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A Reinterpretation of Dense Gas Kinetic Theory

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In dense gas kinetic theory it is standard to express all reduced distribution functions as functionals of the singlet distribution function. Since the singlet distribution function includes aspects of correlated particles as well as describing the properties of freely moving particles, it is here argued that these aspects should more clearly be distinguished and that it is the distribution function for free particles that is the prime object in terms of which dense gas kinetic theory should be expressed. The standard equations of dense gas kinetic theory are rewritten from this point of view and the advantages of doing so are discussed.

KEY WORDS: Gas kinetic theory; generalized Boltzmann equation.

1. INTRODUCTION

The classic work of Boltzmann$^{(1)}$ introduced an equation for the evolution of the one-particle distribution function, taking into account the free motion of a particle and how it is affected by collisions with a second particle. It has been the object of countless efforts to derive Boltzmann's equation in a rigorous way, or, more correctly, to accurately spell out the conditions and range of applicability for which it is valid. As well, the extension to include quantum effects, bound states, and three- and higher-particle collisions have been developed. A general review of the first century of the Boltzmann equation is contained in the proceedings$^{(2)}$ of the conference celebrating the centennial.

In extending the Boltzmann equation to higher density and thus to include three- and higher-particle collisions, it has seemingly been an unwritten rule that a closed equation for the singlet distribution function is required. Obviously this is limited to the case in which the potential supports no bound states, a restriction which is also made in this paper. Thus, the binary, ternary, etc., distribution functions are represented as

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functionals of the singlet distribution function. This philosophy has been especially espoused by Bogoliubov,(3) who postulates that all of the higher-ordered distribution functions have, after an initial transient time, their time dependence determined solely as functionals of the singlet distribution function. The present work questions whether this is the best way of representing the time dependence of a dense gas. It is argued that since the singlet distribution function includes the motion of a particle in the process of interacting with one or more other particles as well as the contribution from particles that are moving freely, it is appropriate to separate these contributions and to treat the free motion part as the basic unit for which a kinetic equation is to be obtained. Laloë and co-workers(4–6) have recently stressed that the free motion should play a more explicit role in the formulation of kinetic equations, but their method of incorporation of free motion differs significantly from that of the present work. In the present paper, connections with the standard approach(7,8) are made and the present work can be considered as a reinterpretation of the standard kinetic equations. However, if the equations are truncated at a particular level of multiparticle collisions, different results are obtained. An advantage of the present scheme is that for any truncation of the kinetic equations (at some multicollisional level), the singlet and pair density operators reduce at equilibrium to their canonical form. While this is true in the standard treatment for classical systems, at least to third order in the density,(9) the standard approach would, in particular, require the equilibrium singlet density operator for a quantum system to be a Maxwellian, which is not true at higher densities.(10,11) In contrast, the correct equilibrium behavior is automatically reproduced by the present method (to the level of multiparticle collisions of the truncation). The same comment is applicable to the expression for the pressure. The correct quantum second virial coefficient is obtained by the present approach, whereas the usual method(12) gives an incorrect result, as emphasized by Laloë and Mullin.(13) This was in fact the motivation for recently introducing(14) a density-corrected quantum Boltzmann equation. The present work shows that this proposed equation is closely related to the standard method of approach,(7,8) differing only in emphasis and method of truncation of the general development.

In this work, a quantum formalism for a gas obeying Boltzmann statistics is used, for example, the singlet density operator $\rho^{(1)}$ is normalized by tracing to the number of particles N according to

$$\mathrm{Tr}_1\, \rho_1^{(1)} = N \tag{1}$$

The results are also applicable to classical systems if the associations

$$\rho_1^{(1)} \leftrightarrow h^3 f^{(1)}(\mathbf{r}_1, \mathbf{p}_1) \quad \text{and} \quad \mathrm{Tr}_1 \leftrightarrow h^{-3} \iint d\mathbf{r}_1\, d\mathbf{p}_1$$

are made. Here $\mathbf{r}_1$ and $\mathbf{p}_1$ are the position and momentum of particle 1. This association is the same as that involved in the Weyl(15) correspondence of quantum operators and phase space functions, in particular the Wigner function.(16) But of course for a classical system, the quantum Liouville superoperator (see below) must be replaced by its classical counterpart, the Liouville operator. A shortened derivation of the equations for dense gas kinetic theory is given in Section 2 based on the initial time development of the reduced density operators, assuming that the N-particle density operator completely factors at the initial instant of time ($t=0$). This provides a setting on which to base the subsequent discussion connecting the different kinetic equations (see Section 3).

