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Kinetic Equations for Autocorrelation Functions in Dilute Gases

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We show that in the case of a dilute gas of neutral particles kinetic equations for autocorrelation functions such as

$$\langle \hat{f}(\mathbf{r}, \mathbf{v}, t)\hat{f}(\mathbf{r}', \mathbf{v}', t')\rangle, \qquad \text{where} \qquad \hat{f}(\mathbf{r}, \mathbf{v}, t) = \textstyle\sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t))\, \delta(\mathbf{v} - \mathbf{v}_i(tt)),$$

can be obtained in a very simple manner by the use of the truncated BBGKY hierarchy. The resulting equations correspond to the low-density limit of the results of van Leeuwen and Yip. Moreover, the derivation does not make use of the Bogoliubov adiabatic approximation, and therefore includes non-Markovian effects which can be important in describing light scattering from gases and the collisional narrowing of atomic dipole radiation. The resulting equations in the long-wavelength limit correspond to the non-Markovian Boltzmann equation for the self-correlation part and the non-Markovian, linearized Boltzmann equation for the total autocorrelation function.

KEY WORDS: Kinetic equations; autocorrelation; light scattering; BBGKY hierarchy; non-Markovian; Liouville equation; Boltzmann equation.

1. INTRODUCTION

In recent years, there has been considerable interest in the use of techniques such as light scattering, slow neutron scattering, and spectral line shapes to investigate the kinetic properties of neutral and ionized gases. These techniques all have the common property of probing certain autocorrelation functions in the system. In the case of neutron and light scattering,$^{(1)}$ the quantity of interest is the density autocorrelation function

$$\langle \hat{\rho}(\mathbf{r}, t)\, \hat{\rho}(\mathbf{r}', t')\rangle = \sum_{i,j} \langle \delta(\mathbf{r} - \mathbf{r}_i(t))\, \delta(\mathbf{r}' - \mathbf{r}_i(t'))\rangle$$

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where $\mathbf{r}_i(t)$ is the position of the ith particle at time t. In the case of atomic line shapes, the quantity of interest is $\langle \mathbf{d}(\mathbf{r}, t) \cdot \mathbf{d}(\mathbf{r}', t')\rangle$, where $\mathbf{d}(\mathbf{r}, t)$ is the dipole current density at the point $\mathbf{r}$ and time t. In certain cases, this quantity is proportional to the density autocorrelation function.(2)

Since autocorrelation functions are of great interest, several authors,(3–11) have developed kinetic equations for these quantities. In particular, Rostoker,(5) Klimontovich,(6) and Dupree(7) have developed rather general techniques for calculating such quantities for plasmas. In the neutral-gas case, Van Leeuwen and Yip(8) and Blum and Lebowitz(9) have considered the problem in equilibrium systems. As Montgomery(10) recently pointed out, the methods used for the neutral-gas case are quite different from those used for the plasma and are in many ways much more complex and much less physically obvious then in the plasma case.

Montgomery used an approach very similar to that developed by Rostoker for the plasma case. In addition, he made use of the multitime method.(12) The problem with this latter technique is that it does not include non-Markovian effects, which can be important for the scattering or emission of light having frequencies greater than the inverse of the duration of a collision.

The purpose of this paper is to show that there is a very simple way to obtain the results for a homogeneous, dilute gas of natural atoms in the low-density limit which, although similar in spirit to Montgomery's approach, does include non-Markovian effects. This method is based on the methods used in the plasma case by Rostoker, Klimontovich, and Dupree. Moreover, we believe (as Montgomery emphasized) that these methods offer a much simpler approach to the problem than those of Refs. 8 and 9. This method may also have an additional advantage of being easily generalized to treat nonequilibrium systems if such systems ever become of interest. This treatment is presently somewhat restricted (as was that of Montgomery) in that it is very hard to account for initial correlation effects and triple and higher-order collisions. Thus, it is, perhaps, somewhat less appropriate for dense gases.

