Journal of Statistical Physics, Vol. 59, Nos. 3/4, 1990

Linear Quantum Enskog Equation. I. Homogeneous Quantum Fluids

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Received March 28, 1989; revision received May 22, 1989

The quantum-statistical generalization of the well-known classical, linear revised Enskog equation is derived for spatially uniform systems. This new quantum kinetic equation allows the study of equilibrium time correlation functions and their associated transport coefficients of normal quantum fluids where static correlations and degeneracy effects due to particle statistics (both are treated exactly) are important. Furthermore, we derive the quantum-statistical analog of the classical ring operator. These microscopic and systematic derivations are based on a recently developed superoperator formalism (including cluster expansion techniques) that, as a main feature, allows a clear distinction between static and dynamic correlations, which is crucial in the discussion of the Enskog approximation.

KEY WORDS: Quantum kinetic theory, linear; equilibrium time correlation functions, transport coefficients; superoperators, cluster expansion; static, dynamic, and quantum-statistical correlations; quantum Enskog equation, linear.

1. INTRODUCTION

Equilibrium time correlation functions and transport coefficients are of central interest in the modern kinetic theory of fluids near equilibrium. They provide a suitable language for the description of dynamic phenomena of many-particle systems and allow a direct comparison between theoretical and experimental results. The main objective in kinetic theory, therefore, is the microscopic evaluation of these quantities, which is equivalent to deriving linear kinetic equations from first principles, i.e., from the Schrödinger equation in the quantum case or from the Newtonian

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0022-4715/90/0500-0691$06.00/0

equations of motion in the classical regime. A well-known example of such a kinetic equation is the linear Boltzmann equation, which describes the dynamics of a dilute system. However, if one considers systems of higher density, the Boltzmann equation can no longer be used and one has to look for more general kinetic equations. By considering a dense gas of hard spheres, Enskog[1,2] was the first to propose a kinetic equation for one-particle reduced distribution functions that generalizes the Boltzmann equation to higher densities. The main feature of this Enskog equation is that, in contrast to the Boltzmann equation, it includes static (i.e., equilibrium) correlations and thereby takes account of excluded-volume effects (colliding particles cannot occupy a region of space where another particle is located). A revised (linear) version of this Enskog equation was then found by several authors[3–9] using more systematic arguments. Probably the most systematic and extensive discussion of (linear) kinetic equations of classical hard-sphere systems was given by van Beijeren and Ernst[6,7] using a diagram technique that is based on binary collision expansions in terms of pseudo-Liouville operators.[10]

It is a well-known fact that for moderately dense systems Enskog's theory gives fairly good results for transport coefficients such as the heat conductivity and the shear and bulk viscosity. The agreement with molecular dynamics calculations is within a few percent[11] and the measurements of transport coefficients in noble gases also agree fairly well with the result of Enskog's theory.[11,12],[2]

However, all these theoretical investigations are restricted to (hard-sphere) systems obeying the laws of classical mechanics. In particular, an extension of Enskog's theory to quantum system has not yet been given as far as we know, although the physical picture underlying the Enskog approximation (see below) makes sense also in the quantum regime where degeneracy effects become important. Thus, it is to be expected that in this approximation the evaluation of transport coefficients of normal quantum fluids (such as ^{3}He, ^{4}He, spin-polarized hydrogen, etc.) also leads to a good agreement between theoretical and experimental results.

It is the purpose of the present paper to fill this gap, i.e., to derive the fully quantum-statistical generalization of the linear revised Enskog equation (known from classical kinetic theory) for spatially uniform (homogeneous) systems. The extension to nonuniform fluids will be presented in a subsequent paper. The many-body system under consideration here consists of identical particles which pairwise interact via a continuous, translationally invariant, short-range potential and which obey Fermi–Dirac (FD) or Bose–Einstein (BE) statistics. The central quantities of interest

[2] For the interpretation of neutron scattering data on classical liquids with the help of Enskog's theory see also ref. 33 and the references given therein.

to us are space-independent one-particle equilibrium time correlation functions and their associated transport coefficients. For such correlation functions we shall derive a kinetic equation in the Enskog approximation which reduces to the homogeneous linear revised Enskog equation in the classical limit and for hard spheres. (Henceforth we call this equation the linear equations Enskog equation.) The same procedure leads also to transport coefficients (such as the shear viscosity and the thermal conductivity) expressed in terms of the linear quantum Enskog collision operator, denoted by B_1^{QE}. Now the aforementioned Enskog approximation is characterized by the fact that dynamic correlations are neglected (as in the Boltzmann description), and only uncorrelated binary collisions are taken into account, whereas the static correlations originating from the equilibrium distribution (i.e., from the canonical density matrix) arte treated exactly. In other words, this means that the short-time limit of the correlation function obtained in the Enskog approximation agrees with the exact correlation function at time t equal to zero. We shall briefly discuss also the opposite case where (certain) dynamic but no static correlations are retained. This will lead us to the quantum-statistical generalization of the well-known classical ring operator[13-15] (without static corrections). The simultaneous treatment of both static and dynamic correlations is also possible and will be discussed elsewhere.

The method we use is based on a powerful superoperator formalism recently developed in refs. 16–18 (hereafter denoted by I–III, respectively). The main feature of this microscopic approach is the utilization of projectors in combination with cluster expansion techniques which allow a systematic reduction of the many-body problem to a few-body problem. Thereby degeneracy effects due to particle statistics are fully taken into account by the help of a resummation procedure leading to renormalized cluster expressions.

The starting point in our evaluation of the correlation function is given by a Dyson-equation-like formula for superoperators derived in II. Rewriting this formula in a form appropriate to carrying out the Enskog approximation, we arrive at the desired result with the aid of the abovementioned resummation procedure which slightly generalizes the one extensively discussed in III. It is at this point where the advantage of our method over other formalisms (especially over the Green's function approach) fully shows up, namely the fact that dynamic and static contributions are clearly separated in our treatment, which therefore immediately allows us to identify the terms being relevant in the approximation considered. The linear quantum Enskog equation thus obtained is still quite complicated, as was, of course, to be expected in view of the nontrivial structure of its classical counterpart. This is partly due to

the fact that static correlations, which occur in the form of reduced distribution operators, still contain the full many-body Hamiltonian (as in the classical case), partly due to the noncommutability of quantum operators, and partly due to the quantum-statistical correlations resulting from FD or BE statistics. Nevertheless, a further reduction of the involved collision operator B_1^{QE} in a specific application seems to present no prohibitive difficulties and shall be considered elsewhere. It should be noted in this connection that B_1^{QE} will be given here in a form that allows a further analysis without detailed knowledge of our formalism.

The paper is organized as follows. In Section 2, basic definitions will be introduced together with a short summary of some results obtained in II and needed here. In Section 3, a linear generalized kinetic equation is derived, the memory kernel of which serves as starting point for the renormalization procedure performed in Section 4 (in the Appendix, respectively). There we also discuss the Enskog approximation that leads to the linear quantum Enskog collision operator B_1^{QE} in its most compact form [Eq. (4.18)]. In Section 5, then, going over to the Markovian limit, we arrive at the linear quantum Enskog equation [Eq. (5.13)], and at transport coefficients expressed in terms of B_1^{QE}. Section 6 deals with the Boltzmann and classical limits of B_1^{QE}. In Section 7 we sketch the derivation of the quantum analog of the classical ring operator and discuss some of its properties in connection with long-time tails of correlation functions. Some conclusions are gathered in the final Section 8.

2. EQUILIBRIUM TIME CORRELATION FUNCTION

In this section, besides introducing some definitions, we give a brief resume of some results obtained in a previous work (II) and which form the starting point for our derivation of a linear Enskog equation for normal quantum fluids.

The central quantity of interest here is the equilibrium (one-particle, one-particle) time correlation function of the form

$$C(t) = \langle a(t)b \rangle = \mathrm{Tr}\, \rho a(t) b \tag{2.1}$$

where ρ is the canonical density matrix,

$$\rho = Z^{-1} e^{-\beta H}, \qquad Z = \mathrm{Tr}\, e^{-\beta H} \tag{2.2}$$

at temperature $T = (\beta k_B)^{-1}$ (k_B is Boltzmann's constant). The system we consider consists of N identical, pairwise interacting fermions or bosons of mass m contained in a periodicity volume Ω. For notational simplicity, the spin of the particles shall not be taken into account explicitly in the

following; see, however, the remarks given in Section 8. The Hamiltonian of this system reads

$$H = H_0 + V = \sum_{i=1}^{N} H_0(i) + \sum_{1 \leqslant i < j \leqslant N} V_{ij} \tag{2.3}$$

with

$$H_0(i) = \frac{\hat{\mathbf{p}}_i^2}{2m} \tag{2.4}$$

and

$$V_{ij} = V(|\mathbf{r}_i - \mathbf{r}_j|) \tag{2.5}$$

$\hat{\mathbf{p}}_i$ is the momentum operator of the ith particle and V is a short-range pair-interaction potential that depends only on the relative coordinates of the particles i and j, i.e., the system is translationally invariant. The observables a and b are given by sums of one-particle operators, i.e.,

$$a = \sum_{i=1}^{N} a_i, \qquad b = \sum_{i=1}^{N} b_i \tag{2.6}$$

with $\langle a \rangle = 0$, which can always be achieved by replacing a by $\delta a = a - \langle a \rangle$. In this work, as mentioned before, we restrict our consideration to the spatially uniform case, i.e., to the case where a_i and b_i are only functions of the momentum operator $\hat{\mathbf{p}}_i$. Therefore a and b are diagonal in the momentum eigenstates. As a consequence, the kinetic equation governing the time evolution of the considered correlation function $C(t)$ does not contain spatially nonuniform terms (see below). The extension of the present formalism to inhomogeneous situations (arising form nondiagonal observables such as the particle density or current density operators) will be discussed in a subsequent paper. Let us also mention here (for details, see Section 5) that such homogeneous correlation functions occur, e.g., in the kinetic part of the Green–Kubo formulas for transport coefficients (such as the shear viscosity or thermal conductivity) or in forms of the fluctuation-dissipation theorem.[19,20]

The Heisenberg operator $a(t)$ is given by (we set $\hbar = 1$)

$$a(t) = e^{iHt} a e^{-iHt} = e^{iLt} a \tag{2.7}$$

In the last equation we introduced the Liouville operator L defined by $La = [H, a]$ with

$$L = L_0 + L_V = \sum_{i=1}^{N} L_0(i) + \sum_{1 \leqslant i < j \leqslant N} L_{ij} \tag{2.8}$$

where

$$L_0(i)a = [H_0(i), a] \tag{2.9}$$

$$L_{ij}a = [V_{ij}, a] \tag{2.10}$$

The Liouville operator belongs to the class of superoperators[19–21] which are formally defined as linear operators acting on ordinary Hilbert-space operators. Further superoperators will be introduced below.

Since we consider a fluid consisting of fermions (bosons), the trace occurring in Eq. (2.1) has to be taken over a complete set of anti-symmetrized (symmetrized) states, which we will choose as eigenstates of the total momentum. It is then not difficult to see [see, e.g., II, Eqs. (II2.11–17)] that this restriction due to the statistics can be avoided by introducing the projector π that (anti-)symmetrizes the product states:

$$\pi = \frac{1}{N!}\pi^{1\cdots N} = \frac{1}{N!}\sum_{\sigma \in S_N} \pi_\sigma \tag{2.11}$$

$$\pi_\sigma |\mathbf{k}_1 \cdots \mathbf{k}_N\rangle = \eta^{|\sigma|} |\mathbf{k}_{\sigma(1)} \cdots \mathbf{k}_{\sigma(N)}\rangle \tag{2.12}$$

Here,

$$|\mathbf{k}_1 \cdots \mathbf{k}_N\rangle = |\mathbf{k}_1\rangle \times \cdots \times |\mathbf{k}_N\rangle \equiv |k\rangle \tag{2.13}$$

is the direct product of single-particle momentum eigenstates. The sum in Eq. (2.11) runs over all permutations σ of N particles, and $\eta^{|\sigma|}$ equals 1 for bosons, whereas for fermions it equals 1 (-1) for even (odd) permutations σ. Using this, the correlation function (2.1) can then be rewritten as

$$C(t) = \mathrm{Tr}_1\, b_1 h_1(t) \tag{2.14}$$

where the one-particle time correlation operator $h_1(t)$ is defined by

$$h_1(t) = N\,\mathrm{Tr}_{2\cdots N}(fa)(t) \tag{2.15}$$

and correlations due to the statistics are now completely absorbed in f:

$$f = \rho\pi = \pi\rho \tag{2.16}$$

$\mathrm{Tr}_{i\cdots j} = \mathrm{Tr}_i \cdots \mathrm{Tr}_j$ denotes the trace for Boltzmann (i.e., classical) statistics. Note that in deriving Eq. (2.14) we have used the fact that $fa(t) = (fa)(t)$.

