

# A Density-Corrected Quantum Boltzmann Equation

R. F. Snider<sup>1</sup>

*Received December 14, 1989; final May 10, 1990*

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Binary correlations are a recognized part of the pair density operator, but the influence of binary correlations on the singlet density operator is usually not emphasized. Here free motion and binary correlations are taken as independent building blocks for the structure of the nonequilibrium singlet and pair density operators. Binary correlations are assumed to arise from the collision of two *free* particles. Together with the first BBGKY equation and a retention of all terms that are second order in gas density, a generalization of the Boltzmann equation is obtained. This is an equation for the *free* particle density operator rather than for the (full) singlet density operator. The form for the pressure tensor calculated from this equation reduces at equilibrium to give the correct (Beth-Uhlenbeck) second virial coefficient, in contrast to a previous quantum Boltzmann equation, which gave only part of the quantum second virial coefficient. Generalizations to include higher-order correlations and collision types are indicated.

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**KEY WORDS:** Boltzmann equation; kinetic theory; binary correlations.

## 1. INTRODUCTION

The Boltzmann equation was first introduced<sup>(1)</sup> to take into account how binary collisions affect the momentum distribution of a monatomic ideal gas. Quantum systems have two nonclassical features that complicate the Boltzmann equation. The first is the noncommutation of position and momentum, which necessitates the classical distribution function being replaced by a density operator, which is also required for the description of molecular systems with internal (rotation, vibration, etc.) states. Such effects are central to this paper. The other quantum effect is the role of exchange symmetry (Bose-Einstein or Fermi-Dirac). For low density and

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<sup>1</sup>Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6.

moderate temperatures these latter effects play a very minor role and in the present work they will be ignored. Thus, it is assumed throughout this work that the system obeys Boltzmann statistics.

If degenerate internal molecular states are present, it is necessary to have an appropriate collision (super)operator for the Boltzmann equation. With a comparison to classical mechanics in mind, Waldmann,<sup>(2)</sup> and independently the author,<sup>(3)</sup> obtained a form for this collision term in which the molecular state is described by a quantity which is simultaneously a density operator in internal states and a Wigner function<sup>(4)</sup> in translational states. The formulation of spin relaxation<sup>(5)</sup> and the resultant expressions for the spin relaxation rates was one of the early uses for this equation. However, total angular momentum was not conserved, because the loss of (e.g., nuclear) spin angular momentum could not be accounted for by an increase of translational angular momentum. The reason for this failure is essentially because the form of the collision term that was introduced approximates both colliding particles as being at the same (macroscopic) position. Without introducing this localization approximation, the quantum Boltzmann equation can be written in operator form and all of the operators entering into this equation conserve angular momentum. Thus, the lack of angular momentum conservation is associated with the localization assumption of the collision term rather than any inherent difficulty with binary collisions or with the molecular chaos assumption used in factoring the pair density operator. With this motivation, the purely operator form for the quantum Boltzmann equation<sup>(6)</sup> was taken as primitive and certain properties of this equation described.<sup>(6,7)</sup> Yvon<sup>(8)</sup> arrived at the same operator equation by different arguments. While the conservation of angular momentum requires the retention of some of the nonlocality of the collision process, an expansion containing the minimal amount of nonlocality was introduced.<sup>(7)</sup> But to the same order of collision nonlocality, the kinetic energy is not conserved and the equation of motion (momentum balance) derived from the Boltzmann equation with retention of the same degree of nonlocality<sup>(7)</sup> gives an expression for the pressure that has a collisional contribution.

Energy conservation was attained<sup>(7)</sup> by adding an expression for the rate of change of the potential energy, evaluated within the binary collision regime. At equilibrium, the only flux that is nonzero is the momentum flux (pressure tensor). For the expression derived,<sup>(7)</sup> the equilibrium pressure has the classic contribution  $nkT$  due to kinetic motion and a term quadratic in the density that reduces in the classical mechanics limit to the correct second virial coefficient contribution. However, for quantum systems, the Beth-Uhlenbeck<sup>(9,10)</sup> form for the second virial coefficient is not obtained. Rainwater and Snider<sup>(11)</sup> showed that the quantum correc-

tion to the equilibrium momentum distribution has exactly the form needed to account for the difference between the expression for the pressure derived from the Boltzmann equation<sup>(7)</sup> and the Beth-Uhlenbeck formula. The first mention of such quantum corrections to the kinetic pressure seem to be by deBoer<sup>(12)</sup> and by Green.<sup>(13)</sup> Recently, Laloë and Mullin<sup>(14)</sup> have pointed out that since the second virial coefficient expression derived from the quantum Boltzmann equation is not correct, then the quantum Boltzmann equation<sup>(6)</sup> is of questionable validity in correctly describing nonlocal collision processes. Another difficulty that they<sup>(14)</sup> raise is the lack of consistency between the approximate form for the pair density operator introduced<sup>(3,6)</sup> to close the BBGKY<sup>(15-18)</sup> hierarchy in deriving the quantum Boltzmann equation and the singlet density operator. These are valid criticisms. The question about the second virial coefficient has never been addressed from a kinetic theory point of view, while for the form for the pair density operator, my standard reply has been that the form used for the pair density operator in the collision term is valid only in the midst of a collision and, moreover, is the quantum analogue of the Bogolubov<sup>(15)</sup> initial condition. But surely it is possible to do better than this, which is what is attempted in the present paper. While the role of density corrections was not of interest in the initial formulation of the quantum Boltzmann equation,<sup>(3,6)</sup> here it is shown how all terms to second order in gas density can be retained in an equation of Boltzmann type (which includes all equilibrium properties to second order in density). Triple collisions are not discussed, but some indication is given as to how the present treatment could be generalized to higher density.

At all but the lowest density, particles are correlated, especially at equilibrium. The present approach is based on the effect such correlations have on the various reduced density operators of a dilute gas system. Standard equilibrium cluster theory<sup>(10,19-21)</sup> is used in Section 2 to provide a motivation for relating nonequilibrium reduced density operators and particle correlations. Only binary correlations are considered, since the object is to describe low-density behavior. The approach taken in order to obtain a kinetic equation is to first express the singlet and pair density operators in terms of quantities representing "independent" free particle motion and binary correlations. Then, since the correlations in a dilute gas are considered to be weak (bound states are disallowed in the present treatment), and to arise only from (binary) collision processes, it is reasonable to expect that the correlations are determined by the *free* particle density operator. An ansatz for such a relation is given in Section 3 and a moderately dense gas quantum Boltzmann equation is "derived" from these considerations. This is viewed as an equation that is fully consistent to second order in particle density. In comparison with the

previously presented quantum Boltzmann equation,<sup>(6)</sup> the present equation contains density corrections to the free motion. The equations of change deduced from this equation are discussed in Section 4.

