Before ending this section let us finally remark that in a completely analogous way the theory can be developed for smooth potentials. Without entering into details, we give here only the final result, i.e., the form of the kinetic equation that is the analog of Eq. (87) for hard spheres. It reads

$$\begin{aligned}\frac{\partial}{\partial t} F_1(\mathbf{v}_1, t) = \int dx_2\, (-\delta\mathscr{L}^{12}) S^{12}_{-t}\{(-\delta\mathscr{L}^{12}) + W_2(12)\mathscr{L}^{12}_0 Y_2(12)\} \\ * \prod_{j=1}^{2} F_1(\mathbf{v}_j, t) + \int dx_2 \int dx_3 (-\delta\mathscr{L}^{12}) \Big\{ -S^{123}_{-t} Y_3(123)\mathscr{L}^{123} W_3(123) \\ + S^{12}_{-t} Y_3(123) W_2(13) W_2(23) \mathscr{L}^{12} W_2(12) \\ + S^{12}_{-t} * \sum_{b=1}^{2} (-\delta\mathscr{L}^{b3}) S^{b3}_{-t} Y_2(b3) \mathscr{L}^{b3} W_2(b3) \Big\} * \prod_{j=1}^{3} F_1(\mathbf{v}_j, t) \quad (98)\end{aligned}$$

In I we have shown that the first term in the rhs of Eq. (98) corresponds to the Enskog collision term. In the low-density limit, by retaining terms of order n^2 and n^3 we get from Eq. (98) the Choh–Uhlenbeck equation, if additionally the time convolutions are treated as in passing from Eq. (93) to Eq. (94).

6. DISCUSSION

We have analyzed in the thermodynamic limit the evolution of the distribution $F_1(\mathbf{v}_1, t)$, showing how to distinguish in the complete expression determining its rate of change $[=(\partial/\partial t)F_1(\mathbf{v}_1, t)]$ three contributions of different nature: $\Lambda^{(s)}_{\mathrm{corr}}$, $\Lambda^{(s)}_{\mathrm{coll}}$, and $\Lambda^{(s)}_{\mathrm{med}}$ [Eq. (58)]. Limiting the discussion to the cases of $s = 2$ and $s = 3$ and using the results obtained by Dorfman and Cohen[6] (see also Ref. 10) we could drop in the long-time regime term $\Lambda^{(s)}_{\mathrm{corr}}$, representing the effect of the initial s-particle correlations. We then interpreted the term $\Lambda^{(s)}_{\mathrm{coll}}$ as describing the rate of change of $F_1(\mathbf{v}_1, t)$ resulting from collisions within s-particle clusters, without taking into account higher order collisions, coupling them to the remaining particles. The third contribution $\Lambda^{(s)}_{\mathrm{med}}$ should thus introduce the necessary correction to $\Lambda^{(s)}_{\mathrm{coll}}$ due to the

[2] We use here the terminology of Ferziger and Kaper.[8] In fact, Eq. (97) was also obtained by Green.[12]

influence of the gaseous medium on the dynamics of s-particle clusters. We approximated this term in accordance with the ideas developed in I by assuming the equilibrium structure and spatial dependence in the relevant expressions [Eqs. (65)–(68)]. In this way we arrived at kinetic equations (70), (77) with the collision operators depending uniquely on s-particle dynamics, $s = 2$, 3, the effect of more complicated dynamical events showing only through the presence of equilibrium distributions Y_2, Y_3. For $s = 2$, in the case of a hard-sphere gas, we obtained the Enskog equation. The analogous equation for a smooth, repulsive interaction has been derived in I. The analysis of the case $s = 3$ has led us to a new kinetic equation both for hard spheres [Eq. (87)] and for a smooth potential [Eq. (98)]. In the low-density, long-time limit it corresponds to the Choh–Uhlenbeck theory [Eq. (97)], and can be thus looked upon as its generalization for a dense system.

Because of the explicit separation of the Enskog collision term in Eq. (87), its form is well adapted for the study of the deviations of various quantities like the self-diffusion coefficient or kinetic parts of the transport coefficients from their values resulting from the Enskog theory. In fact such a study has been already performed at the level of three-particle dynamics by Sengers *et al.*[5] (for details of the calculations see Ref. 11), and it seems to us that the use of Eq. (87) [or (89)] to extend the analysis to dense systems would be worth trying.