2. EVOLUTION HIERARCHY FOR AN N-PARTICLE SYSTEM

An isolated N-particle system (in a box of volume V with some appropriately prescribed boundary conditions) is completely described by a density operator $\rho^{(N)}$. As an isolated system, the time dependence of $\rho^{(N)}$ is governed by the von Neumann or quantum Liouville equation and the associated superoperator $\mathscr{L}^{(N)}$, namely

$$i\frac{\partial\rho^{(N)}}{\partial t}=\mathscr{L}^{(N)}\rho^{(N)}\equiv\hbar^{-1}[H^{(N)}\rho^{(N)}-\rho^{(N)}H^{(N)}] \tag{2}$$

defined in terms of the N-particle Hamiltonian $H^{(N)}$. The latter is assumed to consist of a sum of one-particle kinetic energy operators K_j, for the jth particle, and pair potentials V_{jk} acting between particles j and k. Standardly, $\rho^{(N)}$ is normalized to 1,

$$\mathrm{Tr}_{1,\dots,N}\,\rho^{(N)}=1 \tag{3}$$

Reduced density operators are defined

$$\rho^{(s)}\equiv\frac{N!}{(N-s)!}\,\mathrm{Tr}_{s+1,\dots,N}\,\rho^{(N)} \tag{4}$$

so that these are normalized to the number of ordered sets of s-particles in the N-particle system. It follows that the reduced density operators satisfy the BBGKY(3,17–19) hierarchy

$$i\frac{\partial\rho^{(s)}}{\partial t}=\mathscr{L}^{(s)}\rho^{(s)}+\mathrm{Tr}_{s+1}\,\mathscr{V}_{(s,1)}\rho^{(s+1)} \tag{5}$$

Here $\mathscr{L}^{(s)}$ is the Liouville superoperator for s-particles and the potential superoperator $\mathscr{V}_{(s,1)}$ is the sum

$$\mathscr{V}_{(s,\ 1)} \equiv \sum_{j=1}^{s} \mathscr{V}_{j,s+1} \tag{6}$$

of individual potential superoperators, each associated with a pair potential according to

$$\mathscr{V}_{jk} A \equiv \hbar^{-1}[V_{jk} A - A V_{jk}] \tag{7}$$

for action on an arbitrary operator A.

Since all observables of standard interest consist of a sum of one- or two-particle quantities, it is sufficient to calculate the time evolution of the singlet and pair density operators. These are then connected by the first BBGKY equation. It is assumed in the following that the N-particle density operator factors completely at the zero of time, so that it can be written

$$\rho^{(N)}_{1,\ldots,N}(0) = \prod_{j} \left(\frac{\rho^{(1)}_j(0)}{N} \right) \tag{8}$$

As always, a superscript denotes the number of particles, while the subscripts label the particular particles involved in the operator. Essentially this is thought of as representing N free (independent) particles.

The quantum Liouville equation (2) can be formally solved as

$$\rho^{(N)}(t) = e^{-i\mathscr{L}^{(N)}t} \rho^{(N)}(0) \tag{9}$$

If there was no potential of interaction, then the N-particle system would evolve with each particle moving freely. Under such motion the factored initial density operator remains factored and the singlet density operator for particle j becomes

$$\wp_{fj}(t) = e^{-i\mathscr{K}_j t} \rho^{(1)}_j(0) \tag{10}$$

where $\mathscr{K}_j$, defined as acting on an arbitrary operator A by

$$\mathscr{K}_j A \equiv \hbar^{-1}[K_j A - A K_j] \tag{11}$$

is the kinetic superoperator for particle j. The free motion described by Eq. (10) is emphasized by labeling the time-dependent singlet density operator with a subscript f and, in anticipation of latter notation, by a special symbol to emphasize its *completely* free motion, for all time. The effect of the interparticle potential is to correlate the particles and it is this motion which must be approximated in developing a kinetic theory.