In the following we also need the Laplace transform of $C(t)$ [and $h_1(t)$] defined by

$$C(\varepsilon) = \int_0^\infty dt\, e^{-\varepsilon t} C(t), \qquad \varepsilon > 0 \tag{2.17}$$

Now. in II [see Eq. (II3.45)] we have shown, by making use of projection operators and cluster expansion techniques, that $C(\varepsilon)$ [$h_1(\varepsilon)$, respectively] can be reduced to the following form:

$$C(\varepsilon) = \mathrm{Tr}_1\, b_1 h_1(\varepsilon) \tag{2.18}$$

where

$$h_1(\varepsilon) = \frac{1}{\varepsilon - \bar{D}_1(\varepsilon)} \bar{N}_1(\varepsilon) a_1 \tag{2.19}$$

The one-particle superoperators $\bar{D}_1(\varepsilon)$ and $\bar{N}_1(\varepsilon)$ (acting on everything to their right) are given by

$$\bar{D}_1(\varepsilon) = \varepsilon N\, \mathrm{Tr}_{2\ldots N}\, \bar{P} L_V \frac{1}{\varepsilon - i\bar{Q}L} \bar{P} f \sum_{i=1}^{N} \sigma_{1i} U_1^{-1} \tag{2.20}$$

with

$$U_1 = N\, \mathrm{Tr}_{2\ldots N} f \sum_{i=1}^{N} \sigma_{1i} \tag{2.21}$$

and

$$\bar{N}_1(\varepsilon) = N\, \mathrm{Tr}_{2\ldots N}\, \bar{P}\left(1 + L_V \frac{1}{\varepsilon - i\bar{Q}L} \bar{Q}\right) f \sum_{i=1}^{N} \sigma_{1i} \tag{2.22}$$

Here the superoperator $\bar{P}$ projects onto the diagonal matrix elements of an ordinary operator y as follows:

$$(\bar{P}y)_{kk'} = y_{kk'} \delta_{\{k\},\{k'\}} \tag{2.23}$$

where $y_{kk'} = \langle k | y | k' \rangle$, and $\delta_{\{k\},\{k'\}}$ equals 1 if the sets $\{k\}$ ($= \{\mathbf{k}_1, \ldots, \mathbf{k}_N\}$) and $\{k'\}$ are equal, and 0 otherwise. The complement $\bar{Q}$ is given by $1 - \bar{P}$. For more details we refer to II (Section 2); let us only note that the occurrence of $\delta_{\{k\},\{k'\}}$ in Eq. (2.33) (instead of $\delta_{kk'}$) is a direct consequence of the FD or BE statistics. Finally, σ_{ij} is a permutation superoperator which interchanges the indices i and j. Therefore, the purely static factor U_1 also represents a superoperator.

We conclude this brief review by noting that formula (2.19) is an exact relation only in the thermodynamic limit (characterized by Ω, $N \to \infty$ with finite density $n = N/\Omega$) and holds there for all ε with $\varepsilon > 0$.

3. KINETIC EQUATION

In this section the formula (2.19) will be transformed into a kinetic equation for $h_1(t)$ containing a generalized collision operator as memory kernel. This will be achieved by some simple algebraic manipulations.

Let us first rewrite the expression $\bar{D}_1$ given in Eq. (2.20). Replacing there the last $\bar{P}$ by $1-\bar{Q}$, we find

$$D_1(\varepsilon) = D_1(\varepsilon) - \varepsilon N_1(\varepsilon) \tag{3.1}$$

with

$$D_1(\varepsilon) = N \operatorname{Tr}_{2\ldots N} PL_V \frac{\varepsilon}{\varepsilon - i\bar{Q}L} f \sum_{i=1}^{N} \sigma_{1i} U_1^{-1} \tag{3.2}$$

and

$$N_1(\varepsilon) = N \operatorname{Tr}_{2\ldots N} PL_V \frac{1}{\varepsilon - i\bar{Q}L} \bar{Q} f \sum_{i=1}^{N} \sigma_{1i} U_1^{-1} \tag{3.3}$$

Note that the first $\bar{P}$ in $\bar{D}_1$ has been replaced by the simpler projector $P = P^{1\cdots N}$, defined through

$$P^{i\cdots j} = P^i \cdots P^j, \qquad (P^s y)_{kk'} = y_{kk'} \delta_{\mathbf{k}_s \mathbf{k}'_s} \tag{3.4}$$

since $\operatorname{Tr}_{2\ldots N} \bar{P} = \operatorname{Tr}_{2\ldots N} P$. Actually, this P could even be dropped, for it results automatically due to momentum conservation (see Appendix B of I). For later convenience, however, this P is retained.

Next using (3.3) and the identity $P^1 U_1 a_1 = U_1 a_1$, which follows from momentum conservation and the fact that a_1 is diagonal (i.e., $P^1 a_1 = a_1$), we write for $\bar{N}_1(\varepsilon)$, given in Eq. (2. 22),

$$\bar{N}_1(\varepsilon) a_1 = [1 + N_1(\varepsilon)]\, U_1 a_1 \tag{3.5}$$

Insertion of (3.1) and (3.5) into (2.19) then yields

$$h_1(\varepsilon) = \frac{1}{\varepsilon[1 + N_1(\varepsilon)] - D_1(\varepsilon))} [1 + N_1(\varepsilon)]\, U_1 a_1 \tag{3.6}$$

This expression can finally be rewritten in the following form:

$$h_1(\varepsilon) = \frac{1}{\varepsilon - B_1(\varepsilon)} U_1 a_1 \tag{3.7}$$

$B_1(\varepsilon)$ is a generalized collision operator and reads explicitly

$$B_1(\varepsilon) = \frac{1}{1 + N_1(\varepsilon)} D_1(\varepsilon) \tag{3.8}$$

where $D_1(\varepsilon)$ and $N_1(\varepsilon)$ are given in Eqs. (3.2) and (3.3), respectively. The expressions (3.7) and (3.8) form our basic equations from which all the

following results will be deduced. As we shall see later, a great advantage of our generalized collision operator $B_1(\varepsilon)$ is that the dynamic correlations [coming from the ε-dependent parts in $D_1(\varepsilon)$ and $N_1(\varepsilon)$] and the static correlations (coming from the equilibrium distribution f) are clearly separated. This fact immediately allows us the indentification of those terms in $B_1(\varepsilon)$ that are relevant for obtaining the quantum-statistical analog of the classical Enskog theory.

As a preparation toward this aim, let us first transform (3.7) into a kinetic equation for $h_1(t)$. For that purpose multiply Eq. (3.7) from left with $\varepsilon - B_1(\varepsilon)$ and go back to time space. As a result, one obtains the following exact equation:

$$\frac{\partial}{\partial t} h_1(t) = \int_0^t dt'\, B_1(t')\, h_1(t-t') \tag{3.9}$$

with initial condition

$$h_1(t=0) = U_1 a_1 \tag{3.10}$$

This equation can be interpreted as a non-Markovian generalized kinetic equation for $h_1(t)$. The memory kernel $B_1(t)$ is the inverse Laplace transform of the generalized collision operator (3.8). Note that in (3.9) there is no free-streaming term of the form $iL_0(1)\, h_1(t)$ as would occur in spatially nonuniform systems (see subsequent paper). This, of course, is a direct consequence of the fact that we consider only diagonal observables a and b (being space independent), since then $h_1(t)$ is diagonal, too [i.e., $P^1 h_1(t) = h_1(t)$] and hence $L_0(1)\, h_1(t) = 0$.

In order to get a better feeling for the static factor U_1 (and its inverse U_1^{-1}) defined in (2.21), we conclude this section by briefly stating some of its properties (although they will not be needed in the following sections). Thereby we closely follow ref. 22 (see Appendix B there). First we note that U_1 can be written as

$$U_1 = f_1 + \mathrm{Tr}_2\, f_{12}\sigma_{12} \tag{3.11}$$

where the reduced distribution operator $f_{1\ldots s}$ has been introduced:

$$f_{1\ldots s} = \frac{N!}{(N-s)!}\, \mathrm{Tr}_{s+1\ldots N} f \tag{3.12}$$

Now, the second term in (3.11) also contains a one-particle part f_1 which comes about by the statistics. More explicitly, with the help of the identity $\mathrm{Tr}_i\, \pi_{ij} = \eta$ (η equals -1 for fermions and 1 for bosons) and the cluster expansion

$$f_{12} = g_{12} + \pi^{12} f_1 f_2, \qquad \pi^{12} = 1 + \pi_{12} \tag{3.13}$$

where g_{12} is the two-particle quantum correlation operator, one finds

$$U_1 = F_1 + \mathrm{Tr}_2\, g_{12}\sigma_{12} \tag{3.14}$$

Here, the superoperator F_1 applied to an ordinary operator y is defined as

$$F_1\, y = f_1\, y(1+\eta f_1) \tag{3.15}$$

As in ref. 22, we may express U_1^{-1} in terms of a quantum direct correlation operator c_{12}:

$$U_1^{-1} = F_1^{-1}(1 - \mathrm{Tr}_3\, g_{13} F_3^{-1} c_{32}) \tag{3.16}$$

which fulfills the quantum analog[22] of the classical Ornstein–Zernike relation,

$$\begin{aligned} c_{12} &= g_{12} - \mathrm{Tr}_3\, g_{13} F_3^{-1} c_{32} \\ &= g_{12} - \mathrm{Tr}_3\, c_{13} F_3^{-1} g_{32} \end{aligned} \tag{3.17}$$

This results from the fact that $U_1 U_1^{-1} = U_1^{-1} U_1 = 1$. These relations might be helpful in a further evaluation of the linear quantum Enskog collision operator to be derived below.

4. CLUSTER EXPANSION AND RENORMALIZATION OF $B_1(\epsilon)$

In this section we start the evaluation of the generalized collision operator $B_1(\varepsilon)$ by performing cluster expansions and a renormalization procedure which is necessary to take into account the effects of the FD or BE statistics properly. The aim is to extract the terms relevant for the Enskog approximation. In complete analogy to the classical hard-sphere case (see, e.g., refs. 6–8, 23, and 24) and as stated in the introduction, we mean by this approximation that in the *dynamic* part of the collision operator $B_1(\varepsilon)$ only the binary collision contribution (combined with a certain short-time limit) is retained, whereas the *static* factor f is treated exactly. In this way, all dynamic correlations between collisions are neglected, and, therefore, from this point of view, the Enskog approximation is expected to give a good description of the correlation function $C(t)$ at high densities, but only for short times.