APPENDIX A

In order to prove Eq. (24) we notice that its rhs can be written as

$$R = \int d\mathbf{v}^{N-1}\left\{\sum_{a=2}^{s}\frac{N!}{(N-a)!}\mathscr{D}_{-t}^{1\cdots a} + \frac{N!}{(N-s)!}\mathscr{D}_{-t}^{1\cdots s} * [\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots N}]\mathscr{P}_{-t}^{1\cdots N}\right\} \tag{A.1}$$

Indeed, let us insert into Eq. (A.1) the relation

$$\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots N} = \sum_{j=s+1}^{N}(\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots sj}) - \sum_{i=s+1}^{N}\sum_{j=i+1}^{N}\delta\mathscr{L}^{ij} \tag{A.2}$$

Then the second term containing $\delta\mathscr{L}^{ij}$, $s < j < i \leqslant N$, does not contribute because of Eq. (8), whereas the first can be replaced by $(N - s)(\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots s+1})$, which follows from the symmetry in variables $x_{s+1} \cdots x_N$. (All the operators are considered in the space of functions symmetric in phases $x_1 \cdots x_N$.)

From definition (25) we have

$$\mathscr{D}_{-t}^{1\cdots s} = \mathscr{D}_{-t}^{1\cdots s-1} * (\mathscr{L}^{1\cdots s-1} - \mathscr{L}^{1\cdots s})\mathscr{P}_{-t}^{1\cdots s} \tag{A.3}$$

Hence the relation

$$\mathscr{P}^{1\cdots N}_{-t} = \mathscr{P}^{1\cdots s}_{-t} + \mathscr{P}^{1\cdots s}_{-t} * (\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots N})\mathscr{P}^{1\cdots N}_{-t} \tag{A.4}$$

[see identity (23)] implies that

$$\begin{aligned} &\mathscr{D}^{1\cdots s}_{-t} + \mathscr{D}^{1\cdots s}_{-t} * (\mathscr{L}^{1\cdots s} - \mathscr{L}^{1\cdots N})\mathscr{P}^{1\cdots N}_{-t} \\ &\quad = \mathscr{D}^{1\cdots s-1}_{-t} * (\mathscr{L}^{1\cdots s-1} - \mathscr{L}^{1\cdots s})\mathscr{P}^{1\cdots N}_{-t} \end{aligned} \tag{A.5}$$

Inserting this into Eq. (A.1), we find the rhs of Eq. (24) with s replaced by $s - 1$. It is thus sufficient to prove the validity of Eq. (24) for $s = 2$. In this case Eq. (A.5) takes the form

$$\mathscr{D}^{12}_{-t} + \mathscr{D}^{12}_{-t} * (\mathscr{L}^{12} - \mathscr{L}^{1\cdots N})\mathscr{P}^{1\cdots N}_{-t} = P(\mathscr{L}^{1} - \mathscr{L}^{12})\mathscr{P}^{1\cdots N}_{-t} \tag{A.6}$$

and from Eq. (A.1) ($s = 2$) we get

$$\begin{aligned} R &= N(N-1)\int d\mathbf{v}^{N-1}\, P(\mathscr{L}^{1} - \mathscr{L}^{12})\mathscr{P}^{1\cdots N}_{-t} \\ &= N\int d\mathbf{v}^{N-1}\, P(-\mathscr{L}^{1\cdots N})\mathscr{P}^{1\cdots N}_{-t} \end{aligned} \tag{A.7}$$

The last equality follows from the relation

$$P\mathscr{L}^{1} = P\mathscr{L}_0^{1} = 0 \tag{A.8}$$

and the symmetry in variables $x_2,\ldots, x_N$. This ends the proof of Eq. (24).

APPENDIX B

In order to analyze the structure of operator

$$\lim_{\infty} \Omega^{a-1}\int d\mathbf{v}_2 \cdots \int d\mathbf{v}_a\, \mathscr{D}^{1\cdots a}_{-t} \tag{B.1}$$

[Section 3, Eq. (49)] we shall make use of the binary operators

$$C^{j,lm}_{-t} = (-\delta\mathscr{L}^{lm})\exp\{-[\mathscr{L}_0^{1\cdots j} + \delta\mathscr{L}^{lm}]t\}, \qquad 1 \leqslant l < m \leqslant j \tag{B.2}$$

They are related to the j-particle streaming operator $S^{1\cdots j}_{-t}$ by the equation

$$(-\delta\mathscr{L}^{lm})S^{1\cdots j}_{-t} = C^{j,lm}_{-t} + C^{j,lm}_{-t} * [\delta\mathscr{L}^{lm} - \delta\mathscr{L}^{1\cdots j}]S^{1\cdots j}_{-t} \tag{B.3}$$