This difference between the free and full motion of the N-particle system is determined by the evolution superoperator

$$\mathscr{W}^{(N)}(t) \equiv e^{-i\mathscr{L}^{(N)}t} e^{i\mathscr{K}^{(N)}t} \tag{12}$$

where $\mathscr{K}^{(N)} = \sum_j \mathscr{K}_j$ is the total kinetic energy superoperator. Thus, the N-particle density operator at time t is given by

$$\rho^{(N)}(t) = \mathscr{W}^{(N)}(t) \prod_j \left(\frac{\wp_{fj}(t)}{N} \right) \tag{13}$$

The time-dependent reduced density operators are found by taking the appropriate trace of Eq. (13) according to Eq. (4).

Evolution superoperators $\mathscr{W}^{(s)}(t)$ associated with the motion of an isolated set of s particles follows as a simple generalization of Eq. (12). Exploiting the analogy between the equilibrium distributions $W_s(1/kT) \equiv \exp(-H^{(s)}/kT)$ and the evolution superoperators generalizing Eq. (9), or better Eq. (12), as discussed, for example, by Cohen,$^{(20)}$ it is possible to consider a hierarchy of cluster evolution superoperators for time t according to the iteration scheme

$$\begin{aligned} \mathscr{U}_j^{(1)} &\equiv \mathscr{W}_j^{(1)} = 1 \\ \mathscr{U}_{jk}^{(2)} &\equiv \mathscr{W}_{jk}^{(2)} - 1 \\ \mathscr{U}_{jkl}^{(3)} &\equiv \mathscr{W}_{jkl}^{(3)} - \mathscr{W}_{jk}^{(2)} - \mathscr{W}_{jl}^{(2)} - \mathscr{W}_{kl}^{(2)} + 2 \\ &\cdots \end{aligned} \tag{14}$$

In this way the evolution of the N-particle system can be written as a cluster expansion

$$\mathscr{W}^{(N)}(t) = \sum_{\text{div}} \prod_l \mathscr{U}^{(l)}(t) \tag{15}$$

with the somewhat standard notation$^{(20)}$ that the sum is over all partitions of the N particles into sets and the product is over all sets l for a given partition. From this, it follows that the singlet density operator is given at time t by

$$\begin{aligned} \rho_1^{(1)}(t) = \wp_{f1}(t) &+ \mathrm{Tr}_2\, \mathscr{U}_{12}^{(2)}(t)\, \wp_{f2}(t) \\ &+ \tfrac{1}{2} \mathrm{Tr}_{23}\, \mathscr{U}_{123}^{(3)}(t)\, \wp_{f2}(t)\, \wp_{f3}(t) + \cdots \end{aligned} \tag{16}$$

In a different notation and for classical mechanics this is the same as

Eq. (2.19) of ref. 8. The analogous expression for the pair density operator is

$$\rho_{12}^{(2)}(t) = \rho_1^{(1)}(t)\,\rho_2^{(1)}(t) + \mathscr{U}_{12}^{(2)}(t)\,\wp_{f2}(t) \\ + \mathrm{Tr}_3\,\mathscr{U}_{123}^{(3)}(t)\,\wp_{f1}(t)\,\wp_{f2}(t)\,\wp_{f3}(t) + \cdots \qquad (17)$$

[compare Eq. (2.20) of ref. 8]. In obtaining these results use has been made of the fact that a trace over all particles in a cluster of two or more particles vanishes for the cluster evolution superoperator, i.e.,

$$\mathrm{Tr}_{1,\ldots,s}\,\mathscr{U}_{1,\ldots,s}^{(s)}(t)\,A = 0 \qquad \text{for} \quad s > 1$$

and that different particles contribute equally after being traced over. The latter property allows sums over differing colliding partners to be replaced by a typical particle times the number of possible colliding partners. The total number of particles N is assumed large, so that such counting factors may be simplified.

