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Mode Coupling from Linear and Nonlinear Kinetic Equations

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The calculation of mode coupling contributions to equilibrium time correlation functions from the nonlinear Boltzmann equation is reconsidered. It is suggested that the use of a nonlinear kinetic equation is not appropriate in this context, but instead such calculations should be reinterpreted in terms of the Klimontovich equation for the microscopic phase space density. For hard spheres the Klimontovich equation is formally similar to the nonlinear Boltzmann equation, and this similarity is exploited to explain the successful calculation of mode coupling effects from the latter. The relationship of the Klimontovich formulation to the linear ring approximation is also established.

KEY WORDS: Kinetic equation; Klimontovich equation; time correlation functions; mode coupling; hard spheres; nonlinear dynamics.

1. INTRODUCTION

The slow decay of equilibrium correlation functions for long times is associated with the coupling of hydrodynamic modes. The most detailed microscopic justification for such mode coupling is a kinetic theory description for gases, in which a selective class of secular collision sequences is summed. This is the "ring" approximation, and is characterized by a linear operator consisting of the usual Boltzmann binary collision operator plus a correction due to the many-body ring collisions.(1) An alternative, and

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considerably simpler, description of the long-time behavior of correlation functions for gases has been given by Hauge.(2) In place of the detailed many-body contributions of the ring approximation, he assumed that these corrections can be incorporated simply by the replacement of the linear Boltzmann kinetic equation with the corresponding nonlinear Boltzmann equation. Indeed, it was shown that the long-time behavior of the Green–Kubo correlation functions for transport coefficients calculated in this way agree in detail with the results of the linear ring kinetic theory. More recently, the method of Hauge has been extended in an attempt to describe higher densities.(3) Such calculations have also been interpreted as showing the existence of slowly decaying solutions to the nonlinear Boltzmann equation.(4) However, Ubbink and Hauge(5) indicated that there are serious conceptual and mathematical problems associated with the justification of the nonlinear Boltzmann equation for equilibrium time correlation functions. The purpose of the discussion here is to clarify in what sense the nonlinear Boltzmann equation applies and show its relationship to the ring kinetic approximation.

In an attempt to relate the linear and nonlinear kinetic descriptions, Ubbink and Hauge showed that the usual derivation of the nonlinear Boltzmann equation for reduced distribution functions fails when applied to time correlation functions. The reason for this is that the nonlinear cluster expansion of the BBGKY hierarchy(6) introduces initial correlations to the lowest order in the density that do not decay in time. In contrast, the linear cluster expansion of the ring kinetic theory(7) is more appropriate for the special initial conditions associated with time correlation functions, and has no such problems. This difference is actually one reflection of a more fundamental difficulty to be expected in any attempt to justify the nonlinear Boltzmann equation in this context. It is shown in the next section that the general symmetry properties of equilibrium time correlation functions require that the kinetic theory be linear. This fact is well known,(8) although not always stated explicitly, as a difference between kinetic theories for reduced distribution functions (which are nonlinear in general) and those for time correlation functions. Consequently the application of any approximate nonlinear kinetic theory for the latter will necessarily entail internal inconsistencies. Here, the point of view is taken that such inconsistencies are too serious to admit the nonlinear Boltzmann equation as a reasonable model for equilibrium correlation functions. Instead, the success of Hauge's calculation of mode-coupling effects is explained by exploiting a close relationship between the nonlinear Boltzmann equation for the *average* phase space density, and the Klimontovich equation for the *microscopic* phase space density. In this way the following questions are addressed:

(1) Is there some sense in which time correlation functions can be calculated from a nonlinear Boltzmann equation?

(2) Can the mode-coupling calculations of Hauge be justified?

(3) How do the many-body ring contributions arise from the nonlinear Boltzmann operator, which apparently describes only binary collisions?

The answers to (1) and (2) are affirmative if the nonlinear Boltzmann equation is reinterpreted as applying to the microscopic phase density, rather than to the dependent variable of the kinetic theory. The answer to (3) is shown to depend on the method used to approximate the nonlinear Klimontovich equation.

2. LINEAR AND NONLINEAR FORMULATIONS

In this section two exact formulations of the time correlation functions are given. The first is in terms of the average dynamics in the single-particle phase space. This dynamics is shown to be linear and defines the linear kinetic theory for time correlation functions. The second formulation is based on the microscopic single-particle phase density which satisfies the nonlinear Klimontovich equation. The precise relationship of these two formulations is established, and the formal similarity of the Klimontovich equation for hard spheres to the nonlinear Boltzmann equation is used to clarify the role of the latter in calculating time correlation functions.