2. THE BBGKY EQUATIONS FOR AUTOCORRELATION FUNCTIONS

We are interested in autocorrelation functions of the form $\langle A(x, t)\, A(x', t')\rangle$, where $A(x, t)$ is a single-particle observable

$$A(x, t) = \sum_{i=1}^{N} a_i\, \delta(x - x_i(t)) \tag{1}$$

and $x = (\mathbf{r}, \mathbf{v})$, $\delta(x - x_i(t)) = \delta(\mathbf{r} - \mathbf{r}_i(t))\, \delta(\mathbf{v} - \mathbf{v}_i(t))$. The quantities $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$ are the exact position and velocity of the ith particle at time t. Any autocorrelation function of this form can be written in terms of the quantity(11)

$$f(x, t; x', t') = n^{-1}\langle \hat{f}(x, t)\, \hat{f}(x', t')\rangle \tag{2}$$

where n is the particle density and

$$\hat{f}(x, t) = \sum_{i=1}^{N} \delta(x - x_i(t)) \tag{3}$$

is the exact, one-particle distribution function.

In some cases, one is not interested in $f(x, t; x', t')$ itself but in only a part of it. For example, in the problem of collisional narrowing of spectral lines,$^{(2)}$ the quantity of interest is

$$\begin{aligned} W_{1,1}(x, \tau; x', t') &= n^{-1} \left\langle \sum_{i=1}^{N} \delta(x - x_i(t))\, \delta(x' - x_i(t')) \right\rangle \\ &= V \langle \delta(x - x_1(t))\, \delta(x' - x_1(t')) \rangle \end{aligned} \tag{4}$$

It is therefore useful to decompose the quantity f as

$$f(x, t; x', t') = W_{1,1}(x, \tau; x', t') + n W_{1,2}(x, \tau; x', t') \tag{5}$$

where

$$\begin{aligned} W_{1,2}(x, \tau; x', t') &= \frac{1}{n^2} \left\langle \sum_{i \neq j} \delta(x - x_i(t))\, \delta(x' - x_j(t')) \right\rangle \\ &= V^2 \langle \delta(x - x_1(t))\, \delta(x' - x_2(t')) \rangle \end{aligned} \tag{6}$$

The quantities $W_{1,1}$ and $W_{1,2}$ are the same as those introduced by Rostoker.$^{(5,10)}$ This decomposition is not, however, the same as that used by van Leeuwen and Yip$^{(8)}$ whose expression also involved a decomposition of the Liouville time-evolution operator $\exp(-iL_N\tau)$.

If we introduce a modified N-particle distribution function

$$F_N(\Gamma_N, \tau; x', t') = \exp(-iL_N\tau)\, \delta(x' - x_1) f_N(\Gamma_N) \tag{7}$$

where $f_N(\Gamma_N)$ is the usual N-particle distribution function and L_N is the Liouville operator, we can show that $W_{1,1}$ and $W_{1,2}$ are one-particle reduced distribution functions related to F_N as

$$W_{1,1}(x_1, \tau; x', t') = V \int \cdots \int dx_2 \cdots dx_N\, F_N(1, 2, 3, ..., N, \tau; x', t') \tag{8}$$

and

$$W_{1,2}(x_1, \tau; x', t') = V^2 \int \cdots \int dx_2 \cdots dx_N\, F_N(2, 1, 3, ..., N; x', t') \tag{9}$$

We note that, although F_N obeys the Liouville equation as a function of the $6N$ coordinates $\mathbf{r}_i$ and $\mathbf{v}_i$, it is not symmetric under the interchange $1 \leftrightarrow i$, but is symmetric under $i \leftrightarrow j$, if $i, j \neq 1$. The quantity $W_{1,1}(x, \tau; x', t')$ is the joint probability density that a particle is at phase point x' at time t' and then at the point x a time τ later. On the other hand, the quantity $W_{1,2}(x, \tau; x', t')$ is the joint probability density that a particle is at x' at time t' and another particle is at point x a time τ later. We will choose to work with an equilibrium system, in which case there is no t' dependence. The following results can, however, be easily generalized to treat nonequilibrium systems.