A distinction between free motion and interacting motion has been made by Laloë and co-workers.<sup>(22-24)</sup> Their objective is very much the same as that presented in this paper. In fact, their paper is the immediate motivation for the present work and their conceptual distinction between full and free density operators directed my thinking. However, their detailed implementation of these ideas is very different from that given here. Essentially, they modify the pair density operator (more precisely, the equivalent Wigner<sup>(4)</sup> function) into a *free* (pair) Wigner function and use this as the prime quantity to obtain a Boltzmann collision integral. In contrast, the present approach emphasizes a *free* singlet density operator together with binary correlations and how the structure of the singlet and pair density operators are influenced by these two quantities.

## 2. BINARY CORRELATIONS

The immediate objective here is to arrive at a reasonable ansatz for the structure of the reduced density operators describing a dilute gas in which binary correlations are important. In a nonequilibrium situation, it is not clear exactly how this should be done. The initial motivation for the structure that is presented was by analogy with the structure of the density operators used in formulating a kinetic theory of recombination and decay.<sup>(25),2</sup> In that work it was recognized that a bound state is described by part of the pair density operator, while the unbound (free) particles are described by part of the singlet density operator. To sort out the form of the reduced density operators, an ideal gas mixture of monomers (free particles) and dimers (bound pairs) was envisaged. For an  $N$ -particle system in which  $M$  of the particles are free and  $2D$  particles are bound ( $N = M + 2D$ ), all possible permutations of which particles are bound and which are free were considered. The immediate structure that results is that the singlet density operator  $\rho^{(1)}$  is related to the free  $\rho_f$  and bound  $\rho_b$  density operators by

$$\rho_1^{(1)} = \rho_{f1} + \text{Tr}_2 \rho_{b12} \quad (2.1)$$

and the pair density operator is

$$\rho_{12}^{(2)} = \rho_1^{(1)} \rho_2^{(1)} + \rho_{b12} \quad (2.2)$$

<sup>2</sup> The normalization of the pair density operator in ref. 25 is one-half of that used here.

In the present case, there are no bound states (assumed), but there are correlated pairs. Thus, by analogy, it is postulated that the appropriate structure for the reduced density operators in the same as above, but a correlation density operator  $\rho_c$  replaces the bound-state operator and the notion of being a free particle is that of being uncorrelated to any other particle in the system; thus,

$$\rho_1^{(1)} = \rho_{f1} + \text{Tr}_2 \rho_{c12} \tag{2.3}$$

and

$$\rho_{12}^{(2)} = \rho_1^{(1)} \rho_2^{(1)} + \rho_{c12} \tag{2.4}$$

Since particles can be negatively correlated, it is not possible to rationalize this structure by the same arguments, namely as a mixture of free particles and correlated pairs, as was made for the bound-state case.

An alternative motivation for the structure proposed in Eqs. (2.3)–(2.4) is obtained by studying the correlation structure of a large system at equilibrium. This is done first for an  $N$ -particle system (canonical ensemble) and then for a grand canonical ensemble. Binary correlations are emphasized and higher correlations (between more than two particles) are ignored. The resulting structure of the reduced density operators is found to be of precisely the above form. Aspects of the well-known structure of the cluster expansions<sup>(10,19–21)</sup> are first reviewed and the consequences of retaining only binary correlations emphasized.

For an  $N$ -particle system, the equilibrium density operator is

$$\rho^{(N)} = \exp(-H^{(N)}/kT)/(N! Q_N) \tag{2.5}$$

involving the  $N$ -particle Hamiltonian  $H^{(N)}$ , Boltzmann’s constant  $k$ , absolute temperature  $T$ , and the partition function

$$Q_N = \frac{1}{N!} \text{Tr} \exp\left(\frac{-H^{(N)}}{kT}\right) \tag{2.6}$$

The free particle and multiparticle correlations associated with the  $N$ -particle system are exhibited by rewriting the Boltzmann factor in terms of the operator equivalent of the Ursell functions,<sup>(26)</sup>

$$\begin{aligned} e^{-H^{(N)}/kT} = & \prod_{i=1}^N e^{-H_i^{(1)}/kT} + \sum_{1 \leq i < j \leq N} U_{ij}^{(2)} \prod_{k \neq i, j} e^{-H_k^{(1)}/kT} \\ & + \sum_{\substack{1 \leq i < j \leq N \\ i < k < l \leq N; l \neq j}} U_{ij}^{(2)} U_{kl}^{(2)} \prod_{v \neq i, j, k, l} e^{-H_v^{(1)}/kT} + \dots + U_{1\dots N}^{(N)} \end{aligned} \tag{2.7}$$

where the Ursell operators are defined by recursion on  $N$  and in particular the pair Ursell operator is

$$U_{12}^{(2)} \equiv \exp(-H_{12}^{(2)}/kT) - \exp(-K_{12}^{(2)}/kT) \quad (2.8)$$

with  $K_{12}^{(2)} \equiv H_1^{(1)} + H_2^{(1)}$  denoting the free pair Hamiltonian. If it is assumed that binary correlations are important but that ternary and higher-order correlations (Ursell operators) are negligible, then only the terms involving  $U^{(2)}$  and the single (free) particle Boltzmann factors in the Ursell expansion, Eq. (2.7), need be retained. The general term involves all possible permutations with all possible numbers  $N_c$  of correlated pairs. Thus, the binary correlation approximation to the  $N$ -particle Boltzmann factor is

$$e^{-H^{(N)}/kT} \approx \sum_{N_c=0}^{[N/2]} \sum_{\alpha, \gamma} \prod_{i \in \alpha} e^{-H_i^{(1)}/kT} \prod_{(jk) \in \gamma} U_{jk}^{(2)} \quad (2.9)$$

Here  $\alpha$  is a listing of which particles are free, while  $\gamma$  is a listing of which  $N_c$  pairs are correlated, and there is a sum over all such listings. The upper limit  $[N/2]$  of the  $N_c$  sum is the largest integer less than or equal to  $N/2$ . Within this approximation, the partition function is

$$Q_N \approx \frac{1}{N!} \sum_{N_c=0}^{[N/2]} g(N, N_c) Q_1^{N-2N_c} (2Q_2^U)^{N_c} \quad (2.10)$$

where  $Q_1 \equiv \text{Tr}_1 \exp(-H_1^{(1)}/kT)$  is the one-particle partition function and

$$\begin{aligned} Q_2^U &\equiv \frac{1}{2} \text{Tr}_{12} U_{12}^{(2)} \\ &= Q_2 - \frac{1}{2} Q_1^2 = -Q_1^2 B_2/V \end{aligned} \quad (2.11)$$

is the trace of the binary Ursell operator, which is in turn related to the second virial coefficient  $B_2$  and the volume  $V$  of the system. The factor

$$g(N, N_c) = \frac{N!}{(N-2N_c)! N_c! 2^{N_c}} = \binom{N}{2N_c} \frac{(2N_c)!}{N_c! 2^{N_c}} \quad (2.12)$$

is the number of ways of having  $N_c$  correlated pairs among  $N$  particles. It is easily verified that the partition functions  $Q_N$  satisfy the recursion relation

$$NQ_N = Q_1 Q_{N-1} + 2Q_2^U Q_{N-2} \quad (2.13)$$

within this binary correlation approximation.

