Journal of Statistical Physics, Vol. 46, Nos. 5/6, 1987

Symmetric Linear Collision Operators in Kinetic Theory

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Received December 2, 1986

We consider a class of equilibrium time correlation functions, in fluids, between local physical quantities. We investigate whether the symmetry these correlation functions display with respect to these quantities on the N-particle level also exists on the one-particle (kinetic) level. In this context we derive a new symmetric kinetic operator for a dense, hard sphere fluid.

KEY WORDS: Time correlation functions; kinetic theory; symmetric collision operator; hard spheres; Boltzmann equation; Enskog equation, decay.

1. INTRODUCTION

Mark Kac's work in kinetic theory was in the traditional mold of Boltzmann, Ehrenfest, and Uhlenbeck, where the dilute gas is described by a one-particle distribution function. This distribution function $f(\mathbf{r}, \mathbf{v}, t)$ is a generalization of Maxwell's equilibrium velocity distribution function and is defined as the average number density of particles with a certain velocity $\mathbf{v}$ at a certain position $\mathbf{r}$ at time t in the gas. The time evolution of this distribution function is, for a dilute gas, given by the Boltzmann equation. The basic problem that fascinated Kac was the nature of the probabilistic ansatz that is made in the collision term of the Boltzmann equation[1] and which is the origin of the apparent paradoxes between kinetic theory and dynamics. This is the assumption of molecular chaos, i.e., the independence of the velocities of two particles that are going to collide. This basic assumption leads immediately to the Stoszzahl Ansatz for the average num-

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ber of (binary) collisions in a dilute gas and to the collision term in the Boltzmann equation itself. While the Ehrenfests had tried to elucidate the probabilistic nature of this ansatz[2,3] by divising two very simple—and in some way related—models: the urn (or dog-flea) model[2-4] and the wind-tree model,[2,3] Kac tried to go further and to actually derive the ansatz as a limiting property of a very large system that was initially chaotic, by proving what he called propagation of chaos.[1,5] In addition, his exceptional aptitude in devising as well as solving simple mathematical models led him not only to a solution of Ehrenfest's urn model,[6] but also to create other models that all illustrated various aspects of the Boltzmann equation.[7-9]

Interestingly, although a rather simple kinetic theory of dense gases due to Enskog was available since 1921[10,11]—a theory based on a generalization of the Boltzmann equation—no simple model exists, as far as we know, that incorporates the new (dense gas) features of this theory. Although the Enskog theory is only applicable to hard spheres, when instantaneous binary collisions occur, and is only an approximate theory, it does contain a number of features that are obviously present in dense as opposed to dilute gases. In particular, the transfer of momentum and energy between two particles at collision—the so-called collisional transfer—as well as the presence of multiple-particle collisions are important physical processes in dense gases not represented in the Boltzmann equation.

A paper containing a simple Ehrenfest–Kac-like model that incorporates some such dense gas features thus elucidating the Enskog rather than the Boltzmann equation would have been a very appropriate contribution to a volume honoring Mark Kac. In the absence of such a model, however, we present the solution to a problem that is related to dense, hard sphere gases and that might facilitate the construction of simple dense gas models. This problem is related to the fact that all collision operators used so far in the kinetic theory for $f(\mathbf{r}, \mathbf{v}, t)$ of dense, hard sphere systems, including the Enskog theory, have been asymmetric, in contradiction to the Boltzmann collision operator for a dilute gas, which is a symmetric operator.

The introduction of a symmetric operator is not done here in the context of distribution functions, but rather in that of time correslation functions, introduced by Onsager, Green, and Kubo (see Ref. 12 for a survey). These functions have come to the foreground as a description of the macroscopic properties of fluids after Kac's work in kinetic theory.

2. STATEMENT OF THE PROBLEM

In this paper, we restrict ourselves to correlation functions of local physical quantities in a fluid in thermal equilibrium, of the general type[12,13]

$$G_{ab}(\mathbf{r}, \mathbf{r}'; t) = \left\langle \sum_{i=1}^{N} a(\mathbf{v}_i)\, \delta(\mathbf{r} - \mathbf{r}_i) \sum_{j=1}^{N} b(\mathbf{v}_j(t))\, \delta(\mathbf{r}' - \mathbf{r}_j(t)) \right\rangle$$
$$= \left\langle \sum_{i=1}^{N} a(\mathbf{v}_i)\, \delta(\mathbf{r} - \mathbf{r}_i)\, e^{tL} \sum_{j=1}^{N} b(\mathbf{v}_j)\, \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle \tag{2.1}$$

where the brackets denote a canonical equilibrium ensemble average at temperature T and number density $n = N/V$, with N the number of particles and V the volume of the fluid, $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$ are the position and velocity, respectively, of particle i at time t with $\mathbf{r}_i(0) = \mathbf{r}_i$, $\mathbf{v}_i(0) = \mathbf{v}_i$, and L is the Liouville operator of the system. $a(\mathbf{v})$ and $b(\mathbf{v})$ are functions of the velocity $\mathbf{v}$ and can, in principle, be part of a complete set of functions in $\mathbf{v}$-space, so that G_{ab} can be considered an element of an infinite matrix.

Apart from obvious symmetry properties with respect to space, velocity, and time reversal, we are particularly interested in the symmetry with respect to a and b, namely

$$G_{ab}(\mathbf{r}, \mathbf{r}'; t) = G_{ba}(-\mathbf{r}, -\mathbf{r}'; t) \tag{2.2}$$

Or, in terms of the Fourier transforms with respect to $\mathbf{r} - \mathbf{r}'$, i.e.,[13]

$$F_{ab}(\mathbf{k}, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} [\exp(i\mathbf{k} \cdot \mathbf{r}_i)]\, a(\mathbf{v}_i) [\exp(tL)] \right.$$
$$\left. \times \sum_{j=1}^{N} [\exp(-i\mathbf{k} \cdot \mathbf{r}_j)]\, b(\mathbf{v}_j) \right\rangle \tag{2.3}$$

the symmetry

$$F_{ab}(\mathbf{k}, t) = F_{ba}(\mathbf{k}, t) \tag{2.4}$$

We confine ourselves here to the case $\mathbf{k} \neq 0$, when Eq. (2.3) not only gives the time correlation functions for the quantities $\sum_{i=1}^{N} [\exp(i\mathbf{k} \cdot \mathbf{r}_i)]\, a(\mathbf{v}_i)$ and $\sum_{j=1}^{N} [\exp(-i\mathbf{k} \cdot \mathbf{r}_j)]\, b(\mathbf{v}_j)$, but also for their fluctuations around equilibrium, since the equilibrium averages of these quantities vanish for $\mathbf{k} \neq 0$. Equation (2.4) implies that the value of the fluctuation in "b" at time t, given that the fluctuation in "a" had a given value at $t = 0$, is on the average the same as the value of "a" at time t, given that "b" had a given value at $t=0$. For the special case that $a(\mathbf{v})=b(\mathbf{v})=1$ one obtains the density–density correlation function $F_{11}(\mathbf{k}, t)=F(\mathbf{k}, t)$, which is experimentally accessible by light and neutron scattering.[13]

Although $F_{ab}(\mathbf{k}, t)$ for $a, b \neq 1$ have not been determined experimentally by light or neutron scattering, they have been determined by computer simulations of hard sphere[14] or Lennard–Jones systems[15] for a and b related to locally conserved quantities (other than $a=b=1$) or to local currents.[16–18]