From the equation of motion for F_N, which is

$$\partial F_N / \partial \tau + iL_N F_N = 0 \tag{10}$$

we obtain in the usual manner of the BBGKY method(13) or by the method of Klimontovich(6) and Dupree(7) the equations

$$\frac{\partial}{\partial\tau} W_{1,1}(1, \tau) = -iL_1{}^0(1)\, W_{1,1}(1, \tau) - in \int dx_2\, L_2{}'(1, 2)\, W_{12,1}(1, 2, \tau) \tag{11}$$

and

$$\begin{aligned}\frac{\partial}{\partial\tau} W_{1,2}(1, \tau) = {}& -iL_1{}^0(1)\, W_{1,2}(1, \tau) - i \int dx_2\, L_2{}'(1, 2)\, W_{12,1}(2, 1, \tau) \\ & -in \int dx_2\, L_2{}'(1, 2)\, W_{13,2}(1, 2, \tau)\end{aligned} \tag{12}$$

where

$$L_1{}^0(1) = -i\mathbf{v}_1 \cdot \partial/\partial\mathbf{r}_1 \tag{13}$$

and

$$L_2{}'(1, 2) = \frac{i}{m} \frac{\partial}{\partial\mathbf{r}_i}\, \phi(\mathbf{r}_1 - \mathbf{r}_2) \cdot \left(\frac{\partial}{\partial\mathbf{v}_1} - \frac{\partial}{\partial\mathbf{v}_2}\right) \tag{14}$$

The quantities $W_{12,1}$ and $W_{13,2}$ are two-particle distribution functions defined by

$$W_{12,1}(x, x'', \tau; x', t') = V^2\langle\delta(x - x_1(t))\, \delta(x'' - x_2(t))\, \delta(x' - x_1(t'))\rangle \tag{15}$$

and

$$W_{13,2}(x, x'', \tau; x', t'') = V^3\langle\delta(x - x_1(t))\, \delta(x'' - x_3(t))\, \delta(x' - x_2(t'))\rangle \tag{16}$$

They can also be written as

$$W_{12,1}(1, 2, \tau) = V^2 \int \cdots \int dx_3 \cdots dx_N\, F_N(1, 2, 3, \ldots, N, \tau; x', t') \tag{17}$$

and

$$W_{12,3}(1, 2, \tau) = V^3 \int \cdots \int dx_3 \cdots dx_N\, F_N(3, 1, 2, 4, \ldots, N, \tau; x', t') \tag{18}$$

We will temporarily suppress the x' dependence in these functions.

Equations (11) and (12) represent the first equations of a BBGKY hierarchy which is obtained from Eq. (10) in the usual manner. This hierarchy differs from the usual one in the lack of complete symmetry of F_N under interchange of particles. We can, of course, obtain equations for $W_{12,1}$ and $W_{13,2}$ in terms of three-body distribution functions. The equation for $W_{12,1}$ is given by

$$\begin{aligned}\frac{\partial}{\partial\tau} W_{12,1}(1, 2, \tau) = {}& -iL_2(1, 2)\, W_{12,1}(1, 2, \tau) \\ & -in \int dx_3\, L_2{}'(1, 3)\, W_{123,1}(1, 2, 3, \tau) \\ & -in \int dx_3\, L_2{}'(2, 3)\, W_{123,1}(1, 2, 3, \tau)\end{aligned} \tag{19}$$

where

$$L_2(1,2) = L_1{}^0(1) + L_1{}^0(2) + L_2{}'(1,2) \tag{20}$$

and

$$W_{123,1}(x, x'', x''', \tau; x', t') = V^3\langle \delta(x - x_1(t))\, \delta(x'' - x_2(t))\, \delta(x''' - x_3(t))\, \delta(x' - x_1(t'))\rangle \tag{21}$$

A similar equation exists for $W_{13,2}$. At this point, we will restrict ourselves to two-body collisions and work to lowest order in the density. In that case, we can ignore the last two terms of Eq. (19), thereby truncating the hierarchy and giving[10]

$$\frac{\partial}{\partial\tau} W_{12,1}(1,2,\tau) = -iL_2(1,2)\, W_{12,1}(1,2,\tau) \tag{22}$$

which is the two-body Liouville equation. In a similar manner, we find

$$\frac{\partial}{\partial\tau} W_{12,3}(1,2,\tau) = -iL_2(1,2)\, W_{12,3}(1,2,\tau) \tag{23}$$