Reduced density operators for  $s$  particles, normalized as  $\text{Tr}_{1\dots s}\rho^{(s;N)} = N!/(N-s)!$ , are derived from Eqs. (2.5), (2.9), and (2.10) according to

$$\begin{aligned} \rho_1^{(1;N)} &\equiv N \text{Tr}_{2\dots N} \rho^{(N)} \\ &= \frac{Q_{N-1}}{Q_N} e^{-H_1^{(1)}/kT} + \frac{Q_{N-2}}{Q_N} \text{Tr}_2 U_{12}^{(2)} \end{aligned} \tag{2.14}$$

and

$$\begin{aligned} \rho_{12}^{(2;N)} &\equiv N(N-1) \text{Tr}_{3\dots N} \rho^{(N)} \\ &= \frac{Q_{N-2}}{Q_N} [e^{-(H_1^{(1)} + H_2^{(1)})/kT} + U_{12}^{(2)}] \\ &\quad + \frac{Q_{N-3}}{Q_N} \text{Tr}_3 [U_{13}^{(2)} e^{-H_2^{(1)}/kT} + U_{23}^{(2)} e^{-H_1^{(1)}/kT}] + \frac{Q_{N-4}}{Q_N} \text{Tr}_{34} U_{13}^{(2)} U_{24}^{(2)} \end{aligned} \tag{2.15}$$

The recursion relation (2.13) is needed in order to verify that Eqs. (2.14) and (2.15) are consistent, namely that

$$\rho_1^{(1;N)} = \frac{1}{N-1} \text{Tr}_2 \rho_{12}^{(2;N)} \tag{2.16}$$

In the thermodynamic limit,  $N \rightarrow \infty$ ,  $V \rightarrow \infty$  with  $N/V \equiv n$  finite, the ratio of partition functions for successive  $N$  is related to the absolute activity  $\lambda$ ,  $Q_{N-1}/Q_N \rightarrow \lambda$ . Now, for large  $N$ , the first two reduced density operators can be approximated as

$$\rho_1^{(1;N)} = \lambda e^{-H_1^{(1)}/kT} + \lambda^2 \text{Tr}_2 U_{12}^{(2)} \tag{2.17}$$

and

$$\rho_{12}^{(2;N)} = \rho_1^{(1;N)} \rho_2^{(1;N)} + \lambda^2 U_{12}^{(2)} \tag{2.18}$$

These have exactly the structure of Eqs. (2.3)–(2.4), but the relation (2.16) is valid only to  $O(1/N)$ , noting that  $\rho^{(1;N)}$  is normalized to  $N$ , while  $\text{Tr}_2 U_{12}^{(2)}/(N-1)$  is normalized to  $Q_2^U/(N-1)$ , which is finite in the thermodynamic limit. These comments follows from the fact that both  $Q_1$  and  $Q_2^U$  are linearly proportional to the volume  $V$  of the system.

For the grand canonical ensemble, the absolute activity is introduced as a fundamental quantity and activity expansions of the reduced density operators<sup>(26,27)</sup> arise naturally. In this case, the probability of having  $N$  particles is  $P_N = \lambda^N Q_N/\Xi$ , where  $\lambda$  is the absolute activity, now an

independent variable, and the grand canonical partition function is  $\Xi = \sum_N \lambda^N Q_N$ . Calculations of all observable quantities occur as power series expansions in  $\lambda$ , the average number of particles being an especially well-known result

$$\begin{aligned} \langle N \rangle &= \sum_N NP_N = \lambda Q_1 + \lambda^2 [2Q_2 - Q_1^2] + \dots \\ &= \lambda \text{Tr}_1 e^{-H_1^{(1)}/kT} + \lambda^2 \text{Tr}_{12} U_{12}^{(2)} + \dots \end{aligned} \quad (2.19)$$

The singlet density operator has an analogous expansion,

$$\begin{aligned} \rho_1^{(1;GCE)} &= \sum_N NP_N \text{Tr}_{2,\dots,N} \rho^{(N)} \\ &= \lambda e^{-H_1^{(1)}/kT} + \lambda^2 \text{Tr}_2 U_{12}^{(2)} + \lambda^3 \text{Tr}_{23} U_{123}^{(3)} + \dots \end{aligned} \quad (2.20)$$

whose trace reproduces Eq. (2.19). Higher-order reduced density operators have greater structure. For the pair density operator, the leading term is obviously proportional to the Boltzmann factor for the pair of particles, but the contributions from  $N > 2$  depend on whether both particles appear in the same or different Ursell operators. In graph theory terminology,<sup>(28)</sup> all doubly-rooted graphs are required with connectivity of all points to at least one root point, but not necessarily to both root points. Since the sum of all singly-rooted connected graphs gives the singlet density operator, the pair density operator is a product of singlets plus the sum of doubly-rooted connected graphs, namely

$$\begin{aligned} \rho_{12}^{(2;GCE)} &= \sum_N N(N-1) P_N \text{Tr}_{2,\dots,N} \rho^{(N)} \\ &= \rho_1^{(1;GCE)} \rho_2^{(1;GCE)} + \lambda^2 U_{12}^{(2)} + \lambda^3 \text{Tr}_3 U_{123}^{(3)} + \dots \end{aligned} \quad (2.21)$$

Within the binary correlation approximation, all Ursell operators for three or more particles vanish, so that all these expansions truncate. It follows that the first two reduced density operators, Eqs. (2.20)–(2.21), are the grand canonical ensemble analogs of Eqs. (2.17)–(2.18). It again immediately follows that  $\rho_1^{(1;GCE)}$  is not just the trace over particle 2 of the pair density operator  $\rho_{12}^{(2;GCE)}$ , but the difference is related to the dispersion in the number of particles in the grand canonical ensemble. In detail, the defining relation for  $\rho^{(2;GCE)}$  shows that

$$\text{Tr}_2 \rho_{12}^{(2;GCE)} = \sum_N \frac{N(N-1)}{N! Q_N} P_N \text{Tr}_{2,\dots,N} e^{-H^{(N)}/kT} \quad (2.22)$$



differs from  $\rho_1^{(1;GCE)}$ , Eq. (2.20), by differing  $N$  factors. If both quantities are multiplied by  $\Xi$ , power series in  $\lambda$  are obtained and an identity can be attained by a suitable choice of differentiating with respect to  $\lambda$ , namely

$$\text{Tr}_2 \rho_{12}^{(2;GCE)} = \frac{\lambda^2}{\Xi} \frac{\partial}{\partial \lambda} \left( \frac{\Xi \rho_1^{(1;GCE)}}{\lambda} \right) \tag{2.23}$$

This identity is satisfied in the binary correlation approximation, Eqs. (2.17)–(2.18), precisely for the grand canonical ensemble and in the limit of large  $N$  for the canonical ensemble. This again points to the fact that  $\rho_1^{(1;GCE)}$  and  $\text{Tr}_2 \rho_{12}^{(2;GCE)}$  differ only because of the dispersion in the number of particles, or equivalently, in the dispersion of the particle density.