[see identity (23)]. The iteration of Eq. (B.3) leads to the expansion

$$\begin{aligned} (-\delta\mathscr{L}^{lm})S^{1\cdots j}_{-t} &= C^{j,lm}_{-t} + \sum_{(np)\neq(lm)}^{j} C^{j,lm}_{-t} * C^{j,np}_{-t} \\ &\quad + \sum_{(np)\neq(lm)}^{j}\ \sum_{(rs)\neq(np)}^{j} C^{j,lm}_{-t} * C^{j,np}_{-t} * C^{j,rs}_{-t} + \cdots \end{aligned} \tag{B.4}$$

well known in the binary collision expansion theory.[9] An analogous procedure can be applied to the hard-sphere gas.[2] In this case, due to Eq. (61), the binary operators have the form

$$\bar{C}^{j,lm}_{-t} = \bar{T}(lm)S^{1\cdots j}_{0,-t} \tag{B.5}$$

Taking additionally Eq. (60) into account, we can write the analog of Eq. (B.4) for hard spheres as

$$\begin{aligned}\bar{T}(lm)\bar{S}^{1\cdots j}_{-t} &= \bar{C}^{j,lm}_{-t} + \sum_{(np)}^{j} \bar{C}^{j,lm}_{-t} * \bar{C}^{j,np}_{-t} \\ &\quad + \sum_{(np)}^{j} \sum_{(rs)}^{j} \bar{C}^{j,lm}_{-t} * \bar{C}^{j,np}_{-t} * \bar{C}^{j,rs}_{-t} + \cdots \end{aligned} \tag{B.6}$$

without any restriction on the summations over pairs (np), (rs),.... Applying expansions (B.4) with $j = 2, 3,..., a$ to the rhs of Eq. (49), we get the representation of operator (B.1) as the sum of terms of the form

$$\begin{aligned}&\lim_{\infty} \int dx_2\, C^{2,12}_{-t} * Q_2 \int dx_3\, C^{3,b3}_{-t} * C^{3,cd}_{-t} * \cdots \\ &\cdots Q_{j-1} \int dx_j\, C^{j,ij}_{-t} * C^{j,kl}_{-t} * \cdots * Q_{a-1} \int dx_a\, C^{a,ra}_{-t} * \cdots * C^{a,uw}_{-t} Q_a \end{aligned} \tag{B.7}$$

Let us consider the operator at the right side of projector Q_{j-1}. It describes the contribution from a sequence of collisions between pairs of particles

$$(ij), (kl),..., (ra),..., (uw) \tag{B.8}$$

taking place during a finite time interval, not exceeding t [see Eq. (22)]. The binary operators $C^{j,lm}_{-t}$ ($\bar{C}^{j,lm}_{-t}$) vanish when the distance $|\mathbf{r}_l - \mathbf{r}_m|$ becomes greater than the range of the potential (hard-sphere diameter). Hence, the sequence of convolutions in Eq. (B.7) gives a nonzero contribution only when, during the time interval $\leqslant t$, there is a consecutive sequence of collision configurations between pairs (B.8). Keeping this in mind, let us analyze the group of particles appearing in sequence (B.8) in a more detailed way. Any two of them, say d and p, will be said to belong to the same dynamical cluster if and only if among pairs (B.8) there can be found a subset (di_1), $(i_1 i_2)$,..., $(i_n p)$, corresponding to a chain of collisions between particles d and i_1, i_1 and i_2,..., and finally between i_n and p. It is clear that because of the finite range of the interaction and finite time interval such a chain of collision configurations "joining" particles d and p becomes impossible (for finite particle velocities) when their distance $|\mathbf{r}_d - \mathbf{r}_p|$ is sufficiently large. Thus, if:

(i) There are two or more particles from the set $\{1,..., j - 1\}$ in sequence (B.8) belonging to the same dynamical cluster, then, when their distance is sufficiently increased, the operator

$$\int dx_j\, C_{-t}^{j,ij} * C_{-t}^{j,kl} * \cdots * \int dx_a\, C_{-t}^{a,ra} * \cdots * C_{-t}^{a,uw} \tag{B.9}$$

equals zero. In this situation the action of projector

$$P_{j-1} = \Omega^{-j+1} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_{j-1} \tag{B.10}$$

on term (B.9) gives zero in the thermodynamic limit since at least one of the volume integrations is restricted to a bounded region. We conclude that in case (i) projector Q_{j-1} applied to (B.9) can be replaced by identity I.