To start with, let us now consider the following expression obtained from Eq. (3.8):

$$B_1(\varepsilon)\, h_1(\varepsilon) = \frac{1}{1+N_1(\varepsilon)}\, D_1(\varepsilon)\, h_1(\varepsilon) \tag{4.1}$$

where $h_1(\varepsilon)$ is the Laplace transform of $h_1(t)$ defined in Eq. (2.15). $D_1(\varepsilon)$ and $N_1(\varepsilon)$ are given in Eqs. (3.2) and (3.3), respectively. Now we perform a cluster expansion of the dynamic parts in $D_1(\varepsilon)$ and $N_1(\varepsilon)$, respectively. Thereby we can use the same steps that take one from Eq. (II3.5) to Eq. (II3.11) in II [see also Eq. (II3.24)]. This gives

$$D_1(\varepsilon) = \sum_{s=2}^{N} \varepsilon \operatorname{Tr}_{2\dots s} P\bar{G}_{1\dots s}(\varepsilon) \frac{N!}{(N-s)!} \operatorname{Tr}_{s+1\dots N} f \sum_{i=1}^{N} \sigma_{1i} U_1^{-1} \tag{4.2}$$

and

$$N_1(\varepsilon) = \sum_{s=2}^{N} \operatorname{Tr}_{2\dots s} P\bar{G}_{1\dots s}(\varepsilon) \frac{N!}{(N-s)!} \operatorname{Tr}_{s+1\dots N} \bar{Q} f \sum_{i=1}^{N} \sigma_{1i} U_1^{-1} \tag{4.3}$$

Here, the s-particle cluster superoperator $\bar{G}_{1\dots s}$ is given by

$$\begin{aligned} \bar{G}_{1\dots s}(\varepsilon) = iL_{12} \frac{1}{\varepsilon - i\bar{Q}(12)\, L(12)} i\bar{Q}(12)(L_{12}+L_{13}) \frac{1}{\varepsilon - i\bar{Q}(123)\, L(123)} \\ \times i\bar{Q}(123)\cdots i\bar{Q}(1\cdots s-1)(L_{1s}+\cdots+L_{s-1s}) \\ \times \frac{1}{\varepsilon - i\bar{Q}(1\cdots s)\, L(1\cdots s)} \end{aligned} \tag{4.4}$$

where $\bar{Q}(1\cdots k)$ denotes the k-particle version of $\bar{Q} = \bar{Q}(1\cdots N)$.

By expanding $[1+N_1(\varepsilon)]^{-1}$ in Eq. (4.1), we see now that in the Enskog approximation for $B_1(\varepsilon)$ the term $N_1(\varepsilon)$ is irrelevant, since it leads to dynamic contributions where at least three particles are involved [e.g., $\bar{G}_{12}(\varepsilon)\cdots\bar{G}_{13}(\varepsilon)\cdots$, etc.]. Thus, we can restrict our considerations to $D_1(\varepsilon)$ in the sequel.

At first sight one might think that in $D_1(\varepsilon)$ only the binary collision term $\bar{G}_{12}(\varepsilon)$ has to be retained in the Enskog approximation. However, as discussed in Section 4 of II and more thoroughly in Section 4 of III, the other collision terms, $\bar{G}_{1\dots s}$, $s>2$, also lead to binary-collision contributions due to the effect of the FD of BE statistics. In III it has been demonstrated with the help of exact resummations how the cluster series in $D_1(\varepsilon)$ can be cast into a renormalized form where the s-particle contributions are grouped together explicitly. This result shall now be used here, too. For that purpose, it is most convenient to exploit the following identity:

$$\left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0} f^{\lambda} = f\bar{h}(\varepsilon) \tag{4.5}$$

with the abbreviation

$$\bar{h}(\varepsilon)=\sum_{i=1}^{N}\sigma_{1i}U_1^{-1}h_1(\varepsilon)=\sum_{i=1}^{N}U_i^{-1}h_i(\varepsilon) \tag{4.6}$$

The generalized distribution operator f^{λ} is defined as

$$f^{\lambda}=Z^{-1}(\lambda)e^{-\beta H}e^{\lambda\bar{h}(\varepsilon)}\pi, \qquad Z(\lambda)=\mathrm{Tr}\, e^{-\beta H}e^{\lambda\bar{h}(\varepsilon)} \tag{4.7}$$

To check the validity of Eq. (4.5), one has to take into account that $\mathrm{Tr}\,\rho\bar{h}(\varepsilon)$ vanishes:

$$\mathrm{Tr}\,\rho\bar{h}(\varepsilon)=\frac{1}{N}\mathrm{Tr}_1\, U_1U_1^{-1}h_1(\varepsilon)=\frac{1}{N}\mathrm{Tr}_1\, h_1(\varepsilon)=\frac{1}{\varepsilon}\langle a\rangle=0 \tag{4.8}$$

In the first equality we have used that Tr can be replaced by $\mathrm{Tr}_{1\cdots N}\pi$ [see the transition from Eq. (2.1) to Eq. (2.14)] and Eq. (2.21). The third equality follows from the identity $\mathrm{Tr}_{i\cdots j}L(i\cdots j)\ldots=0$.

Furthermore, in analogy to Eq. (3.12), we define

$$f_{1\cdots s}^{\lambda}=\frac{N!}{(N-s)!}\mathrm{Tr}_{s+1\cdots N}f^{\lambda} \tag{4.9}$$

Using this and the identity (4.5), we can rewrite $B_1(\varepsilon)\,h_1(\varepsilon)$ as follows:

$$B_1(\varepsilon)\,h_1(\varepsilon)=\frac{1}{1+N_1(\varepsilon)}\frac{\partial}{\partial\lambda}\bigg|_{\lambda=0}d_1^{\lambda}(\varepsilon) \tag{4.10}$$

with

$$d_1^{\lambda}(\varepsilon)=\sum_{s=2}^{\infty}\varepsilon\,\mathrm{Tr}_{2\cdots s}P^{1\cdots s}\bar{G}_{1\cdots s}(\varepsilon)f_{1\cdots s}^{\lambda} \tag{4.11}$$

Note that $d_1^{\lambda}(\varepsilon)$ is an ordinary operator.

Next, performing a cluster expansion of $f_{1\cdots s}^{\lambda}$ and making use of the renormalization procedure discussed in III, we show in Appendix A that (4.11) reduces to the following expression in the Enskog approximation:

$$d_1^{\lambda}(\varepsilon)=-\frac{1}{2}\mathrm{Tr}_2\,P^{12}\hat{T}_{12}^{\lambda}(\varepsilon)\frac{\varepsilon}{\varepsilon-iL_0(12)}f_{12}^{\lambda}+\mathrm{DTC} \tag{4.12}$$

with the renormalized Liouville t-matrix defined by

$$\hat{T}_{12}^{\lambda}(\varepsilon)=-i\pi^{12}L_{12}\frac{1}{\varepsilon-i\hat{L}(12;\lambda)}[\varepsilon-iL_0(12)] \tag{4.13}$$

Here, $\pi^{12} = 1 + \pi_{12}$, and the renormalized Liouville operator $\hat{L}(12; \lambda)$ is defined by

$$\hat{L}(12; \lambda) = L_0(12) + \hat{L}_{12}^{\lambda} \tag{4.14}$$

$$\hat{L}_{12}^{\lambda} y = S_{12}^{\lambda} V_{12} y - y V_{12} S_{12}^{\lambda} \tag{4.15}$$

where the quantum-statistical weighting operator[18,22,25,26] S_{12}^{λ} is of the form

$$S_{12}^{\lambda} = 1 + \eta f_1^{\lambda} + \eta f_2^{\lambda} \tag{4.16}$$

DTC denotes the dynamic triple (or higher) collision terms.

The last step in our Enskog approximation consists in replacing the free resolvent $\varepsilon/[\varepsilon - iL_0(12)]$ occurring in (4.12) by its large-ε (i.e., short-time) limit 1; thereby the corrections of order ε^{-1} are omitted. Since we are interested in systems of arbitrarily strongly interacting particles, the t-matrix $\hat{T}_{12}^{\lambda}(\varepsilon)$ occurring in (4.12), however, must be fully retained and cannot be expanded in powers of ε^{-1}, i.e., in powers of the interaction Liouvillian $\hat{L}_{12}^{\lambda}$. Apart from this, it should be noted that the large-ε limit of $\hat{T}_{12}^{\lambda}(\varepsilon)$ (i.e., $-i\pi^{12}L_{12}$) would lead to a vanishing contribution when static correlations are neglected in Eq. (4.12) (since then $\bar{P}L_{12}\bar{P} = 0$). That means one would not obtain the Boltzmann equation in this case, which, of course, stands in contrast to the natural requirement that this equation should follow from the more general Enskog equation in the limit of no static correlations (see Section 6).

Under these conditions our result is valid for very short times, being much shorter than the mean free time τ_m between collisions. We note that such a short-time limit also has to be introduced in the derivation of the Enskog equation for classical hard-sphere systems.[3-8] The new feature here is that the binary collision operator $\hat{T}_{12}^{\lambda}(\varepsilon)$ is ε dependent (due to the finite duration of a collision), whereas the corresponding classical hard-sphere quantity,[10] describing instantaneous collisions, does not depend on ε.

Therefore, the final form of the generalized collision operator $B_1(\varepsilon)$ reads in the Enskog approximation

$$B_1(\varepsilon)\, h_1(\varepsilon) = B_1^{\mathrm{QE}}(\varepsilon)\, h_1(\varepsilon) + \mathrm{DTC} \tag{4.17}$$

where

$$B_1^{\mathrm{QE}}(\varepsilon)\, h_1(\varepsilon) = -\frac{\partial}{\partial \lambda}\bigg|_{\lambda = 0} \frac{1}{2} \mathrm{Tr}_2\, P^{12} \hat{T}_{12}^{\lambda}(\varepsilon) f_{12}^{\lambda} \tag{4.18}$$

$B_1^{\mathrm{QE}}(\varepsilon)$ is the linear quantum Enskog collision operator given in its most compact form. More explicit representations of $B_1^{\mathrm{QE}}(\varepsilon)$ are given below. In

Section 6, we shall see that in the classical limit (and for $\varepsilon \to 0^+$), $B_1^{\mathrm{QE}}(\varepsilon)$ reduces to the revised linear classical Enskog collision operator (for hard spheres) well known in the literature.[6,7]

In the next sections we shall use our collision operator (4.18) for the derivation of a linear quantum Enskog equation and for the calculation of transport coefficients. This means that we have to assume that (4.18) can be used outside the time regime for which it has been derived. This seems to be a reasonable assumption in view of the fact that in classical Enskog theory such an extension of the time regime leads to very good agreement with experimental data.[8]

5. LINEAR QUANTUM ENSKOG EQUATION

Using the above results, it is now an easy matter to derive the linear quantum Enskog equation for $h_1(t)$. Before doing so, let us first write down a more explicit form of $B_1^{\mathrm{QE}}(\varepsilon)$ given in Eq. (4.18). For this we need the derivatives of f_1^λ, f_{12}^λ, and $\hat{T}_{12}^\lambda(\varepsilon)$ with respect to λ. By means of Eqs. (4.5), (4.6), and (4.9) they are easily found to be

$$\left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0} f_1^\lambda = h_1(\varepsilon) \tag{5.1}$$

$$\left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0} f_{12}^\lambda = [f_{12}(1+\sigma_{12}) + \mathrm{Tr}_3 f_{123}\sigma_{13}]\, U_1^{-1} h_1(\varepsilon) \tag{5.2}$$

and

$$\left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0} \hat{T}_{12}^\lambda(\varepsilon) = \hat{T}_{12}(\varepsilon)\frac{1}{\varepsilon - iL_0(12)} iL_{12}^\eta[h_1(\varepsilon)]\frac{1}{\varepsilon - i\hat{L}(12)}[\varepsilon - iL_0(12)] \tag{5.3}$$

where $\hat{T}_{12}(\varepsilon) = \hat{T}_{12}^{\lambda=0}(\varepsilon)$ and $\hat{L}(12) = \hat{L}(12;\ \lambda = 0)$. The new superoperator $L_{12}^\eta[y_1]$, applied to an arbitrary operator a, is defined as

$$L_{12}^\eta[y_1]a = \eta(y_1 + y_2)V_{12}a - aV_{12}\eta(y_1 + y_2) \tag{5.4}$$

y_1 (and $y_2 = \sigma_{12}y_1$) is also an arbitrary one-particle operator. Note that $L_{12}^\eta[\cdot]$ is of purely quantum-statistical nature and vanishes therefore in the classical limit (i.e., for $\eta = 0$). Collecting these results, we find for $B_1^{\mathrm{QE}}(\varepsilon)$

$$B_1^{\mathrm{QE}}(\varepsilon) = B_1^{\mathrm{QE,cl}}(\varepsilon) + B_1^{\mathrm{QE},\eta}(\varepsilon) \tag{5.5}$$

with

$$B_1^{\mathrm{QE,cl}}(\varepsilon) = -\frac{1}{2}\mathrm{Tr}_2\, P^{12}\hat{T}_{12}(\varepsilon)[f_{12}(1+\sigma_{12}) + \mathrm{Tr}_3 f_{123}\sigma_{13}]\, U_1^{-1} \tag{5.6}$$

and

$$B_1^{\mathrm{QE},\eta}(\varepsilon) = -\frac{1}{2}\,\mathrm{Tr}_2\, P^{12} iL_{12}\,\frac{1}{\varepsilon - i\hat{L}(12)}\, iL_{12}^{\eta}[\,\cdot\,]\,\frac{1}{\varepsilon - i\hat{L}(12)}\,[\varepsilon - iL_0(12)]\, f_{12} \tag{5.7}$$