Within the binary correlation approximation, the grand canonical partition function can be readily summed to give

$$\Xi = \sum_N \lambda^N Q_N = \exp(\lambda Q_1 + \lambda^2 Q_2^U) \tag{2.24}$$

which is directly related to the activity expansion of the equation of state stopping at the second virial coefficient. The average number of particles follows from Eq. (2.19),

$$\langle N \rangle = \lambda Q_1 + 2\lambda^2 Q_2^U \tag{2.25}$$

It is standard to express thermodynamic quantities as density “ $n$ ” expansions rather than activity expansions. This involves inverting Eq. (2.25) and thus eliminating  $\lambda$  from the previous expansions. Only one such density expansion is discussed here, namely that of the singlet density operator. From Eqs. (2.17) and (2.25), it follows that

$$\begin{aligned} \rho_1^{(1)} &= \frac{\langle N \rangle}{Q_1} e^{-H_1^{(1)}/kT} + \frac{\langle N \rangle^2}{Q_1^2} \left[ \text{Tr}_2 U_{12}^{(2)} - \frac{2Q_2^U}{Q_1} e^{-H_1^{(1)}/kT} \right] + \dots \\ &= \frac{\langle N \rangle}{Q_1} e^{-H_1^{(1)}/kT} + \frac{\langle N \rangle^2}{Q_1^2} \left[ \text{Tr}_2 e^{-H_1^{(2)}/kT} - \frac{2Q_2}{Q_1} e^{-H_1^{(1)}/kT} \right] + \dots \end{aligned} \tag{2.26}$$

In the density expansion it is seen that only the first term contributes to the normalization of the singlet density operator, but it is also emphasized that the next term is not just the binary correlation. The activity expansion, on the other hand, is directly associated with particle correlations.

The correlation structure of the singlet and pair density operators is explicitly given in equilibrium by Eqs. (2.17)–(2.18) for an  $N$ -particle system and, as stated, the reduced density operators for the grand canonical ensemble have the same structure. This is the structure emphasized at

the beginning of this section, Eqs. (2.3)–(2.4), and which is used in the following to obtain a density corrected form of the quantum Boltzmann equation.

### 3. BOLTZMANN EQUATION

My view of the philosophy of the Boltzmann equation was stated<sup>(6)</sup> several years ago. This has not changed; as stated then, it is “to consider an approximation which incorporates the assumptions: (i) only binary collisions are used and these are assumed to occur on a time scale that is short compared to both the times between collision  $\tau_f$  and the macroscopic relaxation time  $\tau_r$  of  $\rho$ ; and (ii) the pair density operator factors *before* a collision.” These ideas were implemented in a particular way in that paper, where the lowest gas density effects were emphasized. In the present work this same philosophy is espoused; in particular, only binary collisions are considered, but the possibility of density corrections arising within the binary collision approach to kinetic phenomena is taken into account. The method adopted here is to emphasize the role of binary correlations within the binary collision regime while completely ignoring three-particle correlation and/or collision effects.

The starting point for the “derivation” of the Boltzmann equation is the first member of the BBGKY<sup>(15–18)</sup> hierarchy,

$$i\hbar \frac{\partial \rho_1^{(1)}}{\partial t} = [H_1^{(1)}, \rho_1^{(1)}]_- + \text{Tr}_2[V_{12}, \rho_{12}^{(2)}]_- \quad (3.1)$$

where  $V_{12} = H_{12}^{(2)} - H_1^{(1)} - H_2^{(1)}$  is the interaction potential for particles 1 and 2, assumed short ranged for the validity of the following arguments. In order to close this equation, another relation between  $\rho^{(1)}$  and  $\rho^{(2)}$  is required. The argument used here to obtain a closure relation follows closely those given by Green.<sup>(29)</sup> This requires: first, assuming that only a pair of particles are interacting; second, following the binary collision trajectory back in time to before the collision began; third, assuming the particles are independent at this precollision time; and last, connecting the single-particle probabilities at the precollision time to the time  $t$  of interest by free particle evolution. As a consequence, the pair density operator is standardly written<sup>(3,6,8)</sup> in terms of a product of singlets,

$$\rho_{12}^{(2)} = \Omega_{12} \rho_1^{(1)} \rho_2^{(1)} \Omega_{12}^\dagger \quad (3.2)$$

where  $\Omega$  is the pair Møller operator, which essentially converts a free particle wavefunction into an interacting wavefunction by tracing freely back in time and then forward an equal amount of time according to inter-

acting motion. It is this closure that was used in our previous derivations<sup>(3,6)</sup> of the quantum Boltzmann equation.

As stated in the previous paragraph, the Møller operators convert (a pair) of free particles into an interacting state. Here it is proposed to take this statement more literally—since the particles are to be *free* before the Møller operators act on them, they should not be correlated with any other particles and thus the singlet density operators upon which the Møller operators are to act should be the free states  $\rho_f$  rather than the full singlet density operator  $\rho^{(1)}$ . Thus, in closing the BBGKY hierarchy, the pair density operator used in evaluating the collision term should be

$$\rho_{12}^{(2)} = \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \tag{3.3}$$

rather than Eq. (3.2). But the closure of the BBGKY hierarchy should be made in a manner that is consistent to second order in density! In particular, the time and free flow contributions to the first BBGKY equation involve explicitly the full singlet density operator  $\rho^{(1)}$ , which must be distinguished from the free part  $\rho_f$  of the singlet density operator. This is where Eq. (2.3) enters.

With this motivation, the correlation structure of the singlet and pair density operators is again discussed. At the Boltzmann equation level of description of a gas, the independent (*free*) motion of the particles is dominant. Thus, the present work takes as central the free density operator  $\rho_f$ , and it is then required to find an equation governing how  $\rho_f$  evolves in time. Correlations arise through bimolecular encounters (collisions), and from the arguments leading to Eq. (3.3), it is proposed to take the *correlated* part of the pair density operator as

$$\rho_{c12} = \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger - \rho_{f1} \rho_{f2} \tag{3.4}$$

Note that it is only free particles that should be correlated by binary collision dynamics. To elaborate on this argument, since the *correlated* contribution to  $\rho^{(1)}$  has a ghost interacting with the particle being described, it is unreasonable that such a combination be further correlated (to a third particle) by a *binary* collision process.