The basic question we want to address in this paper is whether the basic a, b symmetry on the N-particle level, as expressed in Eq. (2.4), can be maintained on the one-particle level, which is often used to evaluate the correlation functions $F_{ab}(\mathbf{k}, t)$ theoretically, in order to make a connection between the macroscopic properties of the fluid, as incorporated in F_{ab}, and the microscopic properties, as incorporated in the kinetic theories (see Refs. 19 for surveys) used to evaluate F_{ab}. We know the answer to this question only for a few cases. First, for a dilute gas, where only binary collisions between particles have to be taken into account, one can replace the N-particle expression (2.3) for $F_{ab}(\mathbf{k}, t)$ by the kinetic or one-particle expression

$$F_{ab}^{B}(\mathbf{k}, t)=\langle a(\mathbf{v}_1)\{\exp[L_B(\mathbf{k}, \mathbf{v}_1)t]\}\, b(\mathbf{v}_1)\rangle_1 \tag{2.5}$$

where $L_B(\mathbf{k}, \mathbf{v}_1)$ is the linear inhomogeneous Boltzmann operator defined by

$$L_B(\mathbf{k}, \mathbf{v}_1)=-i\mathbf{k}\cdot\mathbf{v}_1+n\Lambda_B(\mathbf{v}_1) \tag{2.6}$$

with $\Lambda_B(\mathbf{v}_1)$ the Boltzmann binary collision operator acting on functions of $\mathbf{v}_1$ only[19] [cf. Eq. (4.8) for the special case of hard spheres]. In (2.5), $\langle f(\mathbf{v}_1)\rangle_1=\int d\mathbf{v}_1\,\phi(v_1)\, f(\mathbf{v}_1)$ denotes the average of an arbitrary function $f(\mathbf{v}_1)$, with $\phi(v_1)$ the normalized Maxwell velocity distribution function

$$\phi(v_1)=\left(\frac{m}{2\pi k_B T}\right)^{3/2}\exp\frac{-mv_1^2}{2k_B T} \tag{2.7}$$

where m is the mass of the particles and k_B is Boltzmann's constant. Since the Boltzmann operator $L_B(\mathbf{k}, \mathbf{v}_1)$—and in particular the binary collision operator $\Lambda_B(\mathbf{v}_1)$—are symmetric operators, so that

$$\begin{gathered}\langle a(\mathbf{v}_1)\, L_B(\mathbf{k}, \mathbf{v}_1)\, b(\mathbf{v}_1)\rangle_1=\langle b(\mathbf{v}_1)\, L_B(\mathbf{k}, \mathbf{v}_1)\, a(\mathbf{v}_1)\rangle_1\\ \langle a(\mathbf{v}_1)\, \Lambda_B(\mathbf{v}_1)\, b(\mathbf{v}_1)\rangle_1=\langle b(\mathbf{v}_1)\, \Lambda_B(\mathbf{v}_1)\, a(\mathbf{v}_1)\rangle_1\end{gathered} \tag{2.8}$$

$F^B_{ab}(\mathbf{k}, t)$ manifestly satisfies the symmetry relation

$$F^B_{ab}(\mathbf{k}, t) = F^B_{ba}(\mathbf{k}, t) \tag{2.9}$$

also on the one-particle level for a single kinetic operator $L_B(\mathbf{k}, \mathbf{v}_1)$.

We consider next two attempts that have been made to evaluate the N-particle F_{ab} beyond the Boltzmann or low-density limit.

1. As a result of the work of Bogolubov, Choh, and Uhlenbeck (see Refs. 19 for surveys) on a systematic generalization of the Boltzmann binary collision operator $\Lambda_B(\mathbf{v}_1)$ to higher densities, an operator has been obtained for finite-range repulsive forces that includes the effect of ternary, i.e., three-particle, collisions. Since the resulting linear inhomogeneous collision operator $L_B(\mathbf{k}, \mathbf{v}_1) + n^2 M(\mathbf{k}, \mathbf{v}_1)$ is also symmetric, the a, b symmetry relation (2.4) also manifestly holds on the one-particle level for the single kinetic operator $L_B(\mathbf{k}, \mathbf{v}_1) + n^2 M(\mathbf{k}, \mathbf{v}_1)$.[20]

Because of the appearance of divergences when higher order collisions are included,[19] a general statement on the a, b symmetry behavior of one-particle kinetic operators incorporating more than ternary collisions cannot be made at this point.

2. A much used, but approximate kinetic theory, restricted to particles interacting with a hard sphere potential, due originally to Enskog[10,11] and usually now called the standard Enskog theory (SET), has been generalized in the last 15 years to a consistent, yet still approximate, kinetic theory for dense, hard sphere fluids, usually called the revised Enskog theory (RET).[21–27] In particular, this theory enables one—for hard sphere fluids—to approximate the N-particle correlation functions $F_{ab}(\mathbf{k}, t)$ by one-particle expressions $F^E_{ab}(\mathbf{k}, t)$. It is not immediately clear, however, whether the $F^E_{ab}(\mathbf{k}, t)$ are symmetric in a and b, since the revised Enskog theory is approximate, so that the a, b symmetry present on the N-particle level does not necessarily carry over to the one-particle, kinetic, level. Up until now only explicit expressions for $F^E_{ab}(\mathbf{k}, t)$ for $a = b = 1$ have been considered in the literature. These expressions for $F_{11}(\mathbf{k}, t) = F(\mathbf{k}, t)$ [given by Eq. (2.3) with $a = b = 1$] are all of the form

$$F^E(\mathbf{k}, t) = S(k) \langle 1\{\exp[L_E(\mathbf{k}, \mathbf{v}_1)t]\}1\rangle \tag{2.10}$$

where $L_E(\mathbf{k}, \mathbf{v}_1)$ is an asymmetric linear operator and $S(k) = F(\mathbf{k}, 0)$ is the static structure factor. In the literature, a number of different operators $L_E(\mathbf{k}, \mathbf{v}_1)$ occur, all leading to the same result for $F^E(\mathbf{k}, t)$, but all being asymmetric.

Inspired by computer simulations of actual dense, hard sphere fluids by Alley and Alder,[14] we were led to consider other correlation functions where, in particular, $a(\mathbf{v})$ and $b(\mathbf{v})$ are related to other locally conserved quantities, $\mathbf{v}$ and v^2, leading to a symmetric 5×5 matrix of correlation functions $F_{ab}(\mathbf{k}, t)$ with $a(\mathbf{v})$, $b(\mathbf{v})=1$, $\mathbf{v}$, or v^2.

We will be concerned with the following questions: (1) What are the expressions for the $F_{ab}(\mathbf{k}, t)$ on the kinetic, one-particle, level in the RET? (2) What is the symmetry of these expressions $F^E_{ab}(\mathbf{k}, t)$ in a and b? (3) Is there a single, *symmetric*, one-particle operator $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$ that, like the Boltzmann operator $L_B(\mathbf{k}, \mathbf{v}_1)$, manifestly yields $F^E_{ab}(\mathbf{k}, t)=F^E_{ba}(\mathbf{k}, t)$? The main point of this paper is to show that such a symmetric operator indeed exists, and to give the explicit form of this operator $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$.

To illustrate that to obtain an a, b symmetry on the one-particle level is nontrivial, we also show that in the standard Enskog theory the a, b symmetry present on the N-particle level for the $F_{ab}(\mathbf{k}, t)$ is lost on the one-particle level.

The plan of this paper is as follows. In Section 3, we relate the equilibrium time correlation functions F_{ab} to a one-particle nonequilibrium distribution function $f(\mathbf{r}, \mathbf{v}, t)$. We derive explicit kinetic representations for the F_{ab} in Section 4 at low densities using the Boltzmann equation for $f(\mathbf{r}, \mathbf{v}, t)$ and in Section 5 at high densities, using the revised Enskog equation for $f(\mathbf{r}, \mathbf{v}, t)$. The expression for $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$ is also given in this section. We conclude with a discussion of our results in Section 6, which includes the connection with the standard Enskog theory.

3. ONE-PARTICLE DISTRIBUTION FUNCTION

Here we express the N-particle equilibrium time correlation functions $F_{ab}(\mathbf{k}, t)$ in terms of the one-particle nonequilibrium distribution function $f(\mathbf{r}, \mathbf{v}, t)$ in the standard manner.[19,26,28–30] Thus, we write

$$F_{ab}(\mathbf{k}, t)=\int d\mathbf{r}[\exp(-i\mathbf{k}\cdot\mathbf{r})]\int d\mathbf{v}\, b(\mathbf{v}) f(\mathbf{r}, \mathbf{v}, t) \tag{3.1}$$

where

$$f(\mathbf{r}, \mathbf{v}, t)=\left\langle \sum_{i=1}^{N} \delta(\mathbf{r}_i-\mathbf{r})\,\delta(\mathbf{v}_i-\mathbf{v})\right\rangle_t \tag{3.2}$$

is, in general, the number of particles at $\mathbf{r}$ with velocity $\mathbf{v}$ in a (non)-equilibrium ensemble at time t. Here the brackets labeled with t denote an N-particle nonequilibrium ensemble average

$$\langle\cdots\rangle_t=\int d\Gamma\, \rho(\Gamma, t)\cdots \tag{3.3}$$

where $\Gamma = (\mathbf{r}_1, \mathbf{v}_1, ..., \mathbf{r}_N, \mathbf{v}_N)$ is the phase of the fluid and, with (2.3),

$$\rho(\Gamma, t) = [\exp(t\bar{L})]\, \rho_0(\Gamma) \left\{ 1 + \frac{1}{N} \sum_{i=1}^{N} [\exp(i\mathbf{k}\cdot\mathbf{r}_i)]\, a(\mathbf{v}_i) \right\} \tag{3.4}$$

Here $\rho_0(\Gamma)$ is the N-particle equilibrium canonical ensemble distribution function and $\bar{L}$ the transpose of L, generally defined by

$$\int d\Gamma\, A(\Gamma)\, LB(\Gamma) = \int d\Gamma\, B(\Gamma)\, \bar{L}A(\Gamma) \tag{3.5}$$

for any two phase functions A and B.