It is now desirable to examine the large-time limit, $t \to \infty$, of Eqs. (16) and (17). For the interaction of pairs of particles, the limit of $\mathscr{W}^{(2)}(t)$ has been treated in detail by Jauch *et al.*[21] and the limit gives the Møller superoperator $\Omega^{(2)}$ provided that the potential is short-ranged and there are no bound states. Analogous limits of $\mathscr{W}^{(s)}(t)$ for arbitrary s can be considered to give the Møller superoperators $\Omega^{(s)}$. Cohen[8] has used the equivalent classical expressions and interpreted the results when inserted into Eqs. (16) and (17) as a convergent density expansion of the evolution of the (classical) distribution functions. However Eqs. (16) and (17) involve an expansion in terms of the number of collisions undergone by the particles over all time, so that truncating these equations to retain only the first few terms is valid only over the course of the equivalent number of collisional mean free times. To account for the sequence of successive collisions that the gas particles undergo in macroscopic times requires keeping an inordinate number of terms. In contrast, for example, the Boltzmann equation takes into account the change that occurs due to one collision in terms of the present state singlet density operator, with all of the effects of the previous collisions incorporated into the present state of the singlet density operator. To get such a description, it is necessary to rearrange the infinite series to isolate the effect of the latest collision. It should also be remarked that the natural interpretation of the large-time limit of the $\mathscr{W}^{(s)}(t)$ is for an isolated (s-particle) collision, with the effects of previous (isolated) collisions treated by some other method. Green[7] derived the classical analog of Eqs. (16) and (17) [his Eqs. (15a) and (15b)], but he then introduced a concept of connectedness which is interpreted as the notion that a set of particles is connected if they have all collided *within a* *time* τ prior to the time t. The time interval τ is taken "to be long compared to a representative duration of a collision but short compared to the mean interval between collisions." It is a basic assumption of Green's work that such a τ exist so that collisions are localized in space and time, which is possible only if the gas is dilute. Green$^{(7)}$ then divides phase space into maximally connected parts and uses this division to resum expansions of the form of Eqs. (16) and (17) over disconnected parts. In this way, the singlet distribution function (Green's ξ) is replaced by its resummation $\bar{\xi}$ leaving only connected sets of particles appearing explicitly in the correlation functions for two or more particles. It is assumed here that such a resummation can be accomplished so that the completely free $\wp_f(t)$ is resummed to obtain a "locally" free singlet density operator $\rho_f(t)$, that is, describing a particle that has been free for a time period τ. It is an aspect of the same resummation, that the "full" singlet density operator $\rho^{(1)}(t)$ and the higher-ordered density operators may be expressed in terms of ρ_f by equations analogous to Eqs. (16) and (17). The difference in form occurs because the cluster correlation (collision) superoperators are now to describe only the latest correlating effect (collision). Thus, it is appropriate to set the time t appearing in the $\mathscr{U}(t)$ as not the macroscopic time, but the period τ associated with a time long compared to a typical collision duration but short to the average time between collisions; thus, for the singlet and pair,

$$\begin{aligned}\rho_1^{(1)}(t) = {} & \rho_{f1}(t) + \mathrm{Tr}_2\, \mathscr{U}_{12}^{(2)}(\tau)\, \rho_{f1}(t)\, \rho_{f2}(t) \\ & + \tfrac{1}{2}\, \mathrm{Tr}_{23}\, \mathscr{U}_{123}^{(3)}(\tau)\, \rho_{f1}(t)\, \rho_{f2}(t)\, \rho_{f3}(t) + \cdots \end{aligned} \tag{18}$$

and

$$\begin{aligned}\rho_{12}^{(2)}(t) = {} & \rho_1^{(1)}(t)\, \rho_2^{(1)}(t) + \mathscr{U}_{12}^{(2)}(\tau)\, \rho_{f1}(t)\, \rho_{f2}(t) \\ & + \mathrm{Tr}_3\, \mathscr{U}_{123}^{(3)}(\tau)\, \rho_{f1}(t)\, \rho_{f2}(t)\, \rho_{f3}(t) + \cdots \end{aligned} \tag{19}$$

Since only a single isolated s-particle collision is described by $\mathscr{U}(\tau)$ in these equations, it is appropriate to interpret the large-τ limit of $\mathscr{W}^{(s)}(\tau)$ as the corresponding Møller superoperator $\Omega^{(s)}$. In this way only isolated collision events appear explicitly, while the previous history of the particles that are about to collide (including the effect of their prior collisions) is contained entirely in the properties of $\rho_f(t)$. Equations (18) and (19) describe how the singlet and pair density operators are determined by (are functionals of) the free density operator ρ_f. In the following section these equations are used as the basis for discussing different forms for generalizing the Boltzmann equation.