Now the full singlet  $\rho^{(1)}$  and pair  $\rho^{(2)}$  density operators are given in terms of the free density operator by Eqs. (2.3) and (2.4). In a way the free singlet density operator gets *dressed* or *renormalized* by binary correlations. On inserting *all* terms up to second order in the density into the first BBGKY equation, it is noted that for the pair density operator, Eq. (2.4), the product of singlet density operators is to this order in density just the product of the free operators, so that

$$\rho_{12}^{(2)} = \rho_1^{(1)} \rho_2^{(1)} + \rho_{c12} \approx \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \tag{3.5}$$

and this is exactly Eq. (3.3), which is to be used in the collision term. The density corrected Boltzmann equation is thus given to second order in density as

$$\begin{aligned}
 i\hbar \frac{\partial \rho_{f1}}{\partial t} + i\hbar \frac{\partial \text{Tr}_2(\Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger - \rho_{f1} \rho_{f2})}{\partial t} \\
 = [H_1^{(1)}, \rho_{f1}]_- + [H_1^{(1)}, \text{Tr}_2(\Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger - \rho_{f1} \rho_{f2})]_- \\
 + \text{Tr}_2[V_{12}, \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger]_- \quad (3.6)
 \end{aligned}$$

This is a closed equation for the free singlet density operator  $\rho_f$ , in terms of which the full singlet and the pair density operators are determined by Eqs. (2.3), (2.4), and (3.4).

For sufficiently low density, the correlation contribution to the full singlet density operator should be negligible. Under these conditions, the free and full singlet density operators can be equated and the correlation corrections for the time and free flow terms in Eq. (3.6) dropped, to arrive at the usual quantum Boltzmann equation.<sup>(6)</sup> As the density increases,  $\rho^{(1)}$  needs to be distinguished from  $\rho_f$  and the time and free motion differences between these two quantities play a role. At equilibrium, it is the free density operator that is Maxwellian. The intertwining property of the Møller operator

$$H^{(2)}\Omega = \Omega K^{(2)} \quad (3.7)$$

implies that at equilibrium the pair correlation operator of Eq. (3.4) becomes proportional to the second Ursell operator, Eq. (2.8), it being assumed in the present work that the potential does not support any bound states. In this way, both the singlet and pair density operators as defined for the density corrected quantum Boltzmann equation reduce at equilibrium to their exact equilibrium forms. Of particular note is the fact that the correlation correction to the singlet density operator dominates the large-momentum behavior of the distribution function for quantum systems,<sup>(11,30)</sup> but merely renormalizes the Maxwellian if the system obeys classical mechanics. That classically, both the free and full density matrices (classically—distribution functions) are Maxwellian may be the reason that the singlet density operator is usually associated with *free* particles.

The distinction, Eq. (3.5), between the full pair density operator and the usual<sup>(6)</sup> collision ansatz, Eq. (3.2), solves the first of Laloë and Mullin's criticisms<sup>(14)</sup> and I believe also the second. Their third criticism concerning the form of the second virial coefficient is addressed in the following section.

### 4. EQUATIONS OF CHANGE

For a one-particle observable  $\phi$ , usually a density in gas kinetic theory (physical attribute per unit of volume in position space), it is desirable to have an equation of change for its expectation value  $\langle \phi \rangle$ . This can be obtained exactly from the first BBGKY equation (3.1), and approximately from the Boltzmann equation (3.6), the latter being carried out here.

It is first emphasized that the expectation value for a one-particle observable is found from the full singlet density operator  $\rho^{(1)}$ . Since this consists of the two parts, free and correlated, the expectation value can be apportioned according to

$$\langle \phi \rangle = \langle \phi \rangle_f + \langle \phi \rangle_c \tag{4.1}$$

with

$$\langle \phi \rangle_f \equiv \text{Tr}_1 \phi_1 \rho_{f1} \tag{4.2}$$

and a corresponding definition for the correlated contribution. Since the time derivative and free motion parts of the Boltzmann equation involve the full singlet density operator, the equation of change for  $\langle \phi \rangle$  can be written

$$\frac{\partial \langle \phi \rangle}{\partial t} - \left\langle \frac{\partial \phi}{\partial t} \right\rangle = \frac{1}{i\hbar} \langle [\phi, H^{(1)}]_- \rangle + \frac{1}{i\hbar} \text{Tr}_{12} [\phi_1, V_{12}]_- \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \tag{4.3}$$

Allowance has been made for the possibility that  $\phi$  has an explicit time dependence. Particular cases are now considered.

First is the number density  $n$ , for which the observable operator is the Dirac delta function  $\phi_1 = \delta_1 \equiv \delta(\mathbf{r} - \mathbf{r}_1)$ . Here  $\mathbf{r}$  denotes the position variable at which the particle is to be observed, while  $\mathbf{r}_1$  is the position operator for particle 1. Since this operator commutes with the (local) potential, there is no collision contribution to the equation of change. On the assumption that the single-particle Hamiltonian has the standard form

$$H_1^{(1)} = \frac{\mathbf{p}_1^2}{2m} + H_{\text{int},1} \tag{4.4}$$

in terms of momentum and internal variables, the free motion commutator can be evaluated and the well-known equation of continuity

$$\frac{\partial n}{\partial t} = -\nabla \cdot (n \mathbf{v}_0) \tag{4.5}$$

results with stream velocity defined by

$$n\mathbf{v}_0 \equiv \text{Tr}_1 \frac{1}{2m} (\mathbf{p}_1 \delta_1 + \delta_1 \mathbf{p}_1) \rho_1^{(1)} \quad (4.6)$$

It is moreover important to recognize that the particle density consists of two parts,  $n = n_f + n_c$ , corresponding to the free and correlated parts of the singlet density operator.

At equilibrium in a homogeneous system, the free density operator becomes the Boltzmann distribution (Maxwellian in momentum)

$$\rho_{f1} = \frac{n_f \Lambda^3}{q_{\text{int}}} e^{-H_1^{(1)}/kT} \quad (4.7)$$

where  $\Lambda \equiv h/(2\pi mkT)^{1/2}$  is the thermal deBroglie wavelength and  $q_{\text{int}}$  in the internal state partition function. The correlation contribution to the particle density becomes proportional to the second virial coefficient,

$$n_c = \text{Tr}_{12} \delta_1 \rho_{c12} = \text{Tr}_{12} \delta_1 \left( \frac{n_f \Lambda^3}{q_{\text{int}}} \right)^2 U_{12}^{(2)} = -2n_f^2 B_2 \quad (4.8)$$

Combined together, it is seen that  $n_f$  is related to the gas density  $n$  by

$$n = n_f - 2B_2 n_f^2 \quad (4.9)$$

Since the present treatment is a density expansion to terms quadratic in the density, it is appropriate to approximately solve Eq. (4.9) for  $n_f$  as  $n_f \approx n + 2B_2 n^2$ .