It is convenient at this point to introduce a Fourier transform with respect to the suppressed variable $\mathbf{r}'$. We define

$$\tilde{W}_{1,1}(x_1, \tau; \mathbf{k}, \mathbf{v}') = \int d\mathbf{r}' (\exp i\mathbf{k}\cdot\mathbf{r}')\, W_{1,1}(x_1, \tau; \mathbf{r}', \mathbf{v}') \tag{24}$$

with a similar definition for $\tilde{W}_{1,2}$. The scattering cross sections and line shapes are all expressed in terms of a Fourier transform of $W_{1,1}$ and $W_{1,2}$ with respect to both position variables.[1,2]

We next introduce correlation functions corresponding to $\tilde{W}_{12,1}(1, 2, \tau)$ and $\tilde{W}_{12,3}(1, 2, \tau)$ which have the property that they vanish when $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$. In the case of an equilibrium system, we have (see the appendix)

$$\tilde{W}_{12,1}(1,2,\tau; x', t') = \phi_1(2)\, \tilde{W}_{1,1}(1,\tau) + \tilde{G}_2(1,2,\tau) \tag{25}$$

and

$$\tilde{W}_{12,3}(1,2,\tau; x', t') = \phi_1(1)\, \tilde{W}_{1,2}(2,\tau) + \phi_1(2)\, \tilde{W}_{1,2}(1,\tau) + \tilde{H}_2(1,2,\tau) \tag{26}$$

where we have assumed that $\mathbf{k} \neq 0$. The quantity $\phi_1(1)$ is the usual Maxwell–Boltzmann distribution function. If the system is not in equilibrium, $\phi_1(1)$ is replaced by $\phi_1(1, t' + \tau)$, which obeys the Boltzmann equation to the order of density we are concerned with here. The quantities $\tilde{G}_2$ and $\tilde{H}_2$ are two-particle correlation functions.

From Eqs. (22) and (23), we obtain, to lowest order in density, the equations

$$\frac{\partial}{\partial\tau} \tilde{G}_2(\tau) = -iL_2{}'(1,2)\, \tilde{G}_2 - iL_2{}'(1,2)\, \phi_1(2)\, \tilde{W}_{1,1}(1,\tau) \tag{27}$$

and

$$\frac{\partial}{\partial\tau}\tilde{H}_2(\tau) = -iL_2(1,2)\,\tilde{H}_2(\tau) - iL_2'(1,2)[\phi_1(1)\,\tilde{W}_{1,2}(2,\tau) + \phi_1(2)\,\tilde{W}_{1,2}(1,\tau)] \tag{28}$$

For nonzero **k**, which are the cases of interest, we also have

$$\frac{\partial}{\partial\tau}\tilde{W}_{1,1}(1,\tau) = -\,iL_1{}^0(1)\,\tilde{W}_{1,1}(1,\tau) - in\int dx_2\,L_2'(1,2)\,\tilde{G}_2(1,2,\tau) \tag{29}$$

and

$$\begin{aligned}\frac{\partial}{\partial\tau}\tilde{W}_{1,2}(1,\tau) = &-\,iL_1{}^0(1)\,\tilde{W}_{1,2}(1,\tau) - i\int dx_2\,L_2'(1,2)\,\tilde{G}_2(2,1,\tau)\\ &-\,in\int dx_2\,L_2'(1,2)\,\tilde{H}_2(1,2,\tau)\end{aligned} \tag{30}$$

3. KINETIC EQUATIONS FOR $W_{1,1}$

Since Eqs. (27) and (28) form a closed set for $W_{1,1}$ and G_2, we begin by obtaining a kinetic equation for $W_{1,1}$. We can solve Eq. (27) formally as

$$\begin{aligned}\tilde{G}_2(1,2,\tau) = &\exp(-iL_2\tau)\,\tilde{G}_2(0)\\ &-i\int_0^\tau d\tau_1\exp[-iL_2(\tau-\tau_1)]\,L_2'(1,2)\,\tilde{W}_{1,1}(1,\tau_1)\,\phi_1(2)\end{aligned} \tag{31}$$

We shall assume henceforth that there are no initial correlations between the particles. Consequently, the first term in Eq. (31) vanishes. (The initial correlations give rise to the Enskog correction, which can be important for dense systems.) If we then define the operator

$$S_2(t) = \exp(-iL_2t)\exp(iL_2{}^0t) \tag{32}$$

where

$$L_2{}^0 = L_1{}^0(1) + L_1{}^0(2) \tag{33}$$

and substitute the resulting expression into Eq. (29), we obtain

$$\begin{aligned}\frac{\partial}{\partial\tau}W_{1,1}(\tau) + iL_1{}^0(1)\,W_{1,1}(\tau) = &-\,in\int dx_2\int_0^\tau d\tau_1\,L_2'(1,2)\\ &\times\frac{\partial S_2(\tau_1)}{\partial\tau_1}\exp(-iL_2{}^0\tau_1)\,\phi(2)\,\tilde{W}_{1,1}(1,\tau-\tau_1)\end{aligned} \tag{34}$$