2.1. Linear Kinetic Theory

The utility of kinetic equations is due to the fact that many observables of interest are represented by sums of single-particle functions,

$$A = \sum_{i=1}^{N} a(x_i), \quad B = \sum_{i=1}^{N} b(x_i), \quad \text{etc.} \tag{2.1}$$

where x_i denotes the position and momentum of the ith particle. The equilibrium time correlation function for two such observables is defined by

$$C_{AB}(t) = \langle A^*(t)[B - \langle B\rangle]\rangle \tag{2.2}$$

The brackets denote an equilibrium ensemble average, and the asterisk indicates complex conjugation. Because of the form of the phase functions, A, B, Eq. (2.2) defines a time-dependent functional of the single-particle quantities, $a(x)$ and $b(x)$:

$$C_t[a,b] \equiv C_{AB}(t) \tag{2.3}$$

The class of single-particle functions is taken to be the elements of a Hilbert space, H, with scalar product

$$(a,b) = \int dx\, F_0(x) a^*(x) b(x) \tag{2.4}$$

where $F_0(x)$ is the Maxwell–Boltzmann distribution function. The following properties of $C_t[a,b]$ then hold:

$$\begin{gathered} C_t[a,b] \leqslant (a,a)(b,b)^{1/2} \\ C_t[a, \beta_1 b_1 + b_2] = \beta_1 C_t[a,b_1] + \beta_2 C_t[a,b_2] \\ C_t[\alpha_1 a_1 + \alpha_2 a_2, b] = \alpha_1^* C_t[a_1,b] + \alpha_2^* C_t[a_2,b] \end{gathered} \tag{2.5}$$

where α_1, α_2, β_1, and β_2 are arbitrary complex scalars. These properties characterize $C_t[a,b]$ as a bounded bilinear (sesquilinear) functional on H. It follows from the Reisz representation theorem$^{(9)}$ that there exist y_t, z_t such that

$$C_t[a,b] = (a, y_t) = (z_t, b)$$

or

$$C_t[a,b] = (a, U_t b) \tag{2.6}$$

where U_t is a linear operator. This result may be written more explicitly as

$$C_t[a,b] = \int dx\, F_0(x) a^*(x) \psi(x,t) \tag{2.7}$$

with

$$\psi(x,t) = (U_t b)(x) \tag{2.8}$$

Therefore the correlation functions, when represented in terms of the average dynamics in the single-particle phase space, are determined from a linear kinetic equation. Conversely, any nonlinear approximation to U_t necessarily violates one of the general properties, (2.5). The above results are exact for all times, and are not restricted to low-density. [Actually, (2.6) is even more general than the discussion here indicates, and applies to the quantum case as well with suitable changes in the scalar product$^{(10)}$.]

An explicit but formal representation of the operator, U_t, is possible in terms of the microscopic phase space density,

$$f(x,t) = \sum_{i=1}^{N} \delta(x - x_i(t)) \tag{2.9}$$

where x is a field point in the single-particle phase space. As the name indicates, $f(x,t)$ is the exact number density for particles with momentum and position, x, at time, t. It is convenient to define the normalized deviation of $f(x,t)$ from its equilibrium average by

$$\phi(x,t) = \frac{f(x,t) - F_0(x)}{F_0(x)} \tag{2.10}$$

Then the correlation function can be expressed as

$$C_t[a,b] = \int dx\, F_0(x) a^*(x) \int dx'\, F_0(x') G(x,t;x',0) b(x) \tag{2.11}$$

with

$$G(x,t;x',0) = \langle \phi(x,t)\phi(x') \rangle \tag{2.12}$$

Comparison of Eqs. (2.11) and (2.8) shows that

$$\psi(x,t) = \int dx' \, F_0(x') G(x,t;x',0) b(x') \tag{2.13}$$

so that $G(x,t;x',0)$ is now identified as the kernel of the linear operator, U_t. It follows that $G(x,t;x',0)$ satisfies the same linear kinetic equation as $\psi(x,t)$, except with different initial conditions. For completeness, the formal linear kinetic equation for $G(x,t;x',0)$ is obtained in Appendix B. The result is

$$\left(\frac{\partial}{\partial t} + \Omega\right) G(t) + \int_0^t dt' \, K(t-t') G(t') = 0 \tag{2.14}$$

where Ω and $K(t)$ are linear operators whose formal definition is also given in Appendix B. The analysis of these operators is the principal problem in the linear kinetic theory approach to equilibrium time correlation functions. In particular, Ω can be determined exactly(8,11) and is known as the generalized Enskog operator. The mode-coupling effects are contained in the operator, $K(t)$.