Next is the equation of motion, in which the observable is the momentum density and whose expectation value is related to the stream velocity [see Eq. (4.6)]. Commutators can again be evaluated and the result cast in the standard form<sup>(31,32)</sup>

$$nm \frac{\partial \mathbf{v}_0}{\partial t} + nm \mathbf{v}_0 \cdot \nabla \mathbf{v}_0 = -\nabla \cdot \mathbf{P} \quad (4.10)$$

where the pressure tensor  $\mathbf{P} = \mathbf{P}^K + \mathbf{P}^V$  consists of a kinetic contribution

$$\mathbf{P}^K \equiv \frac{1}{4m} \langle \delta_1 \mathbf{p}_1 \mathbf{p}_1 + \mathbf{p}_1 \delta_1 \mathbf{p}_1 + (\mathbf{p}_1 \delta_1 \mathbf{p}_1)^t + \mathbf{p}_1 \mathbf{p}_1 \delta_1 \rangle - nm \mathbf{v}_0 \mathbf{v}_0 \quad (4.11)$$

(with superscript  $t$  denoting the tensor transpose) and a collisional transfer contribution

$$\begin{aligned} \mathbf{P}^V \equiv & \frac{-1}{4} \text{Tr}_{12} (\mathbf{r}_1 - \mathbf{r}_2) \nabla_1 V_{12} \\ & \times \int_{-1}^1 \delta \left( \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} + \frac{\lambda}{2} (\mathbf{r}_1 - \mathbf{r}_2) - \mathbf{r} \right) d\lambda \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \end{aligned} \quad (4.12)$$

The kinetic part of the pressure tensor involves the full singlet density operator, whereas the collisional contribution has only the product of the free density operators. This is precisely of the form of the exact pressure tensor, except that the collisional part involves an approximate form for the pair density operator, namely that correct to second order in density and within the proposed correlation creation procedure of Eq. (3.4).

At equilibrium in a homogeneous system, the pressure tensor is a multiple of the tensor identity, with the scalar pressure  $P$  being 1/3 of the (tensor) trace. Moreover, the delocalization integral over  $\lambda$  can be trivially performed and the operator  $\Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger$  becomes proportional to the Boltzmann factor  $\exp(-H_{12}^{(2)}/kT)$ . Thus, the equilibrium collisional transfer contribution to the scalar pressure is

$$\begin{aligned} P^V &= \frac{-n_f^2 A^6}{6q_{\text{int}}^2} \text{Tr}_{12} \delta_1(\mathbf{r}_1 - \mathbf{r}_2) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_1} e^{-H_{12}^{(2)}/kT} \\ &= \frac{-n_f^2 A^3(2)^{3/2}}{6q_{\text{int}}^2} \text{Tr}_{12}^{\text{rel}}(\mathbf{r}_1 - \mathbf{r}_2) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_1} e^{H_{12}^{(2,\text{rel})}/kT} \end{aligned} \quad (4.13)$$

In the second from the center-of-mass dependence has been explicitly traced over to leave only the relative “rel” motion trace. For the kinetic contribution to the pressure, which arises from the full singlet density operator, there is first of all the *free* contribution, which is immediately evaluated as  $n_f kT$ , and the correlation contribution

$$\begin{aligned} P_c^K &= \frac{n_f^2 A^6}{12mq_{\text{int}}^2} \text{Tr}_{12} [\mathbf{p}_1^2 \delta_1 + 2\mathbf{p}_1 \cdot \delta_1 \mathbf{p}_1 + \delta_1 \mathbf{p}_1^2] U_{12}^{(2)} \\ &= \frac{n_f^2 A^3(2)^{3/2}}{3mq_{\text{int}}^2} \text{Tr}_{12}^{\text{rel}} \left( \mathbf{p}^2 + \frac{3}{2} mkT \right) U_{12}^{(2,\text{rel})} \end{aligned} \quad (4.14)$$

Correctly the stream velocity enters as a displacement in the Maxwellian, which is necessary to compensate the  $\mathbf{v}_0$  terms in Eq. (4.11), but the resulting pressure is the same as if  $\mathbf{v}_0$  was zero, so that this elaboration is ignored here for simplicity of presentation. To get the second form of Eq. (4.14), it is necessary to express the operators in terms of relative and center-of-mass variables and then trace over the center-of-mass motion. This is conveniently done using the Weyl<sup>(33)</sup> correspondence, but the end result is that the delta function restricts the position integral and the momentum integration cancels a  $A^3$  factor and on converting to center-of-mass and relative  $[\mathbf{p} \equiv \frac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2)]$  momenta, the center-of-mass kinetic energy contributes the  $3mkT/2$  term to the relative motion trace.

If position and momentum operators commute (classical mechanics),

then the correlation part of the kinetic pressure becomes proportional to the second virial coefficient, namely

$$P_c^K|_{\text{class}} = -2n_f^2 kTB_{2,\text{class}} \quad (4.15)$$

which corrects the free condition to the kinetic pressure so as to arrive at the classical kinetic pressure,

$$P^K|_{\text{class}} = n_f kT - 2n_f^2 kTB_{2,\text{class}} = nkT \quad (4.16)$$

Within this classical approximation, the collisional transfer contribution to the pressure is

$$P^V|_{\text{class}} = \frac{-n_f^2}{6} \int \mathbf{r} \cdot \frac{\partial V}{\partial \mathbf{r}} e^{-V/kT} d\mathbf{r} = n^2 kTB_{2,\text{class}} \quad (4.17)$$

using the classical virial expression for the second virial coefficient. Here  $n_f^2$  has been replaced by  $n^2$ , correct to second order in the gas density.

For quantum systems (that is, keeping the noncommutation of position and momentum) and using the relation (4.9) between  $n$  and  $n_f$ , one can write the kinetic pressure conveniently as

$$P^K = nkT + \frac{n^2 A^3 (2)^{3/2}}{3mq_{\text{int}}^2} \text{Tr}_{12}^{\text{rel}} \left( p^2 - \frac{3}{2} mkT \right) U_{12}^{(2),\text{rel}} \equiv nkT + \frac{1}{3} n^2 kT \varepsilon_1 \quad (4.18)$$

Here the  $\varepsilon_1$  notation of Imam-Rahajoe and Curtiss<sup>(34)</sup> has been introduced and it is noted that the leading term is  $nkT$  rather than  $n_f kT$ . This is exactly the form for the kinetic pressure discussed earlier<sup>(11)</sup> from the viewpoint of equilibrium cluster theory. It was also shown there<sup>(11)</sup> how the kinetic, Eq. (4.18), and collisional, Eq. (4.13), contributions to the pressure combine to give the standard equilibrium expression for the quantum second virial coefficient. In classical mechanics  $\varepsilon_1$  vanishes and the separation of kinetic and collisional pressure contributions is the same as the separation of first and second virial coefficients. If position and momentum do not commute, these divisions are not the same. What is seen in the present formulation of density corrections to the Boltzmann equation is that the separation of kinetic and collisional contributions to the pressure is the same as that at equilibrium.