3. GENERALIZED BOLTZMANN EQUATIONS

The classic Boltzmann equation(1) is an equation describing the time evolution of the singlet (classical) distribution function. Green(7) obtains such an equation from the classical analog of Eq. (18) by looking at how the terms in this expansion change in a time interval Δt [see his Eq. (56a) and the subsequent development]. This is equated to a surface integral of particles entering a collision through a variation of the parameter τ used to define connectedness. Green uses the same argument to get a Boltzmann equation for his free distribution function ξ [see his Eq. (48)]. For a quantum system, the definition of a precise interaction region seems contrary to the uncertainty principle, so that this procedure appears inappropriate. Even in the classical case of a dense gas I think of τ as a fuzzily defined quantity and arguments based on small variations of τ need to be treated carefully. In any event, this is not the method of proceeding that is pursued in the following.

The singlet and pair density operators are expressed as power series in the free motion density operator ρ_f according to Eqs. (18) and (19). Moreover, the singlet and pair density operators are also related by the first member of the BBGKY hierarchy, Eq. (5), which determines the time rate of change of the singlet density operator in terms of the pair density operator. With these three equations it is appropriate to eliminate two of the three density operators ρ_f, $\rho^{(1)}$, and $\rho^{(2)}$ to give a closed equation for one density operator. The usual choice(3,7,8,22,23) is to look for a closed equation for the singlet density operator (distribution function). Cohen's method(8) is to assume that Eq. (18) can be inverted to express ρ_f as a power series in $\rho^{(1)}$ and to substitute this expansion into Eq. (19) and use the first BBGKY equation to give a generalized Boltzmann equation. Assuming the series in Eq. (18) converges, it is easy to successively carry out its inversion. Using the $\tau \to \infty$ limit behavior of the $\mathscr{W}^{(s)}$, namely

$$\mathscr{W}^{(s)}(\tau) \xrightarrow[\tau \to \infty]{} \Omega^{(s)} \tag{20}$$

appropriate to times long compared to the time of duration of a collision but short compared to the mean free time, and of course short compared to macroscopic times, this expansion is

$$\begin{aligned}\rho_{f1}(t) = {} & \rho_1^{(1)}(t) - \mathrm{Tr}_2[\Omega_{12}^{(2)} - 1]\, \rho_1^{(1)}(t)\, \rho_2^{(1)}(t) \\ & - \tfrac{1}{2}\, \mathrm{Tr}_{23}[\Omega_{123}^{(3)} - \Omega_{12}^{(2)} - (2\Omega_{12}^{(2)} - 1)(\Omega_{13}^{(2)} + \Omega_{23}^{(2)} - 2)] \\ & \times \rho_1^{(1)}(t)\, \rho_2^{(1)}(t)\, \rho_3^{(1)}(t) - \cdots \end{aligned} \tag{21}$$

From this the expansion of $\rho^{(2)}$ in powers of $\rho^{(1)}$ is obtained using Eq. (19),

$$\begin{aligned}\rho_{12}^{(2)}(t) = {} & \Omega_{12}^{(2)}\rho_1^{(1)}(t)\,\rho_2^{(1)}(t)\\ & + \mathrm{Tr}_3[\Omega_{123}^{(3)} - \Omega_{12}^{(2)}\Omega_{13}^{(2)} - \Omega_{12}^{(2)}\Omega_{23}^{(2)} + \Omega_{12}^{(2)}]\\ & \times \rho_1^{(1)}(t)\,\rho_2^{(1)}(t)\,\rho_3^{(1)}(t) + \cdots \end{aligned} \tag{22}$$