For continuous interparticle interactions, $\bar{L} = -L$, while for hard spheres, to which we will restrict ourselves in the following,[23,31,32]

$$L = \sum_{i=1}^{N} \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i<j}^{N} \sum^{N} T(ij) \tag{3.6}$$

and

$$\bar{L} = -\sum_{i=1}^{N} \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i<j}^{N} \sum^{N} \bar{T}(ij) \tag{3.7}$$

with the binary collision operators $T(ij)$ and $\bar{T}(ij)$ given by

$$\begin{aligned} T(ij) &= \sigma \int d\hat{\boldsymbol{\sigma}}\, |\mathbf{v}_{ij}\cdot\boldsymbol{\sigma}|\, \Theta(\mathbf{v}_{ij}\cdot\boldsymbol{\sigma})\, \delta(\mathbf{r}_{ij} + \boldsymbol{\sigma})[b_{\hat{\sigma}}(ij) - 1] \\ \bar{T}(ij) &= \sigma \int d\hat{\boldsymbol{\sigma}}\, |\mathbf{v}_{ij}\cdot\boldsymbol{\sigma}|\, \Theta(\mathbf{v}_{ij}\cdot\boldsymbol{\sigma})[\delta(\mathbf{r}_{ij} - \boldsymbol{\sigma})\, b_{\hat{\sigma}}(ij) - \delta(\mathbf{r}_{ij} + \boldsymbol{\sigma})] \end{aligned} \tag{3.8}$$

Here $\hat{\boldsymbol{\sigma}} = \boldsymbol{\sigma}/\sigma$ is a unit vector defining the geometry of the binary collision between the hard spheres i and j with diameter σ, $\Theta(x)$ is the Heaviside step function, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$. The substitution operator $b_{\hat{\sigma}}(ij)$ acts only on the velocities $\mathbf{v}_i$ and $\mathbf{v}_j$ and replaces them by the velocities $\mathbf{v}_i'$, $\mathbf{v}_j'$ after the binary collision,

$$\begin{aligned} b_{\hat{\sigma}}(ij)\mathbf{v}_i &= \mathbf{v}_i' = \mathbf{v}_i - \hat{\boldsymbol{\sigma}}(\hat{\boldsymbol{\sigma}}\cdot\mathbf{v}_{ij}) \\ b_{\hat{\sigma}}(ij)\mathbf{v}_j &= \mathbf{v}_j' = \mathbf{v}_j + \hat{\boldsymbol{\sigma}}(\hat{\boldsymbol{\sigma}}\cdot\mathbf{v}_{ij}) \end{aligned} \tag{3.9}$$

We note that $\bar{T}(ij)$ is the transpose of $T(ij)$, i.e.,

$$\int d\Gamma\, A(\Gamma)\, T(ij)\, B(\Gamma) = \int d\Gamma\, B(\Gamma)\, \bar{T}(ij)\, A(\Gamma) \tag{3.10}$$

so that $T(ij)$ and $\bar{T}(ij)$ are not symmetric operators.

To obtain kinetic representations for the $F_{ab}(\mathbf{k}, t)$, we introduce the relative deviation $h(\mathbf{r}, \mathbf{v}, t)$ of $f(\mathbf{r}, \mathbf{v}, t)$ from its equilibrium value $n\phi(v)$, defined by

$$f(\mathbf{r}, \mathbf{v}, t) = n\phi(v)[1 + h(\mathbf{r}, \mathbf{v}, t)] \tag{3.11}$$

Then, the basic assumption made in kinetic theory is that $h(\mathbf{r}, \mathbf{v}, t)$ is described at low densities by the linear Boltzmann equation and at high densities by the linear revised Enskog equation. On the basis of these assumptions, we derive kinetic representations for the $F_{ab}(\mathbf{k}, t)$, which we call $F_{ab}^{B}(\mathbf{k}, t)$ at low densities and $F_{ab}^{E}(\mathbf{k}, t)$ at high densities.

In the next section, we give a short derivation and discussion of the kinetic representations $F_{ab}^{B}(\mathbf{k}, t)$ at low densities, which we will use as a guideline to derive kinetic representations at high densities.

4. LOW DENSITIES

At low densities we start from the nonlinear Boltzmann equation for $f(\mathbf{r}, \mathbf{v}, t)$, i.e.,[(11),3]

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1}\right) f(\mathbf{r}_1, \mathbf{v}_1, t) = \int d\mathbf{r}_2 \int d\mathbf{v}_2 \, T_B(12) \, f(\mathbf{r}_1, \mathbf{v}_1, t) \, f(\mathbf{r}_2, \mathbf{v}_2, t) \tag{4.1}$$

with the Boltzmann collision operator given by

$$T_B(12) = \sigma \int d\hat{\boldsymbol{\sigma}} \, |\mathbf{v}_{12} \cdot \boldsymbol{\sigma}| \, \Theta(\mathbf{v}_{12} \cdot \boldsymbol{\sigma}) \, \delta(\mathbf{r}_{12})[b_{\hat{\sigma}}(12) - 1] \tag{4.2}$$

We remark that $T_B(12)$ follows from $T(12)$ and $\bar{T}(12)$ when in Eq. (3.8) $\delta(\mathbf{r}_{12} + \boldsymbol{\sigma})$ and $\delta(\mathbf{r}_{12} - \boldsymbol{\sigma})$ are replaced by $\delta(\mathbf{r}_{12})$, i.e., when the difference in position of the colliding particles 1 and 2 is neglected. As a consequence, $T_B(12)$ is a symmetric operator, i.e.,

$$\int d\Gamma \, A(\Gamma) \, T_B(12) \, B(\Gamma) = \int d\Gamma \, B(\Gamma) \, T_B(12) \, A(\Gamma) \tag{4.3}$$

unlike $T(12)$ and $\bar{T}(12)$ [cf. Eq. (3.10)].

[3] See Refs. 29 and 30, where the consequences for equilibrium time correlation functions of the nonlinear Boltzmann equation as opposed to the linear Boltzmann equation are discussed.

Next we substitute the expression (3.11) for $f(\mathbf{r}, \mathbf{v}, t)$ into (4.1) and keep the terms linear in $h(\mathbf{r}, \mathbf{v}, t)$ only. Then, we obtain the linear Boltzmann equation for $h(\mathbf{r}, \mathbf{v}, t)$, i.e.,

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1}\right) h(\mathbf{r}_1, \mathbf{v}_1, t)$$

$$= n \int d\mathbf{r}_2 \int d\mathbf{v}_2 \phi(v_2)\, T_B(12)(1 + P_{12})\, h(\mathbf{r}_1, \mathbf{v}_1, t) \tag{4.4}$$

where we used that

$$T_B(12)\, \phi(v_1)\, \phi(v_2) = \phi(v_1)\, \phi(v_2)\, T_B(12)$$

and where the permutation operator P_{12} replaces $\mathbf{r}_1$ and $\mathbf{v}_1$ by $\mathbf{r}_2$ and $\mathbf{v}_2$ in functions of $\mathbf{r}_1$ and $\mathbf{v}_1$. Therefore, $h(\mathbf{r}, \mathbf{v}, t)$ can be expressed in terms of $h(\mathbf{r}, \mathbf{v}, 0)$ as

$$h(\mathbf{r}, \mathbf{v}, t) = \{\exp[L_B(\mathbf{r}, \mathbf{v})\, t]\} h(\mathbf{r}, \mathbf{v}, 0) \tag{4.5}$$