It is next convenient to introduce a Fourier transform of $W_{1,1}(1,\tau)$ with respect to the remaining position vector. We define

$$W_{1,1}(\mathbf{k},\mathbf{v}_1,\tau) = \int d\mathbf{r}_1\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\,\tilde{W}_{1,1}(\mathbf{r}_1,\mathbf{v}_1,\tau) \tag{35}$$

From Eq. (34), we then obtain

$$\begin{aligned}\frac{\partial}{\partial\tau} W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) &+ i\mathbf{k}\cdot\mathbf{v}_1 W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau)\\ &= -in \int d\mathbf{v}_2 \int_0^\tau d\tau_1 \left\langle \mathbf{k}, 0 \,\middle|\, L_2'(1, 2) \frac{\partial S_2(\tau_1)}{\partial\tau_1} \exp(-iL_2{}^0\tau_1) \,\middle|\, \mathbf{k}, 0 \right\rangle\\ &\quad\times \phi_1(v_2)\, W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau - \tau_1) \qquad (36)\end{aligned}$$

where the Dirac-like notation follows that introduced by van Leeuwen and Yip,[(8)]

$$\begin{aligned}&\langle \mathbf{k}_1, \mathbf{k}_2 \mid A(1, 2) \mid \mathbf{k}_1', \mathbf{k}_2' \rangle\\ &\quad= (1/V) \int d\mathbf{r}_1 \int d\mathbf{r}_2 \times (\exp -i\mathbf{k}_1\cdot\mathbf{r}_1 \exp -i\mathbf{k}_2\cdot\mathbf{r}_2)\, A(1, 2) \exp i\mathbf{k}_1'\cdot\mathbf{r}_1 \exp i\mathbf{k}_2'\cdot\mathbf{r}_2 \qquad (37)\end{aligned}$$

From Eq. (36), we see that the kinetic equation has the form

$$\frac{\partial}{\partial\tau} W_{1,1} + i\mathbf{k}\cdot\mathbf{v}_1 W_{1,1} = \int_0^\tau d\tau_1\, \mathbf{M}(k, \tau_1) \exp(-i\mathbf{k}\cdot\mathbf{v}_1\tau_1)\, W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau - \tau_1) \qquad (38)$$

where

$$M(\mathbf{k}, \tau_1) = -in \int d\mathbf{v}_2 \left\langle \mathbf{k}, 0 \,\middle|\, L_2'(1, 2) \frac{\partial S_2(\tau_1)}{\partial\tau_1} \,\middle|\, \mathbf{k}, 0 \right\rangle \phi_1(\mathbf{v}_2) \qquad (39)$$

Equation (39) reduces to the result obtained by Blum and Lebowitz if the system is in equilibrium and there are no initial correlations. Equation (39) is essentially the non-Markovian Boltzmann equation. The kernel $M(\mathbf{k}, \tau_1)$ vanishes if τ_1 is much larger than the duration of a collision. Consequently, if there is a large separation between the duration of a collision and the time between collisions, we can approximate $\exp(-i\mathbf{k}\cdot\mathbf{v}_1\tau_1)\, W_{1,1}(\tau - \tau_1)$ by $W_{1,1}(\tau)$ over the range for which the kernel is not zero. Furthermore, if τ is large compared to the duration of a collision, we can write

$$\frac{\partial}{\partial\tau} W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) + i\mathbf{k}\cdot\mathbf{v}_1 W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) = \left[\int_0^\infty M(\mathbf{k}, \tau_1)\, d\tau_1\right] W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) \qquad (40)$$

This equation differs from the Markovian form obtained by Blum and Lebowitz because we absorbed the $\exp -i\mathbf{k}\cdot\mathbf{v}_1\tau$ factor into $W_{1,1}$. This is necessary because $W_{1,1}(\tau)$ varies as $\exp -i\mathbf{k}\cdot\mathbf{v}_1\tau$ even for τ of the order of the duration of a collision τ_d. This time dependence is significant unless $kv_0\tau_d \ll 1$, where v_0 is a typical velocity.