As suggested by the superscripts, $B_1^{\mathrm{QE,cl}}(\varepsilon)$ represents the quantum analog of the revised linear classical Enskog collision operator (see Section 6), whereas $B_1^{\mathrm{QE},\eta}(\varepsilon)$ results from purely quantum-statistical effects and therefore has no classical counterpart. Note also that the static correlations, represented by f and U_1^{-1}, are exact in the sense that they contain the full many-body Hamiltonian. In contrast to this, the dynamic part contains only two-particle Liouville operators, in which, however, the influence of the other particles via the quantum statistics is taken into account through the statistical weighting factor S_{12} [$=S_{12}^{\lambda=0}$; see Eq. (4.16)] occurring in $\hat{L}(12)$.

We remark that if one wants to express $B_1^{\mathrm{QE}}(\varepsilon)$ in terms of the more familiar ordinary Hilbert-space operators (instead of superoperators), it is more convenient to do so before performing the derivative in Eq. (4.18) with respect to λ. As a matter of fact, $\hat{T}_{12}^{\lambda}(\varepsilon)$ can directly be expressed in terms of the exchange-modified t-matrix as shown in II [see Eq. (IID.13)]. As a consequence, $B_1^{\mathrm{QE}}(\varepsilon)$ may also be written as

$$\begin{aligned} B_1^{\mathrm{QE}}(\varepsilon)\, h_1(\varepsilon) = \frac{\partial}{\partial\lambda}\bigg|_{\lambda=0} \frac{i}{2\pi}\int_{-\infty}^{+\infty} dE\, \mathrm{Tr}_2\, P^{12} \\ \times \{\hat{t}_{12}^{-}(E^-;\lambda)[f_{12}^{\lambda}\, g_{12}^{0}(E^+) + g_{12}^{0}(E^-)\, f_{12}^{\lambda}] \\ - [f_{12}^{\lambda}\, g_{12}^{0}(E^+) + g_{12}^{0}(E^-)\, f_{12}^{\lambda}]\hat{t}_{12}^{+}(E^+;\lambda) \\ - i\hat{t}_{12}^{-}(E^-;\lambda)[f_{12}^{\lambda}\, g_{12}^{0}(E^+) + g_{12}^{0}(E^-) f_{12}^{\lambda}] \\ \times \hat{t}_{12}^{+}(E^+;\lambda)\, S_{12}^{\lambda}[g_{12}^{0}(E^+) + g_{12}^{0}(E^-)]\} \end{aligned} \tag{5.8}$$

Here, $\hat{t}_{12}^{\pm}(E^{\pm};\lambda)$ is the exchange-modified t-matrix (see, e.g., ref. 25) defined as

$$\hat{t}_{12}^{-}(E^-;\lambda) = V_{12}\,\frac{1}{\varepsilon/2 - i[\hat{H}(12;\lambda) - E]}\left\{\frac{\varepsilon}{2} - i[H_0(12) - E]\right\} \tag{5.9}$$

and $\hat{t}_{12}^{+}(E^+;\lambda) = [\hat{t}_{12}^{-}(E^-;\lambda)]^+$, where $E^{\pm} = E \pm i\varepsilon/2$. The new Hamiltonian $\hat{H}(12;\lambda)$ (which is not self-adjoint) is given by

$$\hat{H}(12;\lambda) = H_0(12) + S_{12}^{\lambda} V_{12} \tag{5.10}$$

Here $g_{12}^0(E^{\pm})$ is a free propagator and reads

$$g_{12}^0(E^{\pm}) = \frac{1}{\varepsilon/2 \pm i[H_0(12) - E]} \tag{5.11}$$

Note that $\frac{1}{2}\pi^{12}$ has been absorbed in f_{12}^{λ} since $\frac{1}{2}\pi^{12} f_{12}^{\lambda} = f_{12}^{\lambda}$.

The representation (5.8) should be well suited for an approximate treatment of $B_1^{\mathrm{QE}}(\varepsilon)$ as given, e.g., by a scattering length expansion of $\hat{t}_{12}^{\pm}$. This, however, shall not be further discussed in this work. Finally, let us note that in the Boltzmann limit, (5.8) reduces to the linear quantum Boltzmann collision operator (see Section 6).

Next, we shall determine the kinetic equation for $h_1(t)$ in the Enskog approximation. For this we insert (4.17) into (3.9), which yields

$$\frac{\partial}{\partial t} h_1(t) = \int_0^t dt' \, B_1^{\mathrm{QE}}(t') \, h_1(t - t') + \mathrm{DTC} \tag{5.12}$$

where $B_1^{\mathrm{QE}}(t)$ is the inverse Laplace transform of $B_1^{\mathrm{QE}}(\varepsilon)$. With the initial condition (3.10) for $h_1(t)$ and with $B_1^{\mathrm{QE}}(\varepsilon)$ given in Eqs. (4.18), (5.5), or (5.8), respectively, this non-Markovian kinetic equation determines $h_1(t)$ within the Enskog approximation.

An interesting limiting case of this equation is obtained in the Markovian limit.[3] This limit makes sense if the kernel $B_1^{\mathrm{QE}}(t)$ decays rapidly to zero for times larger than a typical binary collision time τ_c. We shall now assume that this condition is fulfilled here. One may then extend the upper limit of the time integral to infinity with negligible error and expand $h_1(t - t')$ around t. Thereby only the first term, $h_1(t)$, must be retained in the Enskog approximation, since the other terms (describing retardation efects due to the finite duration of a collision) lead to dynamic processes involving at least three particles. Thus, we eventually arrive at (dropping now the term DTC)

$$\frac{\partial}{\partial t} h_1(t) = B_1^{\mathrm{QE}} h_1(t) \tag{5.13}$$

with

$$B_1^{\mathrm{QE}} = \lim_{\varepsilon \to 0^+} B_1^{\mathrm{QE}}(\varepsilon) \tag{5.14}$$

where $B_1^{\mathrm{QE}}(\varepsilon)$ is given in (4.18) or more explicitly in (5.5) or (5.8). This equation, together with the initial condition (3.10), is now interpreted as

[3] As mentioned at the end of Section 4, Eq. (5.12) shall now be considered for times t outsides the time regime for which it has been derived, in particular for $t \gtrsim \tau_m \gg \tau_c$.

the linear quantum Enskog equation for the equilibrium one-particle time correlation operator $h_1(t)$. It represents the generalization of the revised linear classical Enskog equation for hard-sphere systems (see Section 6) to a normal quantum fluid consisting of fermions or bosons which interact via a continuous short-range potential. It is also worth mentioning in this connection that our Enskog operator B_1^{QE} as, e.g., given in Eq. (5.8) includes the possibility of bound states resulting from short-range attractive forces between the particles.

We conclude this section by giving the Green–Kubo formula for transport coefficients in the Enskog approximation. First we note that for spatially uniform microscopic currents the general form of a transport coefficient is given by (see ref. 20, p. 85)

$$\lambda_{ab} = \frac{\beta}{2\Omega} \int_0^\infty dt \, \langle [\delta a(t) b + b \delta a(t)] \rangle \tag{5.15}$$

with $\delta a = a - \langle a \rangle$. Under the assumption that the observables a and b are self-adjoint, (5.15) can also be written as

$$\lambda_{ab} = \frac{\beta}{\Omega} \lim_{\varepsilon \to 0^+} \mathrm{Re}\, C(\varepsilon) \tag{5.16}$$

Here, Re means real part and $C(\varepsilon)$ is the equilibrium correlation function given in Eqs. (2.17) and (2.1), respectively. Making use of Eqs. (2.18), (3.7), and (4.17), one immediately obtains the transport coefficient λ_{ab} in the Enskog approximation:

$$\lambda_{ab}^{\mathrm{QE}} = \frac{\beta}{\Omega} \lim_{\varepsilon \to 0^+} \mathrm{Re}\, C^{\mathrm{QE}}(\varepsilon) \tag{5.17}$$

with

$$C^{\mathrm{QE}}(\varepsilon) = \mathrm{Tr}_1 \, b_1 \frac{1}{\varepsilon - B_1^{\mathrm{QE}}(\varepsilon)} U_1 a_1 \tag{5.18}$$

where the linear quantum Enskog collision operator $B_1^{\mathrm{QE}}(\varepsilon)$ is given in either (4.18), (5.5), or (5.8). U_1 is defined in (2.21) [see also (3.11) and (3.14)]. As physical examples for $\lambda_{ab}^{\mathrm{QE}}$ we mention the kinetic parts of the shear viscosity and of the thermal conductivity, respectively. The former quantity is obtained by setting

$$a = b = \frac{1}{m} \sum_{i=1}^{N} \hat{p}_{ix} \hat{p}_{iy} \tag{5.19}$$

in λ_{ab}, whereas the latter follows from the choice

$$a = b = \frac{1}{2m^2\sqrt{T}} \sum_{i=1}^{N} \hat{\mathbf{p}}_i^2 \hat{\mathbf{p}}_i \tag{5.20}$$

Note that the case $a = \sum_{i=1}^{N} \hat{\mathbf{p}}_i$ is excluded because the total momentum is a conserved quantity in our system [i.e., $a(t) = a$ for all times], which leads to a time-independent correlation function.