Here, the one-particle operator $L_B(\mathbf{r}, \mathbf{v})$ acting on functions of $\mathbf{r}$ and $\mathbf{v}$ is given by

$$L_B(\mathbf{r}, \mathbf{v}) = -\mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + n\Lambda_B(\mathbf{v}) \tag{4.6}$$

where the Boltzmann collision operator $\Lambda_B(\mathbf{v})$ acts on the velocity $\mathbf{v}$ only, and is given by

$$\Lambda_B(\mathbf{v}_1) = \int d\mathbf{r}_2 \int d\mathbf{v}_2 \phi(v_2)\, T_B(12)(1 + P_{12}) \tag{4.7}$$

or

$$\Lambda_B(\mathbf{v}_1)\, f(\mathbf{v}_1) = \sigma \int d\hat{\boldsymbol{\sigma}} \int d\mathbf{v}_2\, \phi(v_2)\, |\mathbf{v}_{12} \cdot \boldsymbol{\sigma}|\, \Theta(\mathbf{v}_{12} \cdot \boldsymbol{\sigma})$$

$$\times [f(\mathbf{v}_1') - f(\mathbf{v}_1) + f(\mathbf{v}_2') - f(\mathbf{v}_2)] \tag{4.8}$$

with $\mathbf{v}_1'$ and $\mathbf{v}_2'$ the restituting velocities [cf. Eq. (3.9)] and $f(\mathbf{v}_1)$ an arbitrary function of $\mathbf{v}_1$.

Substitution of Eq. (3.11) for $f(\mathbf{r}, \mathbf{v}, t)$ [with Eq. (4.5) for $h(\mathbf{r}, \mathbf{v}, t)$] into Eq. (3.1) for $F_{ab}(\mathbf{k}, t)$ yields

$$F_{ab}^B(\mathbf{k}, t) = n \int d\mathbf{r}\, [\exp(i\mathbf{k} \cdot \mathbf{r})] \int d\mathbf{v}\, b(\mathbf{v})\, \phi(v)$$

$$\times (1 + \exp[L_B(\mathbf{r}, \mathbf{v})t]\, h(\mathbf{r}, \mathbf{v}, 0)) \tag{4.9}$$

Using that $\int d\mathbf{r} \exp(i\mathbf{k}\cdot\mathbf{r})=0$ for $\mathbf{k}\neq 0$ and that $h(\mathbf{r}, \mathbf{v}, 0)$ follows from Eqs. (3.11) and (3.2)–(3.4) to be

$$h(\mathbf{r}, \mathbf{v}, 0)=\frac{1}{N}\left[\exp(i\mathbf{k}\cdot\mathbf{r})\right] a(\mathbf{v}) \tag{4.10}$$

one has for the one-particle representation $F^B_{ab}(\mathbf{k}, t)$ for $F_{ab}(\mathbf{k}, t)$

$$F^B_{ab}(\mathbf{k}, t)=\langle b(\mathbf{v}_1)\{\exp[L_B(\mathbf{k}, \mathbf{v}_1)t]\}\, a(\mathbf{v}_1)\rangle_1 \tag{4.11}$$

where

$$\begin{aligned} L_B(\mathbf{k}, \mathbf{v}_1) &= \frac{1}{V}\int d\mathbf{r}_1 \left[\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right] L_B(\mathbf{r}_1, \mathbf{v}_1) \exp(i\mathbf{k}\cdot\mathbf{r}_1) \\ &= -i\mathbf{k}\cdot\mathbf{v}_1 + n\Lambda_B(\mathbf{v}_1) \end{aligned} \tag{4.12}$$

which is the final result for the one-particle representation $F^B_{ab}(\mathbf{k}, t)$ of $F_{ab}(\mathbf{k}, t)$.

Thus, also on the one-particle (kinetic) level $F^B_{ab}(\mathbf{k}, t)=F^B_{ba}(\mathbf{k}, t)$ [cf. Eqs. (2.5) and (4.11)], with a single one-particle operator $L_B(\mathbf{k}, \mathbf{v}_1)$ for all a and b, as $L_B(\mathbf{k}, \mathbf{v})$ is a symmetric operator, since $\Lambda_B(\mathbf{v})$ is symmetric. The symmetry of $\Lambda_B(\mathbf{v})$ follows from Eqs. (4.3) and (4.7), i.e., directly from the symmetry of $T_B(12)$.

In the next section, we consider the F_{ab} at high densities.

5. HIGH DENSITIES

5.1. The Revised Enskog Equation

At high densities we start from the nonlinear revised Enskog equation for $f(\mathbf{r}, \mathbf{v}, t)$, i.e.,[23]

$$\begin{aligned} &\left(\frac{\partial}{\partial t}+\mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}\right) f(\mathbf{r}_1, \mathbf{v}_1, t) \\ &\qquad = \int d\mathbf{r}_2 \int d\mathbf{v}_2\, \bar{T}(12)\, f(\mathbf{r}_1, \mathbf{v}_1, t)\, f(\mathbf{r}_2, \mathbf{v}_2, t)\, g(\mathbf{r}_1, \mathbf{r}_2, t) \end{aligned} \tag{5.1}$$

Here $\bar{T}(12)$ is given by Eq. (3.8), and $g(\mathbf{r}_1, \mathbf{r}_2, t)$ is the pair correlation function at contact of a fluid in inhomogeneous equilibrium at time t, with a one-particle distribution function given by $f(\mathbf{r}, \mathbf{v}, t)$. As a consequence, $g(\mathbf{r}_1, \mathbf{r}_2, t)$ depends functionally on the local number density $n(\mathbf{r}, t)= \int d\mathbf{v}\, f(\mathbf{r}, \mathbf{v}, t)$.

We remark that the revised Enskog equation differs in two respects from the Boltzmann equation. First, through the use of $\bar{T}(12)$ in Eq. (5.1), the difference in position of two colliding particles is taken into account, which introduces, physically, the (instantaneous) collisional transfer of momentum and energy. Second, $g(\mathbf{r}_1, \mathbf{r}_2, t) > 1$ incorporates approximately the increase in binary collisions at high densities, since $g(\mathbf{r}_1, \mathbf{r}_2, t) = 1$ at low densities.

5.2. One-Particle Representation

To obtain the linear revised Enskog equation for $h(\mathbf{r}, \mathbf{v}, t)$, we substitute Eq. (3.11) for $f(\mathbf{r}, \mathbf{v}, t)$ into (5.1) and expand $g(\mathbf{r}_1, \mathbf{r}_2, t)$ around total equilibrium,

$$g(\mathbf{r}_1, \mathbf{r}_2, t) = \chi + \delta g(\mathbf{r}_1, \mathbf{r}_2, t) + \cdots \tag{5.2}$$

Here $\chi = \chi(n)$ is the value of the pair correlation function at contact in total equilibrium at density n and $\delta g(\mathbf{r}_1, \mathbf{r}_2, t)$ is the term in the expansion of g that is linear in $\int d\mathbf{v}\, h(\mathbf{r}, \mathbf{v}, t)$. Then, keeping the terms linear in $h(\mathbf{r}, \mathbf{v}, t)$ only, one obtains the linear revised Enskog equation for $h(\mathbf{r}, \mathbf{v}, t)$, i.e.,

$$\begin{aligned}\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1}\right) h(\mathbf{r}_1, \mathbf{v}_1, t) &\\ = n\chi \int d\mathbf{r}_2 \int d\mathbf{v}_2\, \phi(v_2)\, \bar{T}(12)(1 + P_{12})\, h(\mathbf{r}_1, \mathbf{v}_1, t) &\\ + n \int d\mathbf{r}_2 \int d\mathbf{v}_2\, \phi(v_2)\, \bar{T}(12)\, \delta g(\mathbf{r}_1, \mathbf{r}_2, t) &\end{aligned} \tag{5.3}$$

where one has used that

$$\bar{T}(12)\, \phi(v_1)\, \phi(v_2) = \phi(v_1)\, \phi(v_2)\, \bar{T}(12)$$

and $\int d\mathbf{r}_2\, \bar{T}(12) 1 = 0$. We refer to the first contribution on the right-hand side of Eq. (5.3) as the collision term [cf. Eq. (4.4)] and the second contribution as the mean field term.