If we do assume that the wavelength is large compared to the range of the potential, so that $kv_0\tau_d \ll 1$, we can approximate $M(\mathbf{k}, \tau_1)$ by $M(0, \tau, \tau)$. We then can write the kinetic equation in the form

$$\begin{aligned}\frac{\partial}{\partial\tau} W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) &+ i\mathbf{k}\cdot\mathbf{v}_1 W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau)\\ &= -in \int dv_2\, L_2'(1, 2)\, S_2(\infty)\, \phi_1(\mathbf{v}_2)\, W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) \qquad (41)\end{aligned}$$

The right-hand side of Eq. (41) is simply the Boltzmann collision integral.(14) That is, if we denote the usual Boltzmann collision integral by $J[\phi_1(1)\,\phi_1(2)]$, then the equation for $W_{1,1}$ is

$$\frac{\partial}{\partial\tau} W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) + i\mathbf{k}\cdot\mathbf{v}_1 W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau) = J[W_{1,1}(\mathbf{k}, \mathbf{v}_1, \tau)\,\phi_1(\mathbf{v}_2)] \tag{42}$$

If the system is not in equilibrium, we must simultaneously solve the Boltzmann equation for ϕ_1 as well.

4. KINETIC EQUATION FOR $W_{1,2}$

Equations (27)–(29) form a coupled set of equations for $\tilde{H}_2$, $\tilde{G}_2$, and $\tilde{W}_{1,2}$. We solve Eq. (28) formally as

$$\begin{aligned}\tilde{H}_2(\tau) = \exp(-iL_2\tau)\,\tilde{H}_2(0) - i\int_0^\tau d\tau_1 \exp(-iL_2\tau_1)\,L_2'(1,2)&\\ \times [\phi_1(1)\,\tilde{W}_{1,2}(2, \tau-\tau_1) + \phi_1(2)\,\tilde{W}_{1,2}(1, \tau-\tau_1)]&\end{aligned} \tag{43}$$

If we then substitute this expression for $\tilde{H}_2$ and the expression for $\tilde{G}_2$ given in Eq. (31) into Eq. (30) for $W_{1,2}$, we obtain

$$\begin{aligned}\frac{\partial}{\partial\tau}\tilde{W}_{1,2}(1,\tau) = &- iL_1^0(1)\,\tilde{W}_{1,2}(1,\tau)\\ &- i\int dx_2 \int_0^\tau d\tau_1\, L_2'(1,2)\,\frac{\partial S_2(\tau_1)}{\partial\tau_1} \exp(-iL_2^0\tau_1)\,\phi_1(2)\,\tilde{W}_{1,1}(1, \tau-\tau_1)\\ &- in\int dx_2 \int_0^\tau d\tau_1\, L_2'(1,2)\,\frac{\partial S_2(\tau_1)}{\partial\tau_1} \exp(-iL_2^0\tau_1)\\ &\times [\phi_1(1)\,\tilde{W}_{1,2}(2, \tau-\tau_1) + \phi_1(2)\,\tilde{W}_{1,2}(1, \tau-\tau_1)]\end{aligned} \tag{44}$$

where we have again ignored the effects of initial correlations.

We can then combine Eqs. (34) and (44) to obtain the following equation for $\tilde{f} = n\tilde{W}_{1,1} + n^2\tilde{W}_{1,2}$:

$$\begin{aligned}\frac{\partial}{\partial\tau}\tilde{f} + iL_1^0\tilde{f} = - in\int dx_2\, L_2'(1,2)\int_0^\tau d\tau_1\, \frac{\partial S_2(\tau_1)}{\partial\tau_1}&\\ \times \exp(-iL_2^0\tau_1)[\phi_1(2)\,\tilde{f}(x_1, \tau-\tau_1; \mathbf{k}, \mathbf{v}') + \phi_1(1)\,\tilde{f}(x_2, \tau-\tau_1; \mathbf{k}, \mathbf{v}')]&\end{aligned} \tag{45}$$