6. BOLTZMANN LIMIT AND CLASSICAL LIMIT OF B_1^{QE}

In this section we shall briefly discuss two limiting cases of the linear quantum Enskog equation (5.13). The first case we consider is the Boltzmann approximation, in which B_1^{QE} reduces to the linear quantum Boltzmann collision operator. Since this case has been treated in Section 4 of II, we can be very brief here. The starting point is Eq. (4.18). The Boltzmann approximation of B_1^{QE} is obtained by simply neglecting all static correlations in B_1^{QE}, which amounts to replacing f_{12}^{λ} by $\pi^{12} f_1^{0,\lambda} f_2^{0,\lambda}$, where $f_i^{0,\lambda}$ $(= P^i f_i^{0,\lambda})$ is equal to f_i^{λ} [see Eqs. (4.7) and (4.9)], but with the interaction V put equal to zero. The f's occurring in $\hat{T}_{12}^{\lambda}$ are also to be replaced by f^0. On comparing the resulting expression with Eq. (II4.12) obtained in II and making use of Eq. (II4.20), we arrive at the announced result:

$$\begin{aligned}
[B_1^{\mathrm{QE}} h_1(\varepsilon)]_{\mathbf{k}_1\mathbf{k}_1} &\overset{\rightarrow}{=} \frac{\partial}{\partial\lambda}\bigg|_{\lambda=0} \lim_{\varepsilon\to 0^+} [-\mathrm{Tr}_2\, P^{12} \hat{T}_{12}^{\lambda}(\varepsilon) P^{12} f_1^{0,\lambda} f_2^{0,\lambda}]_{\mathbf{k}_1\mathbf{k}_1} \\
&= -4\pi \sum_{\mathbf{k}_2,\mathbf{k}_1',\mathbf{k}_2'} \hat{\tau}(\mathbf{k}_1\mathbf{k}_2;\mathbf{k}_1'\mathbf{k}_2') \\
&\quad \times (1+\eta f_{\mathbf{k}_1}^0)(1+\eta f_{\mathbf{k}_2}^0) f_{\mathbf{k}_1'}^0 f_{\mathbf{k}_2'}^0 [\tilde{h}_1(\varepsilon;\mathbf{k}_1) \\
&\quad + \tilde{h}_1(\varepsilon;\mathbf{k}_2) - \tilde{h}_1(\varepsilon;\mathbf{k}_1') - \tilde{h}_1(\varepsilon;\mathbf{k}_2')]
\end{aligned} \tag{6.1}$$

where we have introduced the following abbreviations:

$$\begin{aligned}
&\hat{\tau}(\mathbf{k}_1\mathbf{k}_2;\mathbf{k}_1'\mathbf{k}_2') \\
&\quad = |\langle \mathbf{k}_1\mathbf{k}_2|\, \hat{t}_{12}^{-}(\varepsilon_{\mathbf{k}_1}+\varepsilon_{\mathbf{k}_2})\, \tfrac{1}{2}(1+\pi_{12})\, |\mathbf{k}_1', \mathbf{k}_2'\rangle|^2\, \delta(\varepsilon_{\mathbf{k}_1}+\varepsilon_{\mathbf{k}_2}-\varepsilon_{\mathbf{k}_1'}-\varepsilon_{\mathbf{k}_2'})
\end{aligned} \tag{6.1a}$$

and $\tilde{h}_1(\varepsilon;\mathbf{k}_1) = \langle \mathbf{k}_1|\, \tilde{h}_1(\varepsilon)\, |\mathbf{k}_1\rangle$ with $\tilde{h}_1(\varepsilon) = h_1(\varepsilon)[(1+\eta f_1^0) f_1^0]^{-1}$; $f_{\mathbf{k}_1}^0 = \langle \mathbf{k}_1|\, f_1^0\, |\mathbf{k}_1\rangle$ is the FD or BE distribution [see also Eq. (II3.56)]. The scattering cross section is determined by the exchange-modified t-matrix

$$\hat{t}_{12}^{-}(E) = \lim_{\varepsilon\to 0^+} \hat{t}_{12}^{-}(E^-;\lambda=0)$$

which is a functional of f_1^0 and f_2^0 [see Eq. (5.9)]. This linear quantum

Boltzmann collision operator was first obtained by Boercker and Dufty.[22] For the nonlinear version of (6.1) we refer the interested reader to III (see Section 5 there).

Let us now discuss the classical limit of Eq. (5.13) with $B_1^{\mathrm{QE}}(\varepsilon)$ given in Eqs. (5.5)–(5.7). First we note that for Boltzmann (i.e., classical) statistics $B_1^{\mathrm{QE},\eta}(\varepsilon)$ vanishes because in this case we can put $\eta = 0$. The remaining part, $B_1^{\mathrm{QE,cl}}(\varepsilon)$, reduces to

$$B_1^{\mathrm{QE,cl}}(\varepsilon)\, h_1(\varepsilon) \rightleftarrows -\mathrm{Tr}_2\, P^{12} T_{12}(\varepsilon)[\rho_{12}(1+\sigma_{12}) + \mathrm{Tr}_3\, \rho_{123}\sigma_{13}]](U_1^{\mathrm{B}})^{-1}\, h_1^{\mathrm{B}}(\varepsilon) \tag{6.2}$$

since for Boltzmann statistics

$$f \rightleftarrows \rho, \qquad f_{1\ldots s} \rightleftarrows \rho_{1\ldots s} = \frac{N!}{(N-s)!}\,\mathrm{Tr}_{s+1\ldots N}\rho \tag{6.3}$$

and

$$\hat{T}_{12}(\varepsilon) \rightleftarrows T_{12}(\varepsilon) = -iL_{12}\,\frac{1}{\varepsilon - iL(12)}\,[\varepsilon - iL_0(12)] \tag{6.4}$$

U_1^{B} and $h_1^{\mathrm{B}}(\varepsilon)$ are equal to U_1 and $h_1(\varepsilon)$, respectively, with f replaced by ρ. Of course, the semiclassical quantities (6.2)–(6.4) are still quantum operators. A further simplification of (6.2) occurs in the completely classical limit (i.e., $\hbar \to 0$), which, as usual (see, e.g., ref. 19, p. 149), is obtained by simply replacing the quantum operators by their classical counterparts and the trace operation by a phase space integral. Thus, (6.2) obviously reduces to the classical expression:

$$\begin{aligned} B^{\mathrm{E,cl}}(\varepsilon; \mathbf{p}_1)\, h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1) &= -\int dx_2\, T_{12}^{\mathrm{cl}}(\varepsilon)[\rho_2^{\mathrm{cl}}(x_1, x_2)(1+\sigma_{12}) \\ &\quad + \int dx_3\, \rho_3^{\mathrm{cl}}(x_1, x_2, x_3)\sigma_{13}][U_1^{\mathrm{cl}}]^{-1}\, h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1) \end{aligned} \tag{6.5}$$

with the following notations: $T_{12}^{\mathrm{cl}}(\varepsilon)$ is equal to $T_{12}(\varepsilon)$ given in (6.4), but with $L(12)$ replaced by the classical Liouville operator $L^{\mathrm{cl}}(12) = L_0^{\mathrm{cl}}(12) + L_{12}^{\mathrm{cl}}$, where

$$L_0^{\mathrm{cl}}(12) = -\frac{i}{m}\left(\mathbf{p}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{p}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2}\right) \tag{6.6}$$

$$L_{12}^{\mathrm{cl}} = i\,\frac{\partial V_{12}}{\partial \mathbf{r}_1}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right) \tag{6.7}$$

$x_i = (\mathbf{r}_i, \mathbf{p}_i)$ denotes position and momentum of the ith particle. The canonical distribution function is given by

$$\rho^{\mathrm{cl}}(x) = \varphi_0(p)\, \rho_V(r) \tag{6.8}$$

with $x = (x_1, ..., x_N)$, etc., and where $\varphi_0(p) = \varphi_0(\mathbf{p}_1) \cdots \varphi_0(\mathbf{p}_N)$ is the Maxwell–Boltzmann distribution

$$\varphi_0(\mathbf{p}) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left(-\frac{\beta}{2m}\mathbf{p}^2\right) \tag{6.9}$$

The configurational part reads

$$\rho_V(r) = Q^{-1} e^{-\beta V}, \qquad Q = \int dr\, e^{-\beta V} \tag{6.10}$$

ρ_s^{cl} denotes the reduced distribution function:

$$\rho_s^{\mathrm{cl}}(x_1, ..., x_s) = \varphi_0(\mathbf{p}_1, ..., \mathbf{p}_s)\, n_s(\mathbf{r}_1, ..., \mathbf{r}_s) \tag{6.11}$$

with

$$n_s(\mathbf{r}_1, ..., \mathbf{r}_s) = \frac{N!}{(N-s)!} \int d\mathbf{r}_{s+1} \cdots d\mathbf{r}_N\, \rho_V(r) \tag{6.12}$$

The classical version of U_1 is then found to be

$$U_1^{\mathrm{cl}} = n\varphi_0(\mathbf{p}_1) + \int dx_2\, \varphi_0(\mathbf{p}_1, \mathbf{p}_2)\, n_2(\mathbf{r}_1, \mathbf{r}_2)\sigma_{12} \tag{6.13}$$

Finally, the function $h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1)$ is the classical limit of $h_1(\varepsilon)$ defined in Eq. (2.15) and is given by

$$h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1) = N \int dx_2 \cdots dx_N \frac{1}{\varepsilon - iL^{\mathrm{cl}}} \rho^{\mathrm{cl}}(x)\, a^{\mathrm{cl}}(p) \tag{6.14}$$

with $a^{\mathrm{cl}}(p) = \sum_{i=1}^{N} a_i^{\mathrm{cl}}(\mathbf{p}_i)$ the classical limit of a. Note that $h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1)$ is space independent, since $a^{\mathrm{cl}}(p)$ depends only on the momenta. A further consequence of this spatial uniformity is that $(U_1^{\mathrm{cl}})^{-1} h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1)$ reduces to a particularly simple form:

$$[U_1^{\mathrm{cl}}]^{-1} h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1) = [n\varphi_0(\mathbf{p}_1)]^{-1} h^{\mathrm{cl}}(\varepsilon; \mathbf{p}_1) \tag{6.15}$$

as can be seen by iterating $[U_1^{\mathrm{cl}}]^{-1}$ around $[n\varphi_0(\mathbf{p}_1)]^{-1}$ once and making use of the fact that

$$\int d\mathbf{p}\, h^{\mathrm{cl}}(\varepsilon; \mathbf{p}) = \frac{n}{\varepsilon} \langle a^{\mathrm{cl}}(p) \rangle_{\mathrm{cl}} = 0 \tag{6.16}$$

where $\langle \cdot \rangle_{\mathrm{cl}}$ denotes the classical phase average in the canonical ensemble. Moreover, using again (6.16), we see that the second term in (6.5) vanishes. Thus, introducing the pair correlation function

$$v_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{n^2} - 1 \tag{6.17}$$

we finally arrive at the folowing classical kinetic equation for $h^{\mathrm{cl}}(t; \mathbf{p}_1)$ [(see Eq. (5.13)]:

$$\frac{\partial}{\partial t} h^{\mathrm{cl}}(t; \mathbf{p}_1) = B^{\mathrm{E,cl}}(\mathbf{p}_1)\, h^{\mathrm{cl}}(t; \mathbf{p}_1) \tag{6.18}$$

with

$$B^{\mathrm{E,cl}}(\mathbf{p}_1) = \lim_{\varepsilon \to 0^+} B^{\mathrm{E,cl}}(\varepsilon; \mathbf{p}_1) \tag{6.19}$$

$$B^{\mathrm{E,cl}}(\varepsilon; \mathbf{p}_1) = -n \int dx_2\, T_{12}^{\mathrm{cl}}(\varepsilon)[1 + v_2(\mathbf{r}_1, \mathbf{r}_2)](1 + \sigma_{12})\, \varphi_0(\mathbf{p}_2) \tag{6.20}$$

The initial condition simply reads [see Eq. (3.12) and use that $\langle a^{\mathrm{cl}}(p) \rangle_{\mathrm{cl}} = 0$]

$$h^{\mathrm{cl}}(t = 0; \mathbf{p}_1) = n\varphi_0(\mathbf{p}_1)\, a_1^{\mathrm{cl}}(\mathbf{p}_1) \tag{6.21}$$

The kinetic equation (6.18) represents the revised linear classical Enskog equation for the spatially uniform equilibrium one-particle, one-particle time correlation function $h^{\mathrm{cl}}(t; \mathbf{p}_1)$ as obtained by van Beijeren[6] and van Beijeren and Ernst.[7] Indeed, if we redefine our quantities $h^{\mathrm{cl}}(t; \mathbf{p}_1)$ and $B^{\mathrm{E,cl}}(\mathbf{p}_1)$ as $\varphi_0^{-1}(\mathbf{p}_1)\, h^{\mathrm{cl}}(t; \mathbf{p}_1)$ and $\varphi_0^{-1}(\mathbf{p}_1)\, B^{\mathrm{E,cl}}(\mathbf{p}_1)$, respectively, we see that for space-independent correlation functions the linear Enskog equation obtained by these authors [see, e.g., Eqs. (8.16) and (11.3) of ref. 6] formally agrees with our expression (6.20). The only difference is that these authors consider hard-sphere systems and that therefore their Enskog collision operator contains the hard-sphere binary collision operator $T_{12}^{\text{hard sphere}}$, whereas in our formalism the binary collision operator $T_{12}^{\mathrm{cl}}(\varepsilon)$ for continuous interaction potentials occurs:

$$T_{12}^{\mathrm{cl}}(\varepsilon) = -iL_{12}^{\mathrm{cl}} \frac{1}{\varepsilon - iL^{\mathrm{cl}}(12)} [\varepsilon - iL_0^{\mathrm{cl}}(12)] \tag{6.22}$$

This quantity is well known in classical kinetic theory[27,13,14] and reduces to $T_{12}^{\text{hard sphere}}$ for hard-sphere interaction.[4,34]

We note that for hard-sphere interactions the pair correlation function $v_2(\mathbf{r}_1 - \mathbf{r}_2)$ can be shifted to the left of $T_{12}^{\text{hard sphere}}$ with the result that

$v_2(\mathbf{r}_1-\mathbf{r}_2)$ is evaluated at $|\mathbf{r}_1-\mathbf{r}_2|=\sigma$ (σ is the hard-sphere diameter).[8] The expression thus obtained represents a form of the linear revised hard-sphere Enskog collision operator as usually used in the literature. Such a shifting of v_2, however, does not seem to be possible for more general potentials considered here.