Energy conservation is now discussed. The expression for the single-particle energy density is itself complicated by the requirements of operator symmetry. Thus, on subtracting the convective energy, the quantity of interest will be referred to as the kinetic energy density,

$$n\varepsilon^K \equiv \text{Tr}_1 \left[ \frac{1}{8m} (\mathbf{p}_1^2 \delta_1 + 2\mathbf{p}_1 \cdot \delta_1 \mathbf{p}_1 + \delta_1 \mathbf{p}_1^2) + \left( H_{\text{int},1} - \frac{1}{2} m v_0^2 \right) \delta_1 \right] \rho_1^{(1)} \quad (4.19)$$



The rate of change for this quantity is described in more detail than was the continuity equation or the equation of motion. Using the operator form for  $\phi$  as it appears in Eq. (4.19), the general equation of change, Eq. (4.3), becomes

$$\begin{aligned} \frac{\partial n \varepsilon^K}{\partial t} + n m \mathbf{v}_0 \cdot \frac{\partial \mathbf{v}_0}{\partial t} &= -\nabla \cdot \left[ n \mathbf{v}_0 \left( \varepsilon^K + \frac{1}{2} m \mathbf{v}_0^2 \right) + \mathbf{q}^K + \mathbf{P}^K \cdot \mathbf{v}_0 \right] \\ &+ \frac{1}{2} m \mathbf{v}_0^2 \nabla \cdot (n \mathbf{v}_0) + \frac{1}{i\hbar} \text{Tr}_{12} [ \{ H_1^{(1)} \delta_1 \}_s, V_{12} ] - \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \end{aligned} \quad (4.20)$$

To obtain this result, care is needed to recognize that  $\mathbf{v}_0$  depends on position  $\mathbf{r}$  and time  $t$ . The kinetic contribution to the heat flux has the form

$$\mathbf{q}^K = \text{Tr}_1 \left\{ \left( \frac{\mathbf{p}_1}{m} - \mathbf{v}_0 \right) \left[ \frac{(\mathbf{p}_1 - m \mathbf{v}_0)^2}{2m} + H_{\text{int},1} \right] \delta_1 \right\}_s \rho_1^{(1)} \quad (4.21)$$

where in Eqs. (4.20)–(4.21) the  $\{ \cdot \}_s$  designates appropriately operator-symmetrized quantities. To evaluate the effect of the collisional term, a symmetrization is made between the two colliding particles; in particular, the delta function is rewritten in terms of symmetric and antisymmetric combinations, of which the antisymmetric leads to a gradient in the macroscopic position. This naturally divides the collisional term into flux (gradient) and production effects. On carrying out this program, the collisional term in the kinetic energy equation of change can be written

$$\frac{1}{i\hbar} \text{Tr}_{12} [ \{ H_1^{(1)} \delta_1 \}_s, V_{12} ] - \Omega_{12} \rho_{f2} \rho_{f2} \Omega_{12}^\dagger = -\nabla \cdot (\mathbf{q}_{\text{coll}} + \mathbf{P}^V \cdot \mathbf{v}_0) + \sigma^K \quad (4.22)$$

where the collisional contribution to the heat flux is

$$\begin{aligned} \mathbf{q}_{\text{coll}} &= \frac{1}{8} \text{Tr}_{12} \int_{-1}^1 d\lambda (\mathbf{r}_1 - \mathbf{r}_2) \left\{ \delta \left[ \mathbf{r} - \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} - \frac{\lambda}{2} (\mathbf{r}_1 - \mathbf{r}_2) \right] \right. \\ &\times \left( \frac{1}{i\hbar} [ H_{\text{int},1} - H_{\text{int},2}, V_{12} ] - \frac{1}{m} (\mathbf{p}_1 + \mathbf{p}_2 - 2m \mathbf{v}_0) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_1} \right) \Bigg\}_s \\ &\times \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \end{aligned} \quad (4.23)$$

and the production of kinetic energy is

$$\sigma^K = \frac{1}{4} \text{Tr}_{12} \left\{ (\delta_1 + \delta_2) \left( \frac{1}{i\hbar} [H_{\text{int},1} + H_{\text{int},2}, V_{12}]_- \right. \right. \\ \left. \left. - \frac{1}{2m} \left[ (\mathbf{p}_1 - \mathbf{p}_2) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_1} + \frac{\partial V_{12}}{\partial \mathbf{r}_1} \cdot (\mathbf{p}_1 - \mathbf{p}_2) \right] \right) \right\} \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \quad (4.24)$$

On combining Eqs. (4.20) and (4.22) and eliminating the time derivative of  $\mathbf{v}_0$  by use of the equation of motion (4.10), we find for the rate of change for the kinetic energy density

$$\frac{\partial n \varepsilon^K}{\partial t} = -\nabla \cdot (n \mathbf{v}_0 \varepsilon^K + \mathbf{q}^K + \mathbf{q}_{\text{coll}}) - \mathbf{P}' : \nabla \mathbf{v}_0 + \sigma^K \quad (4.25)$$

The pressure tensor contribution is of course responsible for the coupling of convective energy and (internal) kinetic energy, but the presence of the collisional production term  $\sigma^K$  implies that kinetic energy (internal plus convective) is not conserved.

Energy conservation is recovered by examining the potential energy density, which should be calculated and whose rate of change should be evaluated in a manner consistent with the binary-collision, second order in density, way in which the kinetic energy density is treated. This method of dealing with energy conservation is the same as that of Thomas and Snider.<sup>(7)</sup> Since the potential energy density is a two-particle observable, its expectation value is determined entirely by the pair density operator

$$n \varepsilon^V = \frac{1}{4} \text{Tr}_{12} (\delta_1 + \delta_2) V_{12} \rho_{12}^{(2)} \quad (4.26)$$

The time rate of change of the potential energy density is then determined up to second order in particle density by the pair von Neumann equation, the connection with the Boltzmann equation being made in that the various terms in the equation of change for the potential energy density are to be evaluated using Eq. (3.3) for the pair density operator. According to this prescription, the equation of change for the potential energy density is

$$\begin{aligned} \frac{\partial n \varepsilon^V}{\partial t} &= \frac{1}{4i\hbar} \text{Tr}_{12} [(\delta_1 + \delta_2) V_{12}, H_{12}^{(2)}]_- \rho_{12}^{(2)} \\ &= \frac{1}{4i\hbar} \text{Tr}_{12} \{ (\delta_1 + \delta_2) [V_{12}, H_{12}^{(2)}]_- + [\delta_1 + \delta_2, H_{12}^{(2)}]_- V_{12} \} \rho_{12}^{(2)} \\ &= -\sigma^K - \nabla \cdot (n \mathbf{v}_0 \varepsilon^V + \mathbf{q}^V) \end{aligned} \quad (4.27)$$

where the potential contribution to the heat flux is

$$\mathbf{q}^V = \frac{1}{4m} \text{Tr}_{12}(\mathbf{p}_1 \delta_1 + \delta_1 \mathbf{p}_1) V_{12} \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger \quad (4.28)$$

Since the rate of production of potential energy exactly compensates the rate of production of kinetic energy, it follows that the total energy is conserved for the Boltzmann equation, correct to second order in density. At equilibrium the heat fluxes all vanish, but the expressions for these are the same as would be obtained from the exact BBGKY hierarchy if the density expansion of the density operators were cut off at second order and evaluated according to Eqs. (2.3), (2.4), and (3.4).