Equation (5.3) can be rewritten as follows. First, we introduce for the collision term the Enskog collision operator $\bar{\Lambda}_E(\mathbf{r}_1, \mathbf{v}_1)$, which acts on functions of $\mathbf{r}_1$ and $\mathbf{v}_1$, and is given by

$$\bar{\Lambda}_E(\mathbf{r}_1, \mathbf{v}_1) = \int d\mathbf{r}_2 \int d\mathbf{v}_2\, \phi(v_2)\, \bar{T}(12)(1 + P_{12}) \tag{5.4}$$

Next we introduce for the mean field term the mean field operator $\bar{A}(\mathbf{r}_1, \mathbf{v}_1)$ defined by

$$\bar{A}(\mathbf{r}_1, \mathbf{v}_1)\, h(\mathbf{r}_1, \mathbf{v}_1, t) = \int d\mathbf{r}_2 \int d\mathbf{v}_2\, \phi(v_2)\, \bar{T}(12)\, \delta g(\mathbf{r}_1, \mathbf{r}_2, t) \tag{5.5}$$

which has been evaluated explicitly in the literature[23,26] with the result

$$\bar{A}(\mathbf{r}_1, \mathbf{v}_1) = \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} \int d\mathbf{r}_2 \int d\mathbf{v}_2\, \phi(v_2) \{\tilde{C}(r_{12}) - \chi \tilde{C}_0(r_{12})\}\, P_{12} \tag{5.6}$$

Here $\tilde{C}(r)$ is the direct correlation function of the fluid in equilibrium and $\tilde{C}_0(r)$ its low-density limit [*i.e.*, $\tilde{C}_0(r) = -\Theta(\sigma - r)$]. Then Eq. (5.3) can be rewritten in the form[23,25]

$$\frac{\partial}{\partial t} h(\mathbf{r}_1, \mathbf{v}_1, t) = \bar{L}_E(\mathbf{r}_1, \mathbf{v}_1)\, h(\mathbf{r}_1, \mathbf{v}_1, t) \tag{5.7}$$

with

$$\bar{L}_E(\mathbf{r}_1, \mathbf{v}_1) = -\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + n\chi \bar{A}_E(\mathbf{r}_1, \mathbf{v}_1) + n\bar{A}(\mathbf{r}_1, \mathbf{v}_1) \tag{5.8}$$

Using the formal solution

$$h(\mathbf{r}_1, \mathbf{v}_1, t) = \{\exp[\bar{L}_E(\mathbf{r}_1, \mathbf{v}_1) t]\}\, h(\mathbf{r}_1, \mathbf{v}_1, 0) \tag{5.9}$$

of Eq. (5.7) and Eqs. (3.11) and (3.1), one obtains

$$\begin{aligned} F^E_{ab}(\mathbf{k}, t) = n \int d\mathbf{r}\, [\exp(-i\mathbf{k} \cdot \mathbf{r})] \int d\mathbf{v}\, b(\mathbf{v})\, \phi(v) \\ \times (1 + \{\exp[\bar{L}_E(\mathbf{r}, \mathbf{v}) t]\}\, h(\mathbf{r}, \mathbf{v}, 0)) \end{aligned} \tag{5.10}$$

Therefore, using that with Eqs. (3.11) and (3.2)–(3.4)

$$h(\mathbf{r}, \mathbf{v}, 0) = \frac{1}{N} [\exp(i\mathbf{k} \cdot \mathbf{r})]\{a(\mathbf{v}) + [S(k) - 1]\langle a(\mathbf{v}_1)\rangle_1\} \tag{5.11}$$

one finds

$$F^E_{ab}(\mathbf{k}, t) = \langle b(\mathbf{v}_1)\{\exp[\bar{L}_E(\mathbf{k}, \mathbf{v}_1) t]\}\{a(\mathbf{v}_1) + [S(k) - 1]\langle a(\mathbf{v}_1)\rangle_1\}\rangle_1 \tag{5.12}$$

Here

$$\bar{L}_E(\mathbf{k}, \mathbf{v}_1) = -i\mathbf{k} \cdot \mathbf{v}_1 + n\chi \bar{A}_E(\mathbf{k}, \mathbf{v}_1) + n\bar{A}(\mathbf{k}, \mathbf{v}_1) \tag{5.13}$$

is related to $\bar{L}_E(\mathbf{r}_1, \mathbf{v}_1)$ by

$$\bar{L}_E(\mathbf{k}, \mathbf{v}_1) = \frac{1}{V} \int d\mathbf{r}_1 \, [\exp(-i\mathbf{k} \cdot \mathbf{r}_1)] \, \bar{L}_E(\mathbf{r}_1, \mathbf{v}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_1) \tag{5.14}$$

and similar expressions obtain for $\bar{\Lambda}_E(\mathbf{k}, \mathbf{v}_1)$ and $\bar{\Lambda}(\mathbf{k}, \mathbf{v}_1)$. In fact, with Eqs. (3.8) and (5.4), we obtain for $\bar{\Lambda}_E(\mathbf{k}, \mathbf{v}_1)$

$$\begin{aligned} \bar{\Lambda}_E(\mathbf{k}, \mathbf{v}_1) &= \frac{1}{V} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{v}_2 \, \phi(v_2) [\exp(-i\mathbf{k} \cdot \mathbf{r}_1)] \, \bar{T}(12) \\ &\quad \times (1 + P_{12}) \exp(i\mathbf{k} \cdot \mathbf{r}_1) \\ &= \sigma \int d\hat{\boldsymbol{\sigma}} \int d\mathbf{v}_2 \, \phi(v_2) \, |\mathbf{v}_{12} \cdot \boldsymbol{\sigma}| \, \Theta(\mathbf{v}_{12} \cdot \boldsymbol{\sigma}) \\ &\quad \times (b_{\hat{\sigma}}(12) - 1 + \{[\exp(-i\mathbf{k} \cdot \boldsymbol{\sigma})] \, b_{\hat{\sigma}}(12) - \exp(i\mathbf{k} \cdot \boldsymbol{\sigma})\} P_{12}), \end{aligned} \tag{5.15}$$

while with Eq. (5.6) we find for $\bar{\Lambda}(\mathbf{k}, \mathbf{v}_1)$

$$\bar{\Lambda}(\mathbf{k}, \mathbf{v}_1) = [C(k) - \chi C_0(k)] \, i\mathbf{k} \cdot \mathbf{v}_1 \int d\mathbf{v}_2 \, \phi(v_2) \, P_{12} \tag{5.16}$$

Here

$$C(k) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \, \tilde{C}(r) = [S(k) - 1]/nS(k)$$

is the direct correlation function, while $C_0(k) = -4\pi\sigma^2 j_1(k\sigma)/k$ is its low-density limit, where $j_1(x)$ is the spherical Bessel function of order 1.

Equations (5.12) and (5.13) provide a one-particle representation $F^E_{ab}(\mathbf{k}, t)$ for the N-particle correlation functions $F_{ab}(\mathbf{k}, t)$.

5.3. Transposed Representation

Due to the fact that $\bar{T}(12)$ is not a symmetric operator [cf. Eq. (3.10)], neither $\bar{\Lambda}_E(\mathbf{k}, \mathbf{v})$ nor $\bar{\Lambda}(\mathbf{k}, \mathbf{v})$ is symmetric. As a consequence, another representation of F^E_{ab} can be found using the transpose $\Lambda_E(\mathbf{k}, \mathbf{v}_1)$ of $\bar{\Lambda}_E(\mathbf{k}, \mathbf{v})$, defined by

$$\langle f(\mathbf{v}_1) \, \Lambda_E(\mathbf{k}, \mathbf{v}_1) \, g(\mathbf{v}_1) \rangle_1 = \langle g(\mathbf{v}_1) \, \bar{\Lambda}_E(\mathbf{k}, \mathbf{v}_1) \, f(\mathbf{v}_1) \rangle_1 \tag{5.17}$$

and given by [cf. Eqs. (3.10) and (5.15)]

$$
\begin{aligned}
\bar{A}_E(\mathbf{k}, \mathbf{v}_1) &= \frac{1}{V} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{v}_2\, \phi(v_2)\{\exp[i\mathbf{k}\cdot\mathbf{r}_1]\} \\
&\quad \times T(12)(1+P_{12})\exp(-i\mathbf{k}\cdot\mathbf{r}_1) \\
&= \sigma \int d\hat{\boldsymbol{\sigma}} \int d\mathbf{v}_2\, \phi(v_2)\, |\mathbf{v}_{12}\cdot\boldsymbol{\sigma}|\, \Theta(\mathbf{v}_{12}\cdot\boldsymbol{\sigma}) \\
&\quad \times [b_{\hat{\sigma}}(12)-1]\{1+\exp(-i\mathbf{k}\cdot\boldsymbol{\sigma})\, P_{12}\}
\end{aligned}
\tag{5.18}
$$

as well as the transpose $A(\mathbf{k}, \mathbf{v}_1)$ of $\bar{A}(\mathbf{k}, \mathbf{v}_1)$, given by

$$
A(\mathbf{k}, \mathbf{v}_1) = [C(k) - \chi C_0(k)] \int d\mathbf{v}_2\, \phi(v_2)\, i\mathbf{k}\cdot\mathbf{v}_2 P_{12} \tag{5.19}
$$