Let us notice at this point that each of the dynamical clusters must contain at least one of the particles $1, 2, \ldots, j-1$. This follows from the observation that particles $j, \ldots, a$ in sequence (B.8) interact with particles $i, \ldots, r$, respectively, where $i < j, \ldots, r < a$. Hence, for any one of them there is always a chain of collisions ending in the set $\{1, 2, \ldots, j-1\}$. We thus see that apart from case (i) there remains only one possibility, when:

(ii) Each dynamical cluster in sequence (B.8) contains exactly one particle from the set $\{1, 2, \ldots, j-1\}$.

In this situation operator (B.9) does not depend on relative positions of particles $1, 2, \ldots, j-1$. An immediate consequence is that if, moreover:

The function to which operator (B.9) is applied does not depend on distances between particles from different clusters,

then the action of Q_{j-1} gives zero. Indeed, because of the translational invariance of the integrand the result of the integration over phases $x_j, \ldots, x_a$ gives in this case a function independent of positions $\mathbf{r}_1, \ldots, \mathbf{r}_{j-1}$, and projector Q_{j-1} on such a function vanishes. This case, characterized by a complete lack of spatial correlations between particles $1, \ldots, j-1$, is thus eliminated.

Let us illustrate it on an elementary example corresponding to $j = 3$, $a = 5$. The sequence

$$(13), (34), (25) \tag{B.11}$$

decomposes particles $\{1, 2, \ldots, 5\}$ into two dynamical clusters $\{1, 3, 4\}$ and $\{2, 5\}$, each of which contains one particle from the set $\{1, 2\}$. In this case operator (B.9) takes the form

$$\int dx_3\, C_{-t}^{3,13} * \int dx_4\, C_{-t}^{4,34} * \int dx_5\, C_{-t}^{5,25} \tag{B.12}$$

Suppose that it is applied to the function

$$g_2(x_1, x_4, t)g_2(x_2, x_5, t)\prod_{j=1}^{5} f_1(\mathbf{v}_j, t) \tag{B.13}$$

occurring in the cluster decomposition of $f_5(x_1 \cdots x_5, t)$ [see Eq. (37)]. For a homogeneous system, function (B.13) depends on spatial variables $(\mathbf{r}_1 - \mathbf{r}_4)$ and $(\mathbf{r}_2 - \mathbf{r}_5)$. It does not, however, depend on relative positions of particles belonging to different clusters. It follows that

$$Q_2 \int dx_3\, C_{-t}^{3;13} * \int dx_4\, C_{-t}^{4;34} * \int dx_5\, C_{-t}^{5;25} g_2(x_1, x_4, t)g_2(x_2, x_5, t)$$
$$\prod_{j=1}^{5} f_1(\mathbf{v}_j, t) = 0 \tag{B.14}$$

because the function to which projector Q_2 is applied does not depend in this case on $(\mathbf{r}_1 - \mathbf{r}_2)$.

Consider finally the role of Q_{j-1} when:

> Operator (B.9) acts on a function that goes to zero when the distance between at least one pair of particles from different clusters tends to infinity.

In view of our previous analysis, if the distance between two particles from different clusters increases indefinitely, the same must happen for any other such pair, otherwise operator (B.9) vanishes. But each cluster contains a particle from the set $\{1,..., j - 1\}$. Hence, in the case under consideration projector Q_{j-1} is applied to a function that tends to zero when the distance between a pair of particles (at least one) from $\{1,..., j - 1\}$ tends to infinity. Then, for the same reason as in case (i), we can replace Q_{j-1} by identity I.

An example of this situation is obtained by applying operator (B.12) to the function

$$g_2(x_1, x_5, t)\prod_{j=1}^{5} f_1(\mathbf{v}_j, t) \tag{B.15}$$

which also occurs in the cluster decomposition of $f_5(x_1 \cdots x_5, t)$. Function (B.15) vanishes when the distance between particles 1 and 5 tends to infinity. Since 1 and 5 belong to different clusters, we get

$$\lim_{\infty} P_2 \int dx_3\, C_{-t}^{3;13} * \int dx_4\, C_{-t}^{4;34} * \int dx_5\, C_{-t}^{5;25} g_2(x_1, x_5, t)\prod_{j=1}^{5} f_1(\mathbf{v}_j, t) = 0 \tag{B.16}$$

because projector P_2 [see Eq. (B.10)] acts in this case on a function going to zero when $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$. Since $Q_2 = I - P_2$, we can replace Q_2 by identity I.