If the system is in equilibrium, the above equation is the non-Markovian, linearized Boltzmann equation. We can put the above equation into a form similar to that obtained by Van Leeuwen and Yip(8) by defining the quantity

$$\begin{aligned}f(\mathbf{k}, \mathbf{v}_1, \tau; \mathbf{v}') &= \int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})\,f(x_1, \tau; \mathbf{k}, \mathbf{v}')\\ &= \int d\mathbf{r} \int d\mathbf{r}' \exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')]\,f(x_1, t; x')\end{aligned} \tag{46}$$

We then find that

$$
\begin{aligned}
&\frac{\partial}{\partial\tau} f(\mathbf{k}, \mathbf{v}_1, \tau) + i\mathbf{k}\cdot\mathbf{v}_1 f(\mathbf{k}, \mathbf{v}_1, \tau) \\
&\quad = -in \int d\mathbf{v}_2 \int_0^\tau d\tau_1 \left[\left\langle \mathbf{k}, 0 \,\middle|\, L_2'(1,2)\frac{\partial S_2(\tau_1)}{\partial\tau_1}\exp(-iL_2{}^0\tau_1) \middle|\, \mathbf{k}, 0\right\rangle\right. \\
&\qquad \times f(\mathbf{k}, \mathbf{v}_1, \tau-\tau_1)\,\phi_1(\mathbf{v}_2) \\
&\qquad \left. + \langle \mathbf{k}, 0 \mid L_2'(1,2)\frac{\partial S_2(\tau_1)}{\partial\tau_1}\exp(-iL_2{}^0\tau_1) \mid 0, \mathbf{k}\rangle f(\mathbf{k}, \mathbf{v}_2, \tau-\tau_1)\,\phi_1(\mathbf{v}_1)\right] \qquad (47)
\end{aligned}
$$

If the system is in equilibrium, this is the equation obtained by van Leeuwen and Yip(8) and Blum and Lebowitz(9) (neglecting initial correlation). If $\tau \gg \tau_d$ (the duration of a collision) and if the duration of a collision is small compared to the time between collisions, we obtain the Markovian equation

$$
\begin{aligned}
&\frac{\partial}{\partial\tau} f(\mathbf{k}, \mathbf{v}_1, \tau) + i\mathbf{k}\cdot\mathbf{v}_1 f(\mathbf{k}, \mathbf{v}_1, \tau) \\
&\quad = \int d\mathbf{v}_2 \left[M_1(\mathbf{k}, \tau, t') f(\mathbf{k}, \mathbf{v}_1, \tau) + M_2(\mathbf{k}, \tau, t') f(\mathbf{k}_1, \mathbf{v}_2, \tau)\right] \qquad (48)
\end{aligned}
$$

where

$$
M_1(\mathbf{k}, \tau, t') = -in \int_0^\infty d\tau_1 \langle \mathbf{k}, 0 \mid L_2'(1,2)\frac{\partial S_2(\tau_1)}{\partial\tau_1} \mid \mathbf{k}, 0\rangle\,\phi_1(\mathbf{v}_2) \qquad (49)
$$

and

$$
M_2(\mathbf{k}, \tau, t') = -in \int_0^\infty d\tau_1 \langle \mathbf{k}, 0 \mid L_2'(1,2)\frac{\partial S_2(\tau_1)}{\partial\tau_1} \mid 0, \mathbf{k}\rangle\,\phi_1(\mathbf{v}_2) \qquad (50)
$$

Again these equations differ from the Markovian limit used by Blum and Lebowitz(9) because we have absorbed factors of the form exp $-i\mathbf{k}\cdot\mathbf{v}\tau_1$ as in the last section.

In the long-wavelength limit, $kv_0\tau_d \ll 1$, we can set $k = 0$, in which case we obtain

$$
\begin{aligned}
&\left(\frac{\partial}{\partial\tau} + i\mathbf{k}\cdot\mathbf{v}_1\right) f(\mathbf{k}, \mathbf{v}_1, \tau) \\
&\quad = -in \int d\mathbf{v}_2\, L_2'(1,2)\, S_2(\infty)[\phi_1(\mathbf{v}_2) f(\mathbf{k}, \mathbf{v}_1, \tau) + \phi_1(\mathbf{v}_1) f(\mathbf{k}, \mathbf{v}_2, \tau)] \qquad (51)
\end{aligned}
$$

In the case of thermodynamic equilibrium, this equation reduces to the linearized Boltzmann equation

$$
\left(\frac{\partial}{\partial\tau} + i\mathbf{k}\cdot\mathbf{v}_1\right) f(\mathbf{k}, \mathbf{v}_1, \tau) = J[\phi_1(v_2) f(\mathbf{k}, \mathbf{v}_1, \tau) + \phi_1(\mathbf{v}_1) f(\mathbf{k}, \mathbf{v}_2, \tau)] \qquad (52)
$$

which is the result obtained in Refs. 8 and 9.