Then we obtain for the transposed representation of $F^E_{ab}(\mathbf{k}, t)$

$$
\begin{aligned}
F^E_{ab}(\mathbf{k}, t) &= \langle \{a(\mathbf{v}_1) + [S(k)-1]\langle a(v_1)\rangle_1\} \\
&\quad \times \{\exp[L_E(\mathbf{k}, \mathbf{v}_1)t]\}\, b(\mathbf{v}_1)\rangle_1
\end{aligned}
\tag{5.20}
$$

with

$$
L_E(\mathbf{k}, \mathbf{v}_1) = -i\mathbf{k}\cdot\mathbf{v}_1 + n\chi \Lambda_E(\mathbf{k}, \mathbf{v}_1) + nA(\mathbf{k}, \mathbf{v}_1) \tag{5.21}
$$

This representation has been used in Refs. 33 and 34 to study $F^E(\mathbf{k}, t)$ [cf. Eq. (2.10)].

It is not obvious from the form of the expressions (5.12) and (5.20) for $F^E_{ab}(\mathbf{k}, t)$ that they are symmetric in a and b. This is due not only to the different way in which the functions a and b occur in these expressions, but also to the asymmetry of the one-particle operators $\bar{L}_E$ and L_E. In the next subsection, we will not only show that (5.12) and (5.20) are symmetric in a and b, but also that there is yet another expression for $F^E_{ab}(\mathbf{k}, t)$ that uses a single *symmetric* one-particle operator and that is obviously symmetric in a and b.

5.4. Symmetric Representation

We prove first for Eq. (5.20) that the $F^E_{ab}(\mathbf{k}, t)$ are symmetric in a and b. To that end, we introduce a symmetric operator $\mathscr{S}(\mathbf{v}_1)$ and its inverse $\mathscr{S}^{-1}(\mathbf{v}_1)$ defined such that in the expression (5.20) for $F^E_{ab}(\mathbf{k}, t)$, a and b occur symmetrically at $t=0$, i.e., that in the expression

$$
\begin{aligned}
F^E_{ab}(\mathbf{k}, 0) &= \langle \{a(\mathbf{v}_1) + [S(k)-1]\langle a(\mathbf{v}_1)\rangle_1\}\, b(\mathbf{v}_1)\rangle_1 \\
&= \langle \{a(\mathbf{v}_1) + [S(k)-1]\langle a(\mathbf{v}_1)\rangle_1\}\, \mathscr{S}^{-1}(\mathbf{v}_1)\, \mathscr{S}(\mathbf{v}_1)\, b(\mathbf{v}_1)\rangle_1
\end{aligned}
\tag{5.22}
$$

$a(\mathbf{v})$ and $b(\mathbf{v})$ are treated symmetrically, after $\mathscr{S}(\mathbf{v}_1)$ has acted to the right and $\mathscr{S}^{-1}(\mathbf{v}_1)$ to the left. Thus, one obtains for $\mathscr{S}(\mathbf{v}_1)$ the equation

$$\mathscr{S}(\mathbf{v}_1)\, f(\mathbf{v}_1) = \mathscr{S}^{-1}(\mathbf{v}_1)\{f(\mathbf{v}_1) + [S(k) - 1]\langle f(\mathbf{v}_1)\rangle_1\} \tag{5.23}$$

One of the two solutions to this equation is

$$\begin{aligned} \mathscr{S}(\mathbf{v}_1)\, f(\mathbf{v}_1) &= f(\mathbf{v}_1) + [\sqrt{S(k)} - 1]\langle f(\mathbf{v}_1)\rangle \\ \mathscr{S}^{-1}(\mathbf{v}_1)\, f(\mathbf{v}_1) &= f(\mathbf{v}_1) + \left[\frac{1}{\sqrt{S(k)}} - 1\right]\langle f(\mathbf{v}_1)\rangle \end{aligned} \tag{5.24}$$

while the second solution [with $\sqrt{S(k)}$ replaced by $-\sqrt{S(k)}$] will be discussed later.

Then, for finite times, using the identity operator $\mathscr{S}^{-1}(\mathbf{v}_1)\,\mathscr{S}(\mathbf{v}_1)$ in Eq. (5.20) for $F^E_{ab}(\mathbf{k}, t)$, we obtain [cf. Eq. (5.22)]:

$$\begin{aligned} F^E_{ab}(\mathbf{k}, t) = \langle \{a(\mathbf{v}_1) &+ [\sqrt{S(k)} - 1]\langle a(\mathbf{v}_1)\rangle_1\} \\ &\times \{\exp[L_{E,s}(\mathbf{k}, \mathbf{v}_1)t]\}\{b(\mathbf{v}_1) + [\sqrt{S(k)} - 1]\langle b(\mathbf{v}_1)\rangle_1\}\rangle_1 \end{aligned} \tag{5.25}$$

where

$$L_{E,s}(\mathbf{k}, \mathbf{v}_1) = \mathscr{S}(\mathbf{v}_1)\, L_E(\mathbf{k}, \mathbf{v}_1)\, \mathscr{S}^{-1}(\mathbf{v}_1) \tag{5.26}$$

or

$$L_{E,s}(\mathbf{k}, \mathbf{v}_1) = -i\mathbf{k}\cdot\mathbf{v}_1 + n\chi\Lambda_{E,s}(\mathbf{k}, \mathbf{v}_1) + n\Lambda_s(\mathbf{k}, \mathbf{v}_1) \tag{5.27}$$

Here

$$\Lambda_{E,s}(\mathbf{k}, \mathbf{v}_1)\, f(\mathbf{v}_1) = \Lambda_E(\mathbf{k}, \mathbf{v}_1)\, f(\mathbf{v}_1) - \langle \Lambda_E(\mathbf{k}, \mathbf{v}_1)\, f(\mathbf{v}_1)\rangle_1 \tag{5.28}$$

and

$$\Lambda_s(\mathbf{k}, \mathbf{v}_1) = \frac{\sqrt{S(k)} - 1}{n\sqrt{S(k)}} \int d\mathbf{v}_2\, \phi(v_2)\, i\mathbf{k}\cdot(\mathbf{v}_1 + \mathbf{v}_2)\, P_{12} \tag{5.29}$$

The derivation of Eq. (5.27) from (5.26) is straightforward when one uses that $\Lambda_E(\mathbf{k}, \mathbf{v}_1)1 = 0$ and [cf. Eq. (5.18)]

$$\langle \Lambda_E(\mathbf{k}, \mathbf{v}_1)\, f(\mathbf{v}_1)\rangle_1 = C_0(k)\langle i\mathbf{k}\cdot\mathbf{v}_1\, f(\mathbf{v}_1)\rangle_1 \tag{5.30}$$

The inhomogeneous Enskog operator $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$ given in Eq. (5.27) is a symmetric operator, since both $\Lambda_{E,s}(\mathbf{k}, \mathbf{v}_1)$ and $\Lambda_s(\mathbf{k}, \mathbf{v}_1)$ are symmetric operators, as follows from Eqs. (5.4), (5.18),[33] and (5.29), respectively.

Thus, we have found an expression for $F^E_{ab}(\mathbf{k}, t)$ given by Eqs. (5.25) and (5.27) which involves a single symmetric one-particle streaming operator $\exp[L_{E,s}(\mathbf{k}, \mathbf{v}_1)t]$ and which treats a and b symmetrically, so that indeed obviously $F^E_{ab}(\mathbf{k}, t) = F^E_{ba}(\mathbf{k}, t)$.