The above rules when applied systematically to all projectors Q_{a-1}, $Q_{a-2},\dots, Q_3, Q_2$ permit us to calculate the action of terms (B.7), and consequently of the complete operator (B.1), on functions (43). Before ending this appendix let us consider the case of $a = 3$. According to Eq. (49),

$$\begin{aligned}\lim_{\infty} \Omega^2 \int d\mathbf{v}_2 \int d\mathbf{v}_3\, \mathscr{D}^{123}_{-t} \\ = \lim_{\infty} \int dx_2\, C^{2,12}_{-t} * Q_2 \int dx_3\, (-\delta\mathscr{L}^{13} - \delta\mathscr{L}^{23}) S^{123}_{-t} Q_3 \qquad \text{(B.17)}\end{aligned}$$

In the binary collision expansions

$$\begin{aligned}(-\delta\mathscr{L}^{13}) S^{123}_{-t} &= C^{3,13}_{-t} + C^{3,13}_{-t} * (C^{3,12}_{-t} + C^{3,23}_{-t}) + \cdots \\ (-\delta\mathscr{L}^{23}) S^{123}_{-t} &= C^{3,23}_{-t} + C^{3,23}_{-t} * (C^{3,12}_{-t} + C^{3,13}) + \cdots\end{aligned}$$

only the first terms $C^{3,13}_{-t}$ and $C^{3,23}_{-t}$ satisfy condition (ii). We are thus allowed to write

$$\begin{aligned}\lim_{\infty} \Omega^2 \int d\mathbf{v}_2 \int d\mathbf{v}_3\, \mathscr{D}^{123}_{-t} \\ = \lim_{\infty} \int dx_2\, C^{2,12}_{-t} * \int dx_3\, (-\delta\mathscr{L}^{13} - \delta\mathscr{L}^{23}) S^{123}_{-t} Q_3 \\ - \lim_{\infty} \int dx_2\, C^{2,12}_{-t} * P_2 \int dx_3\, (C^{3,13}_{-t} + C^{3,23}_{-t}) Q_3 \qquad \text{(B.18)}\end{aligned}$$

Equation (B.12) is equivalent to Eq. (51) of Section 3 since

$$P_2 \int dx_3\, C^{3,13}_{-t} Q_3 = \int dx_3\, (-\delta\mathscr{L}^{13}) S^{13}_{-t} \Omega^{-1} \int d\mathbf{r}_2\, Q_3$$

and an analogous relation holds after interchanging indices 1 and 2.

APPENDIX C

Here we prove Eq. (84), which reduces to

$$W_2(12)\mathscr{L}^{12}_0 Y_2(12) = n \int d\mathbf{r}_3\, Y_3(123) W_2(12) \mathscr{L}^{12}_0 W_2(13) W_2(23) \qquad \text{(C.1)}$$

when the use of the relation

$$\overline{\mathscr{L}}^{123} = \mathscr{L}^{123}_0 - \overline{T}(12) - \overline{T}(13) - \overline{T}(23) \qquad \text{(C.2)}$$

is made. At equilibrium and for a smooth potential the hierarchy equation (33) with $s = 2$ in the thermodynamic limit yields

$$\mathscr{L}^{12} F^{\mathrm{eq}}_2(x_1, x_2) = \int dx_3\, (\mathscr{L}^{12} - \mathscr{L}^{123}) F^{\mathrm{eq}}_3(x_1, x_2, x_3) \qquad \text{(C.3)}$$

Using Eqs. (66) and (67), we get from this

$$W_2(12)\mathscr{L}_0^{12} Y_2(12) = n \int d\mathbf{r}_3 \, (W_2(12)\mathscr{L}_0^{12} W_2(13) W_2(23) Y_3(123) - W_3(123)\mathscr{L}_0^{123} Y_3(123)) \tag{C.4}$$

But

$$\int d\mathbf{r}_3 \, W_3(123)\mathscr{L}_0^{3} Y_3(123) = 0 \tag{C.5}$$

and

$$W_3(123) = W_2(12) W_2(13) W_2(23) \tag{C.6}$$

Hence, the rhs of Eq. (C.4) is equal to the rhs of Eq. (C.1). We have thus proved Eq. (C.1) for smooth potentials. Its validity for the hard-sphere interaction follows from the possibility of approaching the hard-core potential by a sequence of smooth potentials. A direct proof of Eq. (84) for a hard-sphere gas is also possible.

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