Substitution of this expression for $\rho^{(2)}$ into the first BBGKY equation (5) gives the quantum analog of the generalized Boltzmann equation derived by Choh and Uhlenbeck,$^{(23)}$ Green,$^{(7,9)}$ and Cohen$^{(8,24)}$:

$$\begin{aligned} i\frac{\partial\rho_1^{(1)}}{\partial t} = {} & \mathscr{L}_1^{(1)}\rho_1^{(1)} + \mathrm{Tr}_2\,\mathscr{V}_{12}\Omega_{12}^{(2)}\rho_1^{(1)}\rho_2^{(1)}\\ & + \mathrm{Tr}_{23}\,\mathscr{V}_{12}[\Omega_{123}^{(3)} - \Omega_{12}^{(2)}\Omega_{13}^{(2)} - \Omega_{12}^{(2)}\Omega_{23}^{(2)} + \Omega_{12}^{(2)}]\\ & \times \rho_1^{(1)}\rho_2^{(1)}\rho_3^{(1)} + \cdots \end{aligned} \tag{23}$$

The quantum form for the triple collision term was first derived by Lowry,$^{(25)}$ while a related form without the free evolution superoperators was obtained by Résibois.$^{(26)}$ The latter may be satisfactory for a homogeneous system, but the contrast between free and interacting motion is useful to emphasize even there, since this is crucial for the convergence of the Møller superoperators, Eq. (20).

Alternately, if Eqs. (18) and (19) are directly substituted into the first BBGKY equation (5), with the large-time limit of the $\mathscr{W}^{(s)}(\tau)$ evaluated according to Eq. (20), there results a closed equation for the free density operator ρ_f:

$$\begin{aligned} & \left[i\frac{\partial}{\partial t} - \mathscr{L}_1^{(1)}\right]\{\rho_{f1} + \mathrm{Tr}_2[\Omega_{12}^{(2)} - 1]\,\rho_{f1}\rho_{f2}\\ & \qquad + \tfrac{1}{2}\mathrm{Tr}_{23}[\Omega_{123}^{(3)} - \Omega_{12}^{(2)} - \Omega_{13}^{(2)} - \Omega_{23}^{(2)} + 2]\,\rho_{f1}\rho_{f2}\rho_{f3} + \cdots\}\\ & = \mathrm{Tr}_2\,\mathscr{V}_{12}\Omega_{12}^{(2)}\rho_{f1}\rho_{f2} + \mathrm{Tr}_{23}\,\mathscr{V}_{12}[\Omega_{123}^{(3)} - \Omega_{12}^{(2)}]\,\rho_{f1}\rho_{f2}\rho_{f3} + \cdots \end{aligned} \tag{24}$$

Since it is the same three equations, namely Eqs. (5), (18), and (19), that are involved in obtaining Eqs. (23) and (24), these must be equivalent and Eq. (24) may be considered as a reinterpretation of the standard dense gas kinetic theory given by Eq. (23). It is argued that this is a more adequate way of writing the generalization of the Boltzmann equation since it determines the behavior of an independent (free) particle in the gas. Moreover, at equilibrium, it is ρ_f that is Maxwellian and thus represents free particles. ρ_f determines the total singlet density operator according to Eq. (18). This involves not only free particles, but also correlated sets of particles.

Moreover, these correlations are all determined by the free density operator, as, for example, the pair correlation operator $\rho_{12}^{(2)} - \rho_1^{(1)}\rho_2^{(1)}$ is given in terms of the free density operator by Eq. (19).

4. DISCUSSION

Two generalizations of the Boltzmann equation have been obtained from the same set of starting equations, namely Eqs. (5), (18), and (19). In the standard approach,(3,7,8,22,23) the pair and free density operators (in classical mechanics, distribution functions) are eliminated from these three equations to give Eq. (23) governing the time dependence of the singlet density operator. In contrast, in this paper it has been proposed to eliminate the pair and singlet density operators to give Eq. (24) as an equation determining the free density operator. If the infinite series of multiparticle collisions is kept and convergent, then these equations must be equivalent. However, if they are truncated at a certain level of collision order, then they can give different results.