Finally, it should be noted that due to the noncommutability of quantum operators, the linear semiclassical Enskog collision operator (6.2) contains static correlations (originating from ρ_{123} and U_1^{-1}) which vanish in the classical limit (6.20). But we emphasize again that this simplification of (6.5) to (6.20) due to the spatial uniformity of $h^{\mathrm{cl}}(t;\mathbf{p}_1)$ no longer occurs when $h^{\mathrm{cl}}(t;\mathbf{p}_1)$ becomes space dependent. In this latter case the demonstration of the equivalence between the classical limit of the linear quantum Enskog operator obtained in our formalism and the classical hard-sphere result derived in refs. 6 and 7 is then more involved, as we shall see in a subsequent paper.

7. QUANTUM RING OPERATOR

Up to now dynamic correlations due to s-particle collisions ($s\geqslant 3$) have been neglected; only static correlations originating from the canonical density matrix have been retained, including the many-particle effects due to the FD or BE statistics. Therefore, to obtain a better description for long times, dynamic correlations also have to be taken into account. However, as is well known from the classical[13] or semiclassical[16] case, these dynamic contributions cannot be obtained by simply retaining a few terms in the cluster series occurring, e.g., in (4.2). [Note that apart from the effects due to the FD or BE statistics, only $\bar{G}_{12}(\varepsilon)$ was needed in (4.2) to get the linear quantum Enskog equation.] The reason for this is that for small ε (which corresponds to long times) the dynamic clusters $\bar{G}_{1\ldots s}(\varepsilon)$ contain divergent contributions for $s\geqslant 4$ (in 3 dimensions).[4] In the classical or semiclassical case the strongest divergences are believed to come from the so-called ring events consisting of sequences of s collisions among s particles for $s\geqslant 3$. Therefore, well-defined expressions (as $\varepsilon\to 0^+$) with dynamic correlations from s-particle collisions ($s\geqslant 4$) can only be expected after having performed partial resummations of the relevant, i.e., most divergent terms. In the classical case the resummation of the ring events leads then to the ring collision operator[13–15,28] describing the mode-coupling effects in a fluid. The generalization of this quantity to the semi-

[4] The finite term $\bar{G}_{123}(\varepsilon)$ [$\hat{G}_{123}(\varepsilon)$, respectively], which would contribute to the quantum generalization of the Choh–Uhlenbeck correction, shall not be considered here separately and will therefore simply be included in the following ring summation.

classical case was derived in I, but only for the self-diffusion correlation function, obtained from Eq. (2.1) when one puts $a = b = \hat{\mathbf{p}}_1$.

We shall now briefly present the extension of this result to the case considered here, where a and b are given as sums of one-particle operators. Thereby we shall also include the many-body effects originating from the statistics. However, it must be emphasized here that the quantum ring collision operator thus obtained represents only the quantum analog of its (semi-)classical counterpart. In particular, this means that this quantity alone is probably not sufficient for a proper description of the truly quantum mechanical, dynamic correlation effects occurring in a fluid at low temperatures. This is also suggested by the investigation of the Lorentz gas model,[29] where the quantum long-time tail of the momentum autocorrelation function does not agree with the quantum analog of the corresponding classical quantity.

Now, to single out these ring events, we can proceed similarly to I [see Eqs. (I3.68–88)]. As done there, we shall only consider here ring terms without static correlations originating from the equilibrium distribution f. Hence, looking at the generalized collision operator $B_1(\varepsilon)$ as given in (4.10), we see that there $N_1(\varepsilon)$ can be dropped, for this term vanishes due to the effect of $\bar{Q}$ when static correlations in $f_{1\ldots s}$ are neglected. With the help of Eqs. (A.10) and (4.17), $B_1(\varepsilon)$ then reduces to

$$B_1(\varepsilon)\, h_1(\varepsilon) \rightrightarrows \left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0} d_1^\lambda(\varepsilon)$$

$$\rightrightarrows B_1^{\mathrm{QE}}(\varepsilon)\, h_1(\varepsilon) + \left.\frac{\partial}{\partial\lambda}\right|_{\lambda=0} \sum_{s=3}^{\infty} \varepsilon\, \mathrm{Tr}_{2\ldots s} P^{1\cdots s} \hat{G}_{1\ldots s}^{\lambda}(\varepsilon) f_1^\lambda \cdots f_s^\lambda \tag{7.1}$$

where we have replaced f_{12}^λ by $\pi^{12} f_1^\lambda f_2^\lambda$ in the second term. $\hat{G}_{1\ldots s}^{\lambda}(\varepsilon)$ is the renormalized cluster superoperator defined in (A.11). Note that except in the linear quantum Enskog collision operator $B_1^{\mathrm{QE}}(\varepsilon)$ all static correlations occurring in $B_1(\varepsilon)$ have been omitted.[5]

To extract now the ring events from the second term on the rhs of Eq. (7.1) and to resum them into a closed expression, we introduce the following, symmetrized projection operator:

$$\hat{P}_{\mathbf{k}}^{1\cdots s} = \sum_{\sigma \in S_s} \pi_\sigma P_{\mathbf{k}}^{1\cdots s} \pi_\sigma^{-1} \tag{7.2}$$

with

$$P_{\mathbf{k}}^{1\cdots s} = \sum_{1 \leqslant i < j \leqslant s} P_{\mathbf{k}}^{i} \cdot P_{-\mathbf{k}}^{j} P^{1\cdots \not{i} \cdots \not{j} \cdots s} \tag{7.3}$$

[5] The static correlations of U_1^{-1} which occur in f_1^λ vanish when taking the derivative with respect to λ due to Eq. (5.1) or when setting λ equal to zero.

Its complement $1-\hat{P}_{\mathbf{k}}^{1\cdots s}$ is denoted by $\hat{Q}_{\mathbf{k}}^{1\cdots s}$. The one-particle projector $P_{\mathbf{k}}^{i}$ applied to an ordinary operator y is defined as

$$(P_{\mathbf{k}}^{i}\, y)_{qq'} = y_{qq'}\, \delta_{\mathbf{q}_i',\mathbf{q}_i-\mathbf{k}} \tag{7.4}$$

For a discussion of $P_{\mathbf{k}}^{1\cdots s}$ we refer the interested reader to I (see pp. 213–214 and 220–221) and note that its symmetrized version (7.2) has the same features.

The procedure is now the following. Insert

$$\hat{P}_{\mathbf{k}}^{1\cdots s'} + \hat{Q}_{\mathbf{k}}^{1\cdots s'} = 1 \qquad (2 \leqslant s' \leqslant s)$$

into $\hat{G}_{1\ldots s}^{\lambda}(\varepsilon)$ (after each resolvent) and retain only the $\hat{P}_{\mathbf{k}}^{1\cdots s'}$ parts. Resummation of these terms then yields the quantum ring collision operator we are looking for. However, since the actual realization of this procedure is rather tedious and especially since its result will be obtained as special case of a more general formula derived in a forthcoming paper, let us only quote the final outcome of this calculation:

$$B_1(\varepsilon) \rightleftarrows B_1^{\mathrm{QE}}(\varepsilon) + R_1(\varepsilon) \tag{7.5}$$

$R_1(\varepsilon)$ is the quantum ring collision operator and is given by

$$R_1(\varepsilon) = -\frac{1}{2}\,\mathrm{Tr}_2\, \hat{T}_{12}(\varepsilon)\, \frac{1}{\varepsilon - iL_0(12) - C_{12}(\varepsilon)}\, B_{12}(\varepsilon) \tag{7.6}$$

with the following definitions:

$$C_{12}(\varepsilon) = C_1^{12}(\varepsilon) + C_2^{12}(\varepsilon) \tag{7.7a}$$

$$C_i^{12}(\varepsilon) = -\,\mathrm{Tr}_3\, \hat{T}_{i3}^{123}(\varepsilon)(1+\sigma_{i3}) f_3^0, \qquad i = 1, 2 \tag{7.7b}$$

$$\hat{T}_{12}^{123}(\varepsilon) = -\,i\bar{L}_{12}\, \frac{1}{\varepsilon - i[L_0(123) + \hat{L}_{12}]}\, [\varepsilon - iL_0(123)] \tag{7.8}$$

and $\bar{L}_{12} = \pi^{12} L_{12}$, $\hat{L}_{12} = \hat{L}_{12}^{\lambda=0}$ [see Eq. (4.15)]. Furthermore,

$$\hat{T}_{12}(\varepsilon) = \hat{T}_{12}^{12}(\varepsilon) \tag{7.9}$$

and

$$B_{12}(\varepsilon)\, h_1(\varepsilon) = \frac{\partial}{\partial\lambda}\bigg|_{\lambda=0} i\hat{\bar{L}}_{12}^{\lambda}\, \frac{1}{\varepsilon - i\hat{L}(12;\lambda)}\, f_1^{0,\lambda} f_2^{0,\lambda} \tag{7.10}$$

with $\hat{\bar{L}}_{12}^{\lambda} = \pi^{12}\hat{L}_{12}^{\lambda}$. The $f_i^{0,\lambda}$ is equal to f_i^{λ} defined in Eq. (4.7), but with $V=0$; f_i^0 is the Fermi (Bose) distribution operator.

$R_1(\varepsilon)$ represents the quantum-statistical generalization of the well-known classical (hard-sphere) ring collision operator[13–15,28] (without static corrections). To see this more clearly, let us introduce the phase space representation[30] of (super-) operators (for details see also Section 2 of I).