Second, we note that Eqs. (5.25) and (5.27) can also be derived from the transposed representation for $F^E_{ab}(\mathbf{k}, t)$ given by Eqs. (5.12) and (5.13). Then one inserts $\mathscr{S}(\mathbf{v}_1)\, \mathscr{S}^{-1}(\mathbf{v}_1)$ instead of $\mathscr{S}^{-1}(\mathbf{v}_1)\, \mathscr{S}(\mathbf{v}_1)$ and one finds that

$$\bar{L}_{E,s}(\mathbf{k}, \mathbf{v}_1) = \mathscr{S}^{-1}(\mathbf{v}_1)\, \bar{L}_E(\mathbf{k}, \mathbf{v}_1)\, \mathscr{S}(\mathbf{v}_1) = L_{E,s}(\mathbf{k}, \mathbf{v}_1) \tag{5.31}$$

which also leads to Eq. (5.25) for $F^E_{ab}(\mathbf{k}, t)$.

6. DISCUSSION

We end with a number of remarks.

1. The Enskog expressions $F^E_{ab}(\mathbf{k}, t)$ given by (5.25) tend at low densities to the Boltzmann expressions $F^B_{ab}(\mathbf{k}, t)$ given by Eq. (2.5) as long as $k\sigma \ll 1$. To see this, we note that $\lim_{n\to 0} \chi = 1$, $\lim_{n\to 0} S(k) = 1$, $\lim_{n\to 0} A_s(\mathbf{k}, \mathbf{v}_1) = O(k\sigma)$, and $A_{E,s}(\mathbf{k}, \mathbf{v}_1) = A_B(\mathbf{v}_1) + O(k\sigma)$, so that for low densities and $k\sigma \ll 1$, $L_{E,s}(\mathbf{k}, \mathbf{v}_1) = L_B(\mathbf{k}, \mathbf{v}_1)$ and $F^E_{ab}(\mathbf{k}, t) = F^B_{ab}(\mathbf{k}, t)$.

Thus, we have found continuous extensions $F^E_{ab}(\mathbf{k}, t)$ of the Boltzmann expressions $F^B_{ab}(\mathbf{k}, t)$ to higher densities, still involving a single symmetric one-particle streaming operator $\exp[L_{E,s}(\mathbf{k}, \mathbf{v}_1)t]$, which is a continuous extension of the operator $\exp[L_B(\mathbf{k}, \mathbf{v}_1)t]$ to higher densities.

2. The operators $L_B(\mathbf{k}, \mathbf{v}_1)$ [cf. Eq. (4.12)] and $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$ [cf. Eq. (5.27)] are the *only* symmetric operators that describe *all* $F^B_{ab}(\mathbf{k}, t)$ and $F^E_{ab}(\mathbf{k}, t)$ respectively, when one requires that:

(i) *Each* function $a(\mathbf{v}_1)$ in $F^B_{ab}(\mathbf{k}, t)$ on the one-particle level corresponds, one to one, to the function $\sum_i a(\mathbf{v}_i) \exp(i\mathbf{k} \cdot \mathbf{r}_i)$ on the N-particle level.

(ii) $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$ is a continuous extension of $L_B(\mathbf{k}, \mathbf{v}_1)$ to higher densities.

One needs (i) to exclude the results of the trivial transformations

$$O_\psi a(\mathbf{v}_1) = O_\psi^{-1} a(\mathbf{v}_1) = a(\mathbf{v}_1) - 2\langle a(\mathbf{v}_1)\, \psi(\mathbf{v}_1)\rangle_1 \psi(\mathbf{v}_1)$$

for *any* normalized $\psi(\mathbf{v}_1)$. For, with the O_ψ one can transform the $F^B_{ab}(\mathbf{k}, t)$ into expressions that also involve symmetric one-particle Boltzmann operators $L_B^{(\psi)}(\mathbf{k}, \mathbf{v}_1)$, which are unequal to $L_B(\mathbf{k}, \mathbf{v}_1)$, however. For example, if $\psi(\mathbf{v}_1) = 1$,

$$F_{ab}^B(\mathbf{k}, t) = \langle \{a(\mathbf{v}_1) - 2\langle a(\mathbf{v}_1)\rangle_1\}\{\exp[L_B^{(1)}(\mathbf{k}, \mathbf{v}_1)t]\} \times \{b(\mathbf{v}_1) - 2\langle b(\mathbf{v}_1)\rangle_1\}\rangle_1 \tag{6.1}$$

with $L_B^{(1)} = O_1 L_B O_1$, i.e.,

$$L_B^{(1)}(\mathbf{k}, \mathbf{v}_1) = -i\mathbf{k}\cdot\mathbf{v}_1 + n\Lambda_B(\mathbf{v}_1) + 2\int d\mathbf{v}_2\, \phi(v_2)\, i\mathbf{k}\cdot(\mathbf{v}_1 + \mathbf{v}_2)\, P_{12} \tag{6.2}$$

Here $L_B^{(1)}(\mathbf{k}, \mathbf{v}_1)$ is also symmetric, but the function $\sum_i \exp(i\mathbf{k}\cdot\mathbf{r}_i)$ on the N-particle level corresponds now to -1 on the one-particle level [cf. Eq. (6.1)] instead of to 1.

One needs (ii) to exclude the solution of Eq. (5.23) given by Eq. (5.24) with $\sqrt{S(k)}$ replaced by $-\sqrt{S(k)}$, since this solution leads to expressions for $F_{ab}^E(\mathbf{k}, t)$ involving the symmetric one-particle operator $O_1 L_{E,s}(\mathbf{k}, \mathbf{v}_1) O_1$, which tends at low densities to $L_B^{(1)}(\mathbf{k}, \mathbf{v}_1)$ instead of to $L_B(\mathbf{k}, \mathbf{v}_1)$.

3. The main results of this paper are summarized in Table I. There one sees how the N-particle correlation functions $F_{ab}(\mathbf{k}, t)$ given by Eq. (2.3) translate to the one-particle level. At low densities one uses the expressions for $F_{ab}^B(\mathbf{k}, t)$ given by Eqs. (2.5) and (2.6), while at high densities the expressions for $F_{ab}^E(\mathbf{k}, t)$ given by Eqs. (5.25) and (5.27) are used. Both involve *symmetric* one-particle operators, in contrast to the expressions $F_{ab}^E(\mathbf{k}, t)$ given by Eqs. (5.20) and (5.21), which involve the *asymmetric* operator $L_E(\mathbf{k}, \mathbf{v}_1)$.

Table I. Replacement Rules for the Correlation Functions $F_{ab}(\mathbf{k}, t)$ from the N-Particle to the One-Particle Level at Low Densities $[F_{ab}^B(\mathbf{k}, t)]$ and High Densities $[F_{ab}^E(\mathbf{k}, t)]$[a]

$F_{ab}(\mathbf{k}, t)$	$F_{ab}^B(\mathbf{k}, t)$	$F_{ab}^E(\mathbf{k}, t)$	$F_{ab}^E(\mathbf{k}, t)$
$\langle\ \rangle$	$\langle\ \rangle_1$	$\langle\ \rangle_1$	$\langle\ \rangle_1$
L	$L_B(\mathbf{k}, \mathbf{v}_1)$	$L_{E,s}(\mathbf{k}, \mathbf{v}_1)$	$L_E(\mathbf{k}, \mathbf{v}_1)$
$\sum_{i=1}^N [\exp(i\mathbf{k}\cdot\mathbf{r}_i)]a(\mathbf{v}_i)/\sqrt{N}$	$a(\mathbf{v}_1)$	$a(\mathbf{v}_1) + [\sqrt{S(k)} - 1]\langle a(\mathbf{v}_1)\rangle_1$	$a(\mathbf{v}_1) - [S(k) - 1]\langle a(\mathbf{v}_1)\rangle_1$
$\sum_{i=1}^N [\exp(-i\mathbf{k}\cdot\mathbf{r}_j)]b(\mathbf{v}_j)/\sqrt{N}$	$b(\mathbf{v}_1)$	$b(\mathbf{v}_1) + [\sqrt{S(k)} - 1]\langle b(\mathbf{v}_1)\rangle_1$	$b(\mathbf{v}_1)$

[a] For $F_{ab}^E(\mathbf{k}, t)$ there is a symmetric [with $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$] and an asymmetric representation [with $L_E(\mathbf{k}, \mathbf{v}_1)$].