At equilibrium it is expected that the free particle density operator will be a Boltzmann distribution with free particle Hamiltonian $H^{(1)}$, namely $\rho_f = (n_f/q)\exp(-H^{(1)}/kT)$, where n_f is the free particle density, and $q \equiv V^{-1}\,\mathrm{Tr}_1 \exp(-H_1^{(1)}/kT)$ is the free particle partition function per unit volume in a homogeneous system of volume V with Boltzmann's constant k and absolute temperature T. It follows from the intertwining property of the Møller operators that

$$\Omega_{1,\dots,s}^{(s)}\rho_{f1}\rho_{f2}\cdots\rho_{fs} = n_f^s \exp(-H_{1,\dots,s}^{(s)}/kT)/q^s \tag{25}$$

[Since the restriction has been made to potentials that support no bound states, $\Omega^{(s)}1 = 1$ and the continuous spectrum of $H^{(s)}$ spans the whole space.] It is now easy to show that at equilibrium, Eq. (24) is identically satisfied at each collisional level. Since $\mathscr{L}_1^{(1)}\rho_{f1} = 0$ and there is no time dependence, the left-hand side of Eq. (24) becomes

$$\frac{-n_f^2}{q^2}\,\mathrm{Tr}_2\,\mathscr{L}_1^{(1)} e^{-H_{12}^{(2)}/kT} - \frac{n_f^3}{2q^3}\,\mathrm{Tr}_{23}\,\mathscr{L}_1^{(1)}\left[e^{-H_{123}^{(3)}/kT} - 2e^{-(H_{12}^{(2)}+H_3^{(1)})/kT}\right] + \cdots$$

In the three-particle term, symmetry between particles 2 and 3 has been used to combine terms. The right-hand side of Eq. (24) is similarly reduced to

$$n_f^2 q^{-2}\,\mathrm{Tr}_2\,\mathscr{V}_{12} e^{-H_{12}^{(2)}/kT} + n_f^3 q^{-3}\,\mathrm{Tr}_{23}\,\mathscr{V}_{12}\left[e^{-H_{123}^{(3)}/kT} - e^{-(H_{12}^{(2)}+H_3^{(1)})/kT}\right] + \cdots$$

For the first term in the latter expression, $\mathscr{V}_{12} = \mathscr{L}_{12}^{(2)} - \mathscr{L}_1^{(1)} - \mathscr{L}_2^{(1)}$. On noticing that the $\mathscr{L}_{12}^{(2)}$ term is identically zero and that the trace over particle 2 causes the $\mathscr{L}_2^{(1)}$ contribution to vanish, it is seen that the remaining $\mathscr{L}_1^{(1)}$ contribution is the same as that calculated from the left-hand side of Eq. (24). Thus, the binary interaction terms exactly cancel. A similar but more elaborate identification leads to the cancellation between the three-particle interaction terms. Moreover, the expressions for the singlet and pair density operators, Eqs. (18) and (19), become exactly the expressions based on equilibrium cluster theory(27–29) with n_f/q identified as the absolute activity.

In gas kinetic theory, it is common(30, 31) to consider the binary collision term as determining the local equilibrium distribution function via Boltzmann's H-theorem. Thus, the distribution function (density operator) appearing in the binary collision operator is expected to be the (local) Maxwellian. For Eq. (24) this is the free density operator, which is consistent with the results obtained using an equilibrium canonical ensemble of N particles. For Eq. (23), it is the full singlet density operator that appears in the binary collision term. If $\rho^{(1)}$ is set equal to a (space and time independent) Maxwellian, then it can be shown that this is a solution for Eq. (23). But in carrying out this calculation, extensive use needs to be made of the homogeneity (spatial independence) of various operators that arise in evaluating the terms in Eq. (23). In contrast, the proof that a Maxwellian ρ_f satisfies Eq. (24) can be mostly accomplished using detailed cancellation of free motion and collision terms, with homogeneity invoked only for the vanishing of $\mathscr{L}_1^{(1)}\rho_{f1}$. It can also be shown that if $\rho^{(1)}$ is the correct equilibrium singlet density operator [from Eq. (18) with ρ_f a Maxwellian], then Eq. (23) is satisfied. Again extensive use is required of homogeneity to obtain this result. It is concluded that the condition that the kinetic equation is satisfied by the correct equilibrium density operator is not a very discriminating criterion. But it is emphasized that when Eq. (23) is to be used as the basis for dense gas kinetic theory, the equilibrium (and presumably local equilibrium) form for $\rho^{(1)}$ is not Maxwellian. It thus seems that Eq. (24) is the simpler equation to apply because the (local) equilibrium form for ρ_f is Maxwellian.

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