5. DISCUSSION

We have used the BBGKY method to obtain kinetic equations for autocorrelation functions for a dilute gas of neutral particles. These results can easily be extended to nonequilibrium gases. The basic philosophy of this approach is quite similar to that used by Montgomery.(10) The method of solution is somewhat different and offers some advantages in that it allows us to account for non-Markovian effects. On the other hand, both methods suffer from the difficulty of being hard pressed to account for initial correlations (the Enskog approximation) which are important for dense gases.

In the Markovian limit, the self-part, $W_{1,1}$, can be reduced to the Boltzmann equation in the low-density limit. On the other hand, $W_{1,2}$ obeys the linearized Boltzmann equation. These results have been previously obtained by other authors(8,9) by the use of considerably more complicated methods. It is important to note, however, that van Leeuwen and Yip(8) did not decompose the autocorrelation function in this way (although they mention the result for $W_{1,1}$ in their discussion). This is the reason Montgomery(10) was unable to verify completely some of their results.

APPENDIX

We can obtain the correlation functions corresponding to $W_{12,1}$ and $W_{13,2}$ by the use of a method introduced by Dupree.(7) If we define $\hat{f}_i(x, t) = \delta(x - x_i(t))$ and its fluctuation from the average by

$$\delta\hat{f}_i(x, t) = \hat{f}_i(x, t) - V^{-1}\phi_1(\mathbf{v}) \tag{53}$$

we can write $W_{12,1}$ and $W_{13,2}$ as

$$\begin{aligned} W_{12,1}(x, x'', \tau; x') = &- V^{-1}\phi_1(\mathbf{v})\,\phi_1(\mathbf{v}'')\,\phi_1(\mathbf{v}') + W_{1,1}(x, \tau; x')\,\phi_1(\mathbf{v}'') \\ &+ V^{-1}\phi_1(\mathbf{v}')\,g_2(x, x'') + V^{-1}W_{1,2}(x'', \tau; x')\,\phi_1(\mathbf{v}) \\ &+ V^2\langle\delta\hat{f}_1(x, t)\,\delta\hat{f}_2(x'', t)\,\delta\hat{f}_1(x', t')\rangle \end{aligned} \tag{54}$$

where g_2 is the usual two-body correlation function.

In the limit $V \to \infty$ and $N \to \infty$, the first, third, and fourth terms on the right-hand side of the above equation vanish, leaving us with

$$W_{12,1}(x, x'', \tau; x') = W_{1,1}(x, \tau; x')\,\phi_1(\mathbf{v}'') + \lim_{V\to\infty} V\langle\delta\hat{f}_1(x, t)\,\delta\hat{f}_2(x'', t)\,\delta\hat{f}_1(x', t')\rangle \tag{55}$$

In a similar way, we can show that in the infinite-volume limit

$$\begin{aligned} W_{13,2}(x, x'', \tau; x') = &\ \phi_1(\mathbf{v})\,\phi_1(\mathbf{v}'')\,\phi_1(\mathbf{v}') + W_{1,2}(x, \tau; x')\,\phi_1(\mathbf{v}'') + W_{1,2}(x'', \tau; x')\,\phi_1(\mathbf{v}) \\ &+ \phi_1(\mathbf{v}')\,g_2(x, x'') + \lim_{V\to\infty} V^3\langle\delta\hat{f}_1(x, t)\,\delta\hat{f}_2(x'', t)\,\delta\hat{f}_3(x', t')\rangle \end{aligned} \tag{56}$$

When $t = t'$, the last term of Eq. (55) is proportional to the two-particle correlation function g_2 and the last term of Eq. (56) is related to the three-particle correlation function g_3.

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