## 5. DISCUSSION

Motivated by an attempt to reply to the criticisms of Laloë and Mullin<sup>(14)</sup> and by the distinction of free versus full density operators that Laloë has previously stressed,<sup>(22-24)</sup> this paper reexamines how the Stosszaahlansatz is to be implemented in deriving a quantum Boltzmann equation. Whereas Laloë distinguishes between free and full motion for the pair density operator, here the emphasis is on the singlet density operator. Essential to the approach taken here is the notion that in a binary collision, each of the particles entering into collision must be *free*. In analogy with the equilibrium cluster expansion, the (full) singlet density operator has contributions from correlated particles, so that a product of full singlet density operators should *not* be used as the initial state for a *binary* collision, but rather a product of the *free* part of the singlet density operator. The correlation contribution to the singlet density operator is identified by analogy with the equilibrium cluster expansion, as is the division of the pair density operator into correlated and uncorrelated parts. The interrelations between the free and (binary) correlation contributions to the singlet and pair density operators are spelled out in Eqs. (2.3)–(2.4). At low gas densities, correlations arise (it being assumed that there are no bound states) only by means of binary collisions of free particles and the interaction is described using the Møller operator, Eq. (3.4). In this way the first BBGKY equation can be closed and becomes an equation for the free part  $\rho_f$  of the singlet density operator, Eq. (3.6). Consequences for the equations of change have been given in Section 4.

Bound states have been explicitly excluded in this paper by assuming that the potential is not sufficiently attractive to support bound states. But it is somewhat clear how the possibility of bound states could be included in the formalism. Bound states consist of correlated pairs and thus these should contribute as an extra term in Eq. (3.4). Of course, within the pair

particle description given in this paper, such bound pairs cannot collide, but only contribute to gas properties by their free motion. This has been noted previously by Hawker.<sup>(35)</sup> Collisions of bound pairs require three- and four-particle collisions as have been introduced in our theory of recombination and decay.<sup>(25)</sup> Extension of the present work to cover such a situation is planned.

Bogolubov<sup>(15)</sup> postulates that after an initial transient, the distribution function (density operator  $\rho^{(N)}$ ) for the system is uniquely determined as a functional of the singlet distribution function (density operator  $\rho^{(1)}$ ). Bogolubov's method of determining this functional relation is essentially as follows: each  $s$ th-order density operator is given as a product of  $\rho^{(1)}$  modified by interaction by following the state of the  $s$  particles back in time according to free motion and then forward an equal time interval according to interaction motion, as in Eq. (3.2) for  $s=2$ . Here it is pointed out that if the  $s$  particles are to follow free motion before a collision, then they should be *free* before the collision. It is thus concluded that a more appropriate ansatz is to replace  $\rho^{(1)}$  by  $\rho_f$  in the construction of  $s$ th-order density operators. As a consequence, it is proposed to replace Bogolubov's function dependence of  $\rho^{(N)}$  on  $\rho^{(1)}$  by a functional dependence of  $\rho^{(N)}$  on  $\rho_f$ . Thus, it is the free particle state that determines the state of the whole  $N$ -particle system. Another way of describing this state of affairs is to say that the free particle state carries along with it correlations of all the other particles. To the author, this point of view seems consistent with the Bogolubov philosophy and is an elaboration of that approach to describe gas kinetic behavior.

The present paper includes only binary collisions and the binary correlations that arise from such collisions. But to sort out what part of the singlet density operator is free, it is necessary to identify the role of binary correlations in the whole gas (i.e., for all  $N$  particles). This is done by analogy with the equilibrium Ursell expansion. Appeal to this expansion has been made previously<sup>(36,37)</sup> in deriving the Boltzmann equation and its extension to higher gas density, but the present approach has a different emphasis, which might be described as a binary correlation expansion (see Section 2) with the pair Ursell operator identified as the binary correlation at equilibrium. Because all pairs of particles in the  $N$ -particle system have equal probability of being correlated, the singlet density operator, representing the ensemble average behavior of a particular particle (say 1), has contributions from  $N$ -particle states in which particle 1 is free and from  $N$ -particle states in which 1 is correlated to *any* of the other particles in the system. It is for this reason that the singlet density operator has both free and correlated contributions. For a pair of particles, each can be free, correlated together, or individually correlated to another particle in the

system. At equilibrium this property is explicitly displayed in Eq. (2.15). It is this structure that Eq. (2.4) incorporates.

It is interesting to consider how this structure of the  $s$ -particle density operators could be generalized to include triple and higher-order correlations. Whereas the present treatment truncated the Ursell expansion at  $U^{(2)}$  [see Eq. (2.9)], triple correlations can be included by retaining all  $U^{(3)}$  terms in the expansion of the Boltzmann factor, Eq. (2.7). The resulting structure for the first three reduced density operators would be the generalization of Eqs. (2.20)–(2.21) and this used to generalize the structure of the reduced density operators in nonequilibrium situations, i.e., generalizations of Eqs. (2.3)–(2.4). This requires a three-particle correlation density operator  $\rho_c^{(3)}$  for arbitrary nonequilibrium states. Here Bogolubov's solution to the initial value problem may be used to determine the correlation in terms of the free part of the singlet density operator; thus, in analogy to Eq. (3.4), it may be expected that

$$\begin{aligned} \rho_{c123}^{(3)} = & \Omega_{123} \rho_{f1} \rho_{f2} \rho_{f3} \Omega_{123}^\dagger - \rho_{f1} \Omega_{23} \rho_{f2} \rho_{f3} \Omega_{23} \\ & - \rho_{f2} \Omega_{13} \rho_{f1} \rho_{f3} \Omega_{13}^\dagger - \rho_{f3} \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger + 2\rho_{f1} \rho_{f2} \rho_{f3} \end{aligned} \quad (5.1)$$

Again it has been assumed that no bound states exist. Clearly, this type of scheme can be generalized to include arbitrarily high-order correlation contributions. Insertion of the resulting expressions for the singlet and pair density operators into the first BBGKY equation gives a generalization of the Boltzmann equation to arbitrary density, in which  $\rho_f$  is to be determined and from which the higher-order reduced density operators may be obtained using correlation calculations like Eqs. (3.4) and (5.1). In this way the functional dependence of  $\rho^{(N)}$  on  $\rho_f$  can be determined. It is also immediate that for a Maxwellian free density operator, all the correlation operators immediately take on their equilibrium Ursell operator forms and thus all equilibrium properties of the  $N$ -particle system are obtained. That the quantum Boltzmann equation at low gas density [in the present terminology, at sufficiently low enough density so that the free and complete singlet operators agree, equivalently that  $\text{Tr}_2 \rho_{c12}$  can be neglected in Eq. (2.3)] leads to a Maxwellian singlet density operator has been discussed.<sup>(6)</sup> It is a further question as to whether this can be proved when generalized to higher density.

There may be other ways of closing the BBGKY hierarchy, for example, by allowing both the free and the binary correlation operators to be unknown [i.e., not use Eq. (3.4)]. In such a situation the first and second BBGKY equations might be used with closure attained using a suitable generalization of Eq. (5.1) which includes the pair correlation operator as an independent entity.

## ACKNOWLEDGMENTS

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada. I thank Franck Laloë for preprints of his work and for many discussions about the problems with the density corrections to the quantum Boltzmann equation.

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