A phase function $y^{\mathrm{ph}}(r, p)$, depending on the c-number variables $r=(\mathbf{r}_1,..., \mathbf{r}_N)$ and $p=(\mathbf{p}_1,..., \mathbf{p}_N)$, is defined as the Weyl transform of the ordinary operator y:

$$y^{\mathrm{ph}}(r, p)=\sum_k e^{ikr}\, y_{p+k/2,\, p-k/2} \tag{7.11}$$

A phase operator S^{ph}, which corresponds to a superoperator S and which acts on phase functions, is defined by the relation

$$S^{\mathrm{ph}}\, y^{\mathrm{ph}}(r, p)=(Sy)^{\mathrm{ph}}(r, p) \tag{7.12}$$

Making use of these definitions and of the fact that b_1 and a_1 (and hence $U_1 a_1$) are diagonal, it is not difficult to see that the correlation function $C(\varepsilon)$ [see Eqs. (2.18) and (3.7)] can also be written as

$$C(\varepsilon)=\sum_{\mathbf{p}_1} (b_1)_{\mathbf{p}_1\mathbf{p}_1} \frac{1}{\varepsilon - B_1^{\mathrm{ph}}(\varepsilon)} (U_1 a_1)_{\mathbf{p}_1\mathbf{p}_1} \tag{7.13}$$

with

$$B_1^{\mathrm{ph}}(\varepsilon)\, y_1^{\mathrm{ph}}(\mathbf{p}_1)=[B_1(\varepsilon)\, y_1]_{\mathbf{p}_1\mathbf{p}_1} \tag{7.14}$$

where we have used that $B_1(\varepsilon)=P^1 B_1(\varepsilon) P^1$ and $y^{\mathrm{ph}}(p)=y_{pp}$ [see Eq. (I2.22)]. Next, introducing the Fourier transform of phase operators,

$$S^{\mathrm{ph}}(k\,|\,k')=\frac{1}{\Omega^N}\int dr\, e^{-ikr} S^{\mathrm{ph}} e^{ik'r} \tag{7.15}$$

and noticing that $R_1^{\mathrm{ph}}(\varepsilon)$ may be replaced by $R_1^{\mathrm{ph}}(\varepsilon)(0\,|\,0)$, one obtains with Eqs. (7.5) and (7.6)

$$B_1^{\mathrm{ph}}(\varepsilon)=B_1^{\mathrm{QE,ph}}(\varepsilon)+R_1^{\mathrm{ph}}(\varepsilon) \tag{7.16}$$

with

$$\begin{aligned} R_1^{\mathrm{ph}}(\varepsilon)=&-\frac{1}{2}\sum_{\mathbf{k},\mathbf{p}_2} \hat{T}_{12}^{\mathrm{ph}}(\varepsilon)(0\,|\,\mathbf{k}, -\mathbf{k}) \\ &\times \frac{1}{\varepsilon-(i/m)\mathbf{k}\cdot(\mathbf{p}_1-\mathbf{p}_2)-C_{12}^{\mathrm{ph}}(\varepsilon)(\mathbf{k}, -\mathbf{k}\,|\,\mathbf{k}, -\mathbf{k})} \\ &\times B_{12}^{\mathrm{ph}}(\varepsilon)(\mathbf{k}, -\mathbf{k}\,|\,0) \end{aligned} \tag{7.17}$$

Here, we have used the matrix multiplication rule

$$(S^{\mathrm{ph}}\bar{S}^{\mathrm{ph}})(k\,|\,k') = \sum_{k''} S^{\mathrm{ph}}(k\,|\,k'')\,\bar{S}^{\mathrm{ph}}(k''\,|\,k') \tag{7.18}$$

and momentum conservation. Restricting our further consideration of $C(\varepsilon)$ to small ε (i.e., to long times), we may assume as in the classical case[14,15] that the dominant contribution of $R_1^{\mathrm{ph}}(\varepsilon)$ comes from small $\mathbf{k}$ values and that therefore the quantities $\hat{T}_{12}^{\mathrm{ph}}(\varepsilon)(0\,|\,\mathbf{k},-\mathbf{k})$, $C_{12}^{\mathrm{ph}}(\varepsilon)(\mathbf{k},-\mathbf{k}\,|\,\mathbf{k},-\mathbf{k})$, and $B_{12}^{\mathrm{ph}}(\varepsilon)(\mathbf{k},-\mathbf{k}\,|\,0)$ can be replaced by their $\mathbf{k}=0$ and $\varepsilon=0^+$ values, which we denote by $\hat{T}_{12}^0$, C_{12}^0, and B_{12}^0, respectively. We also replace the linear quantum Enskog operator by its $\varepsilon\to 0^+$ limit $B_1^{\mathrm{QE,ph}}$. In this approximation $R_1^{\mathrm{ph}}(\varepsilon)$ is denoted by $R_1^0(\varepsilon)$ given by

$$R_1^0(\varepsilon) = -\sum_{\mathbf{p}_2,\mathbf{k}} \hat{T}_{12}^0 \frac{1}{\varepsilon(i/m)\mathbf{k}\cdot(\mathbf{p}_1-\mathbf{p}_2)-C_{12}^0} \tag{7.19}$$

with

$$\begin{aligned}
&\hat{T}_{12}^0\, y^{\mathrm{ph}}(\mathbf{p}_1,\mathbf{p}_2)\\
&\quad = \lim_{\varepsilon\to 0^+}[\hat{T}_{12}(\varepsilon)\,y]_{\mathbf{p}_1\mathbf{p}_2;\mathbf{p}_1\mathbf{p}_2}\\
&\quad = 4\pi \sum_{\mathbf{p}_1',\mathbf{p}_2'} \hat{\tau}(\mathbf{p}_1\mathbf{p}_2;\mathbf{p}_1'\mathbf{p}_2')\\
&\qquad \times [y^{\mathrm{ph}}(\mathbf{p}_1,\mathbf{p}_2)(1+\eta f_{\mathbf{p}_1'}^0+\eta f_{\mathbf{p}_2'}^0) - y^{\mathrm{ph}}(\mathbf{p}_1',\mathbf{p}_2')(1+\eta f_{\mathbf{p}_1}^0+\eta f_{\mathbf{p}_2}^0)]
\end{aligned} \tag{7.20}$$

and

$$C_{12}^0 = C_1^0 + C_2^0 \tag{7.21a}$$

$$\begin{aligned}
C_1^0\, y_1^{\mathrm{ph}}(\mathbf{p}_1) &= -\lim_{\varepsilon\to 0^+}[\mathrm{Tr}_2\,\hat{T}_{12}(\varepsilon)(1+\sigma_{12})f_2^0\,y_1]_{\mathbf{p}_1\mathbf{p}_1}\\
&= -4\pi \sum_{\mathbf{p}_2,\mathbf{p}_1',\mathbf{p}_2'} \hat{\tau}(\mathbf{p}_1\mathbf{p}_2;\mathbf{p}_1'\mathbf{p}_2')\\
&\quad \times \{[y_1^{\mathrm{ph}}(\mathbf{p}_1)f_{\mathbf{p}_2}^0 + y_2^{\mathrm{ph}}(\mathbf{p}_2)f_{\mathbf{p}_1}^0](1+\eta f_{\mathbf{p}_1'}+\eta f_{\mathbf{p}_2'})\\
&\quad - [y_1^{\mathrm{ph}}(\mathbf{p}_1')f_{\mathbf{p}_2'}^0 + y_2^{\mathrm{ph}}(\mathbf{p}_2')f_{\mathbf{p}_1'}^0](1+\eta f_{\mathbf{p}_1}^0+\eta f_{\mathbf{p}_2}^0)\}
\end{aligned} \tag{7.21b}$$

C_2^0 is defined analogously. Similarly, one finds from Eq. (7.10)

$$\begin{aligned}
B_{12}^0\, y_1^{\mathrm{ph}}(\mathbf{p}_1) = &-4\pi(1+\eta f_{\mathbf{p}_1}^0+\eta f_{\mathbf{p}_2}^0)\sum_{\mathbf{p}_1',\mathbf{p}_2'} \hat{\tau}(\mathbf{p}_1,\mathbf{p}_2;\mathbf{p}_1'\mathbf{p}_2')\\
&\times (1+\eta f_{\mathbf{p}_1}^0)(1+\eta f_{\mathbf{p}_2}^0) f_{\mathbf{p}_1'}^0 f_{\mathbf{p}_2'}^0 [\bar{y}_1^{\mathrm{ph}}(\mathbf{p}_1)+\bar{y}_2^{\mathrm{ph}}(\mathbf{p}_2)-\bar{y}_1^{\mathrm{ph}}(\mathbf{p}_1')\bar{y}_2^{\mathrm{ph}}(\mathbf{p}_2')]
\end{aligned} \tag{7.22}$$

where $\bar{y}_1^{\rm ph}(\mathbf{p}_1) = y_1^{\rm ph}(\mathbf{p}_1)[f_{\mathbf{p}_1}^0(1+\eta f_{\mathbf{p}_1}^0)]^{-1}$, etc. The quantity $\hat{\tau}(\mathbf{p}_1\,\mathbf{p}_2;\,\mathbf{p}_1'\mathbf{p}_2')$ is given in (6.1a). In deriving these expressions we have made use of some results obtained in Appendix D of II, in particular of Eq. (IID.17) [for (7.20) and (7.21)] and Eq. (IID.19) [for (7.22)]. Note that all three collision operators $\hat{T}_{12}^0$, C_{12}^0, and B_{12}^0 possess a structure very similar to the linear quantum Boltzmann collision operator given in Eq. (6.1).

Comparing now (7.19) with the corresponding quantity obtained in the classical kinetic theory of hard-sphere systems [see, e.g., ref. 24, Eq. (2.22a)], we see that $R_1^0(\varepsilon)$ indeed can be regarded as the quantum statistical generalization of the low-density, classical ring collision operator. The most prominent differences between the quantum and classical expressions are the FD (BE) distribution functions multiplied by η that occur in R_1^0. These factors, which of course have no classical counterparts (η can be put to zero for classical statistics), result from many-body effects due to particle statistics. Further differences from the classical case are the exchange-modified scattering cross sections (occurring in $\hat{T}_{12}^0$, C_{12}^0, and B_{12}^0), which describe the collision between two particles interacting via a continuous potential (with possible bound states).

Although it would be interesting to further analyze $R_1^0(\varepsilon)$ with the help of analogous methods used in classical kinetic theory (see, e.g., ref. 24), this shall not be attempted here. Let us only mention that in the semiclassical regime (i.e., with Boltzmann statistics) $R_1^0(\varepsilon)$ can be expressed in terms of eigenfunctions and eigenvalues of the operator $(i/m)\,\mathbf{k}(\mathbf{p}_1-\mathbf{p}_2)+C_{12}^0$ exactly as in the classical case (see, e.g., ref. 24, p. 271). The only difference is that here the transport coefficients occurring in the corresponding eigenvalues (hydrodynamic modes) are determined by their semiclassical (instead of hard-sphere) Boltzmann equation value. Thus, the same mode-coupling effects as in the classical case result from the semiclassical ring collision operator. In particular, for the time correlation function occurring in the kinematic shear viscosity [see Eqs. (5.16) and (5.19)] one obtains the same long-time tail of the form $t^{-d/2}$ ($d=2, 3$ is the number of dimensions) as found in hard-sphere systems.[14,31]

8. DISCUSSION

In the previous sections we have derived a linear quantum kinetic equation for the homogeneous equilibrium one-particle time correlation operator $h_1(t)$ by means of a superoperator formalism (e.g., Liouville and projecting operators) that is mainly based on cluster expansion techniques. This equation applies to normal quantum fluids consisting of fermions (bosons) which interact pairwise via a short-range, translationally invariant potential with arbitrarily strong interaction strength. It should be noted in

this connection that the formalism presented here (as well as in II and III) allows also the description of particles with spin; only the following minor modifications are necessary. The single-particle state $|\mathbf{k}_i\rangle$ occurring in the direct product state (2.13) is to be replaced by the state $|\mathbf{k}_i, \sigma_i^z\rangle = |\mathbf{k}_i\rangle\,|\sigma_i^z\rangle$, where σ_i^z denotes the spin component of the ith particle along a chosen z axis (e.g., $\sigma_i^z = \pm 1/2$ for a spin-1/2 fermion). Thus, one only has to replace the wave vectors $\mathbf{k}_i$ by $(\mathbf{k}_i, \sigma_i^z)$ everywhere, in particular in the definitions for the diagonal projectors $\bar{P}$ [Eq. (2.23)] and P [Eq. (3.4)], respectively. The observables a and b must then be diagonal in these new states. If, in addition, the interaction potential is spin dependent, it is no longer allowed to drop projectors P^i due to momentum conservation (as we have done several times in the derivation), since the considered quantity need not be diagonal in the spin indices. Now, a careful reexamination shows that the only modification needed in this case simply consists in replacing the static quantity U_1 [given in Eq. (2.21)] by its diagonal part $P^1 U_1$ in all formulas; everything else remains unchanged. Therefore, the whole formalism can also be aplied, for instance, to a magnetization time correlation function of the type $\langle s^z(t) s^z \rangle$, where $s^z = \sum_{i=1}^{N} s_i^z$ is the z component of the total spin operator.