4. To illustrate that the a, b symmetry for the correlation functions $F_{ab}(\mathbf{k}, t)$ present at the N-particle level does not necessarily carry over to the one-particle kinetic level, we consider the predictions of the standard Enskog theory for $F_{ab}(\mathbf{k}, t)$, which we call $F_{ab}^{SE}(\mathbf{k}, t)$.

Enskog originally proposed Eq. (5.1) with the assumption that $g(\mathbf{r}_1, \mathbf{r}_2, t)$ is given by

$$g_{SE}(\mathbf{r}_1, \mathbf{r}_2; t) = \chi\left(n\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}; t\right)\right) \tag{6.3}$$

where

$$n\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}; t\right) = \int d\mathbf{v}\, f\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \mathbf{v}, t\right) \tag{6.4}$$

is the number density at time t in the fluid (out of equilibrium) at the point of contact of the two colliding spheres located at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. Then $g_{SE}(\mathbf{r}_1, \mathbf{r}_2; t)$ is expanded around total equilibrium, i.e.,

$$g_{SE}(\mathbf{r}_1, \mathbf{r}_2; t) = \chi + \delta g_{SE}(\mathbf{r}_1, \mathbf{r}_2; t)$$

where

$$\delta g_{SE}(\mathbf{r}_1, \mathbf{r}_2, t) = \frac{\partial \chi}{\partial n} n \int d\mathbf{v}_3\, \phi(v_3)\, h\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \mathbf{v}_3, t\right) \tag{6.5}$$

Then, by replacing $\delta g(\mathbf{r}_1, \mathbf{r}_2, t)$ in Eq. (5.3) by $\delta g_{SE}(\mathbf{r}_1, \mathbf{r}_2, t)$, one obtains the linearized standard Enskog equation for $h(\mathbf{r}_1, \mathbf{v}_1, t)$, with an *asymmetric* operator $\bar{L}_{SE}(\mathbf{r}_1, \mathbf{v}_1)$, analogous to the operator $\bar{L}_E(\mathbf{r}_1, \mathbf{v}_1)$ in Eq. (5.7).

The derivation of the expressions $F_{ab}^{SE}(\mathbf{k}, t)$ in the SET is straightforward and very similar to that of $F_{ab}^{E}(\mathbf{k}, t)$ in the RET given above. We will only give the final result [cf. Eqs. (5.25) and (5.27)]:

$$\begin{aligned} F_{ab}^{SE}(\mathbf{k}, t) = \Bigg\langle & \left\{a(\mathbf{v}_1) + \left[\frac{S(k)}{\sqrt{\Sigma(k)}} - 1\right] \langle a(\mathbf{v}_1)\rangle_1\right\} \\ & \times \{\exp[L_{SE,s}(\mathbf{k}, \mathbf{v}_1)t]\}\{b(\mathbf{v}_1) + [\sqrt{\Sigma(k)} - 1]\langle b(\mathbf{v}_1)\rangle_1\}\Bigg\rangle_1 \end{aligned} \tag{6.6}$$

with a *symmetric* one-particle operator

$$L_{SE,s}(\mathbf{k}, \mathbf{v}_1) = -i\mathbf{k}\cdot\mathbf{v}_1 + n\chi A_{E,s}(\mathbf{k}, \mathbf{v}_1) + nA_{SE,s}(\mathbf{k}, \mathbf{v}_1) \tag{6.7}$$

Here

$$A_{SE,s}(\mathbf{k}, \mathbf{v}_1) = \frac{\sqrt{\Sigma(k)} - 1}{n\sqrt{\Sigma(k)}} \int d\mathbf{v}_2\, \phi(v_2)\, i\mathbf{k} \cdot (\mathbf{v}_1 + \mathbf{v}_2)\, P_{12} \tag{6.8}$$

and

$$\Sigma(k) = \left\{1 + \frac{4\pi n\sigma^2}{k}\left[\chi j_1(k\sigma) + n\frac{\partial \chi}{\partial n} j_1\left(\frac{k\sigma}{2}\right)\right]\right\}^{-1} \tag{6.9}$$

are analogous to $A_s(\mathbf{k}, \mathbf{v}_1)$ and $S(k)$, respectively, in Eq. (5.29).

Thus, when $\langle a(\mathbf{v}_1)\rangle_1 = \langle b(\mathbf{v}_1)\rangle_1 = 0$ in Eq. (6.6), $F^{SE}_{ab}(\mathbf{k}, t) = F^{SE}_{ba}(\mathbf{k}, t)$ and the basic a, b symmetry is maintained in the standard Enskog theory.

However, if only $\langle b(\mathbf{v}_1)\rangle_1 = 0$ [cf. Eq. (6.6)]

$$F^{SE}_{1,b}(\mathbf{k}, t) = \frac{S(k)}{\Sigma(k)} F^{SE}_{b,1}(\mathbf{k}, t) \tag{6.10}$$

so that then the a, b symmetry is maintained in the SET only when $S(k) = \Sigma(k)$, i.e., for a finite number of k values, including $k = 0$.

5. Finally, we remark that the existence of symmetric operators $L_{E,s}$ and $L_{SE,s}$ in the RET and SET, respectively, facilitates the proof of the decay to zero of all correlation functions $F^{E}_{ab}(\mathbf{k}, t)$ and $F^{SE}_{ab}(\mathbf{k}, t)$ for large times.

A proof then involves only two steps. First, one uses that

$$\operatorname{Re} L_{E,s}(\mathbf{k}, \mathbf{v}_1) = \operatorname{Re} L_{SE,s}(\mathbf{k}, \mathbf{v}_1) = \operatorname{Re} \Lambda_E(\mathbf{k}, \mathbf{v}_1) \tag{6.11}$$

and that $\operatorname{Re} \Lambda_E(\mathbf{k}, \mathbf{v}_1)$ is a seminegative-definite operator, i.e.,[27,33]

$$\langle \psi^*(\mathbf{v}_1)[\operatorname{Re} \Lambda_E(\mathbf{k}, \mathbf{v}_1)]\, \psi(\mathbf{v}_1)\rangle_1 \leqslant 0 \tag{6.12}$$

for any $\psi(\mathbf{v}_1)$, where the equality sign only holds for $\psi(\mathbf{v}_1) = 1$.

Then one uses that the following inequality holds for all eigenvalues z_j and corresponding eigenfunctions $\psi_j(\mathbf{v}_1)$ in a spectral eigenmode decomposition of $L_{E,s}$ or $L_{SE,s}$:

$$\operatorname{Re} z_j = \frac{\langle \psi_j^*(\mathbf{v}_1)[\operatorname{Re} \Lambda_E(\mathbf{k}, \mathbf{v}_1)]\, \psi_j(\mathbf{v}_1)\rangle_1}{\langle \psi_j^*(\mathbf{v}_1)\, \psi_j(\mathbf{v}_1)\rangle_1} < 0 \tag{6.13}$$

where the equality sign is excluded since $\psi_j(\mathbf{v}_1) \neq 1$ for all eigenmodes j. Equation (6.13) implies the decay of $F^{E}_{ab}(\mathbf{k}, t)$ and $F^{SE}_{ab}(\mathbf{k}, t)$ via all its eigenmodes.

We note that a previous proof[33] of the decay of $F^{E}_{ab}(\mathbf{k}, t)$ based on $L_E(\mathbf{k}, \mathbf{v}_1)$ instead of $L_{E,s}(\mathbf{k}, \mathbf{v}_1)$ was much more involved, since in that case the right and left eigenfunctions were not the same and no direct connection, as between Eqs. (6.12) and (6.13), could be used.

Whether or not the correlation functions $F_{ab}(\mathbf{k}, t)$ for a moderately dense gas, as described by the kinetic, symmetric one-particle operator $L_B(\mathbf{k}, \mathbf{v}_1) + n^2 M(\mathbf{k}, \mathbf{v}_1)$, also decay to zero for large times is an open question.

ACKNOWLEDGMENT

We are indebted to Mrs. D. Lott for her help in preparing this manuscript.

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