Next, the many-body effects due to FD (BE) statistics are fully taken into account in the form of a renormalized cluster series of the dynamic (i.e., time-dependent) quantities. Thereby the static correlations originating from the canonical density matrix can always clearly be distinguished from the dynamic ones, which is a great advantage of the method presented here, e.g., over the familiar Green's function formalism, where such a clear distinction is not possible (for this see also ref. 32). As a consequence of this, we have been able to single out the terms relevant to the Enskog approximation of the collision operator. This approximation is, in analogy to the classical case, characterized by the fact that dynamic correlations are neglected (only uncorrelated binary collisions are taken into account as in the Boltzmann equation), whereas static correlations are treated exactly. In this approximation, therefore, the short-time limit of the correlation operator $h_1(t)$ (regarded as solution of the linear quantum Enskog equation) agrees with the exact initial value $h_1(0)$. The kinetic equation thus obtained generalizes the revised linear Enskog equation for classical hard-sphere systems to normal quantum fluids (with more general interaction potentials).

We have also shown how to express Green–Kubo formulas for transport coefficients (such as the shear viscosity or the thermal conductivity) in terms of the linear quantum Enskog collision operator B_1^{QE}. It would now be very interesting to further evaluate these quantities for physical systems such as normal ^{3}He, ^{4}He, spin-polarized hydrogen, etc.

It is clear that such an evaluation will still be complicated mainly due to the fact that, similar to the classical case, one has to find approximate expressions for the static operators f_1, f_{12}, f_{123}, and U_1^{-1} occurring in B_1^{QE} (note that these operators contain the full many-body Hamiltonian). Without going into further details here, let us only mention that approximations which could be interesting in this connection have been studied in Section 3 of ref. 25, where in particular an approximate value for f_{12} has been derived. We intend to come back to this problem in a forthcoming paper.

Finally, by resumming a special class of terms (ring events) in the renormalized cluster series, we arrived at the quantum-statistical analog of the classical hard-sphere ring collision operator (without static corrections). We have seen that in the semiclassical limit (i.e., with Boltzmann statistics) this quantum ring operator leads to the same qualitative behavior of correlation functions (i.e., in particular with the same long-time tails) as known from classical hard-sphere systems. As already announced, these (and other) higher-order dynamic correlations shall be investigated more systematically in a forthcoming paper.

APPENDIX

In this Appendix we derive Eq. (4.12). To begin with, we first perform a cluster expansion of the distribution operator $f^{\lambda}_{1\dots s}$. It should be noted here that $f^{\lambda}_{1\dots s}$ has the same cluster properties as $f_{1\dots s}$ since $\exp[\lambda\bar{h}(\varepsilon)]$ occurring in $f^{\lambda}_{1\dots s}$ decays into a product of one-particle operators that cannot create any additional correlations between the particles. Now, for reasons which will become clear further below, we choose the following cluster decomposition:

$$f^{\lambda}_{1\dots s}=\pi^{1\cdots s}\bar{g}^{\lambda}_{1\dots s}+\tilde{g}^{\lambda}_{1\dots s}, \qquad s\geqslant 2 \tag{A.1}$$

with

$$\bar{g}^{\lambda}_{1\dots s}=\frac{1}{2}\left(\sum_{1\leqslant i<j\leqslant s} g^{\lambda}_{ij}\prod_{l(\neq i,j)}^{s} f^{\lambda}_{l}+\pi^{12}f^{\lambda}_{1}\cdots f^{\lambda}_{s}\right) \tag{A.2}$$

and

$$g^{\lambda}_{ij}=f^{\lambda}_{ij}-\pi^{12}f^{\lambda}_{i}\cdot f^{\lambda}_{j}, \qquad \pi^{12}=1+\pi_{12} \tag{A.3}$$

The cluster operator $\tilde{g}^{\lambda}_{1\dots s}$ (being zero for $s\leqslant 2$) connects (by V_{ij}) more than two particles from the set $\{1,\dots,s\}$; hence, this term, inserted into Eq. (4.11), cannot lead to a dynamic two-particle contribution [see also

Section 4 of II, in particular Eq. (II4.9)]. This term will therefore be put into DTC. The relevant term for our purpose is $\pi^{1\cdots s}\bar{g}_{1\ldots s}$ whose main features are that it contains all correlations resulting from the statistics (i.e., $\pi^{1\cdots s}$) as well as the two-particle correlations created by the interaction V_{ij} (i.e., g^{λ}_{ij}).

Insertion of (A.1) into (4.11) then yields

$$d^{\lambda}_1(\varepsilon)=\sum_{s=2}^{\infty}\varepsilon\,\mathrm{Tr}_{2\ldots s}\,P^{1\cdots s}\bar{G}_{1\ldots s}(\varepsilon)\pi^{1\cdots s}\bar{g}^{\lambda}_{1\ldots s}+\mathrm{DTC} \tag{A.4}$$

Since $\bar{g}^{\lambda}_{1\ldots s}$ is a symmetric operator, $\bar{G}_{1\ldots s}(\varepsilon)\pi^{1\cdots s}$ can be brought to the following form (see Appendix B of II):

$$\bar{G}_{1\ldots s}(\varepsilon)\pi^{1\cdots s}\bar{g}^{\lambda}_{1\ldots s}=\tilde{G}_{1\ldots s}(\varepsilon)\,\bar{g}^{\lambda}_{1\ldots s} \tag{A.5}$$

with

$$\begin{aligned}\tilde{G}_{1\ldots s}(\varepsilon)=i\bar{L}_{12}&\frac{1}{\varepsilon-iL(12)}\,iQ^{12}(\bar{L}_{13}+\bar{L}_{23}+\bar{L}_{12,3})\frac{1}{\varepsilon-iL(123)}\,iQ^{123}\\&\times(\bar{L}_{14}+\bar{L}_{24}+\bar{L}_{34}+\bar{L}_{12,4}+\bar{L}_{13,4}+\bar{L}_{23,4})\\&\times\frac{1}{\varepsilon-iL(1234)}\,iQ^{1234}\cdots\frac{1}{\varepsilon-iL(1\cdots s-1)}\\&\times iQ^{1\cdots s-1}\left(\bar{L}_{1s}+\cdots+\bar{L}_{s-1\,s}+\sum_{1\leqslant i<j\leqslant s-1}\bar{L}_{ij,s}\right)\frac{1}{\varepsilon-iL(1\cdots s)}\end{aligned} \tag{A.6}$$

where $Q^{1\cdots k}=1-P^{1\cdots k}$ [see Eq. (3.4)] and where

$$\bar{L}_{ij}\,y=[\bar{V}_{ij},\,y],\qquad \bar{V}_{ij}=V_{ij}(1+\pi_{12}) \tag{A.7a}$$

$$\bar{L}_{ij,k}\,y=(\pi_{ik}+\pi_{jk})\,V_{ij}\,y-yV_{ij}(\pi_{ik}+\pi_{jk}) \tag{A.7b}$$

Next we note that in $\bar{g}^{\lambda}_{1\ldots s}$ only the term

$$\tfrac{1}{2}(g^{\lambda}_{12}+\pi^{12}f^{\lambda}_1\cdot f^{\lambda}_2)f^{\lambda}_3\cdots f^{\lambda}_s=\tfrac{1}{2}f^{\lambda}_{12}\cdot f^{\lambda}_3\cdots f^{\lambda}_s \tag{A.8}$$

must be retained in the Enskog approximation, since the other terms cannot lead to a dynamic two-particle contribution, for the same reason as above for $\tilde{g}^{\lambda}_{1\ldots s}$. Thus, (A.4) reduces to

$$d^{\lambda}_1(\varepsilon)=\frac{1}{2}\sum_{s=2}^{\infty}\varepsilon\,\mathrm{Tr}_{2\ldots s}\,P^{1\cdots s}\tilde{G}_{1\ldots s}(\varepsilon)f^{\lambda}_{12}f^{\lambda}_3\cdots f^{\lambda}_s+\mathrm{DTC} \tag{A.9}$$

For this expression we can now perform exactly the same resummation procedure as in Appendix A of III (replace there i by $-i$). The fact that here the distribution f_{12}^{λ} is not a product of the form $f_1^{\lambda} f_2^{\lambda}$ (as is the case in III) has no influence. As a result one obtains [see Eq. (III4.4)]

$$d_1^{\lambda}(\varepsilon) = \tfrac{1}{2} \sum_{s=2}^{\infty} \varepsilon \operatorname{Tr}_{2\cdots s} P^{1\cdots s} \hat{G}_{1\cdots s}^{\lambda}(\varepsilon) f_{12}^{\lambda} \cdot f_3^{\lambda} \cdots f_s^{\lambda} + \mathrm{DTC} \tag{A.10}$$

with the renormalized cluster superoperator

$$\begin{aligned} \hat{G}_{1\cdots s}^{\lambda}(\varepsilon) = i\bar{L}_{12} \frac{1}{\varepsilon - i\hat{L}(12;\lambda)} iQ^{12}(\bar{L}_{13} + \bar{L}_{23} + \bar{L}_{12,3}) \frac{1}{\varepsilon - i\hat{L}(123;\lambda)} \\ \times iQ^{123} \cdots iQ^{1\cdots s-1} \left(\bar{L}_{1s} + \cdots + \bar{L}_{s-1s} + \sum_{1 \leqslant i < j \leqslant s} \bar{L}_{ij,s} \right) \\ \times \frac{1}{\varepsilon - i\hat{L}(1\cdots s;\lambda)} - M_s(\varepsilon;\lambda) \end{aligned} \tag{A.11}$$

with

$$\hat{L}(\cdots s;\lambda) = L_0(1\cdots s) + \sum_{1 \leqslant i < j \leqslant s} \hat{L}_{ij}^{\lambda}$$

[see Eq. (4.15)]. Here, $M_s(\varepsilon;\lambda)$ compensates those s-particle contributions in the first term on the rhs of the foregoing equation which can reduce to s'-particle contributions [when inserted into Eq. (A.10)] with $s' < s$. Otherwise, these contributions would be counted twice in the resummation procedure [see also Eqs. (III4.10–12)]. For instance,

$$M_2(\varepsilon;\lambda) = 0 \tag{A.12}$$

$$M_3(\varepsilon;\lambda) = i\bar{L}_{12} \frac{1}{\varepsilon - i\hat{L}(12;\lambda)} i\bar{L}_{12,3} \frac{1}{\varepsilon - i\hat{L}(12;\lambda)} \tag{A.13}$$

etc.

An alternative form of $\hat{G}_{1\cdots s}^{\lambda}(\varepsilon)$ is [see (IIIA.5)]

$$\begin{aligned} \hat{G}_{1\cdots s}^{\lambda}(\varepsilon) = iL_{12} \frac{1}{\varepsilon - i\hat{L}(12;\lambda)} i\bar{Q}^{12}(L_{13} + L_{23}) \frac{1}{\varepsilon - i\hat{L}(123;\lambda)} i\bar{Q}^{123} \\ \times \cdots \frac{1}{\varepsilon - i\hat{L}(1\cdots s-1;\lambda)} i\bar{Q}^{1\cdots s-1}(L_{1s} + \cdots + L_{s-1s}) \\ \times \frac{1}{\varepsilon - i\hat{L}(1\cdots s;\lambda)} \pi^{1\cdots s} - M_s(\varepsilon;\lambda) \end{aligned} \tag{A.14}$$

which holds when applied to a symmetric operator.

$\bar{Q}^{1\cdots k}$ is given by $1-\bar{P}^{1\cdots k}$ with

$$\bar{P}^{1\cdots k}=\sum_{\sigma\in s_k}\pi_\sigma P^{1\cdots k}\pi_\sigma^{-1}\overset{k\ll N}{=}\bar{P}(1\cdots k) \tag{A.15}$$

Retaining in (A.10) only two-particle dynamic contributions (i.e., the $s=2$ term), we arrive at Eq. (4.12).

ACKNOWLEDGMENTS

I am very grateful to A. Thellung for helpful discussions and for his constant interest in this work. I also wish to express my thanks to H. van Beijeren, who drew my attention to the problem of a quantum extension of Enskog's theory. This work was supported by the Swiss National Science Foundation.

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