As a specific example, consider the current–current correlation function associated with the kinetic parts of the Green–Kubo expressions for transport coefficients. This corresponds to the choice

$$a(x) = Vb(x) = j(v) \tag{2.15}$$

where V is the volume of the system and $j(v)$ is a function of the velocity only. In Ref. 5 the correlation function is rewritten using the identity,

$$j(v) = \int dx_0 \, j(v_0) \delta(v - v_0) W(r - r_0) \tag{2.16}$$

for one of the currents. Here, $W(r)$ is an arbitrary function with the normalization,

$$\int dr \, W(r) = 1 \tag{2.17}$$

Then, using the invariance of the equilibrium ensemble under spatial translations, Eq. (2.11) becomes

$$\begin{aligned} C(t) &= \int dv_0 \, F_0(v_0) j(v_0) \int dx \, F_0(x) j(v) \psi_W(x,t) \\ \psi_W(x,t) &= \int dx' \, G(x,t;x',0) \delta(v' - v_0) W(r' - r_0) \end{aligned} \tag{2.18}$$

This representation for $\psi_W(x,t)$ is equivalent to that defined in Ref. 5. As noted in the Introduction, the latter authors assume that the long-time behavior of $C(t)$ for a low-density gas can be calculated from a *nonlinear* Boltzmann equation for $\psi_W(x,t)$. The main point of this section is to emphasize that such an assumption is inconsistent with the fundamental bilinearity of $C(t)$, as expressed by Eq. (2.5). It may be thought that the introduction of the arbitrary function $W(r)$ somehow circumvents the above requirements, to allow a nonlinear representation for this special class of initial conditions. However, Eq. (2.18) clearly shows the linearity in this case. [That is, if W_1 and W_2 have the normalization (2.17), then so does any convex combination, $W = \alpha W_1 + (1 - \alpha) W_2$; consequently $\psi_W = \alpha\psi_{W_1} + (1 - \alpha)\psi_{W_2}$ and the evolution is linear.] Equation (2.18) is a special case of the general linear kinetic theory formulation with the identification,

$$\psi_W(x,t) = U_t\left[\frac{\delta(v - v_0) W(r - r_0)}{F_0(v_0)}\right] \tag{2.19}$$

In summary, correlation functions of the type (2.2) may be represented as averages over the effective dynamics in the single-particle phase space. This dynamics is necessarily linear and consequently the associated kinetic equations are linear. A formal expression for the kinetic theory can be obtained as in Eq. (2.14) where the operators Ω and $K(t)$ are to be evaluated in some approximation suitable for the system considered. A low-density evaluation of Ω and $K(t)$ leads to the linear Boltzmann equation, for times not too large. For asymptotically long times other many-body effects must be included, even for low density, leading to the linear ring approximation.

2.2. Klimontovich Formulation

The kernel for the liner operator, U_t, defined by Eq. (2.12) is closely related to the microscopic phase space density, $f(x,t)$. The time dependence of $f(x,t)$ is governed by Hamilton's equations. However, the special form of $f(x,t)$ as the sum of δ functions in the phase variables allows Hamilton's equations to be converted into an equation for $f(x,t)$ with x and t as variables rather than $\{x_i\}$ and t. In the latter case the equation is called the Klimontovich equation.(12) The two equivalent sets of equations are

$$\begin{aligned}\frac{\partial f}{\partial t} &= \sum_{i=1}^{N}\left(\frac{\partial H}{\partial q_i}\frac{\partial f}{\partial p_i} - \frac{\partial H}{\partial p_i}\frac{\partial f}{\partial q_i}\right)\\ \frac{\partial f}{\partial t} &= -\mathbf{v}\cdot\mathbf{v}f + \fint dx'\,\theta(x,x')f(x)f(x')\end{aligned} \tag{2.20}$$

where H is the Hamiltonian and $\theta(x,x')$ is the operator:

$$\theta(x,x') = \nabla V(r - r')\cdot(\nabla_p - \nabla_{p'}) \tag{2.21}$$

and it has been assumed that the potential, $V(r)$, is continuous and differentiable. The line through the integral denotes a principal part with the point $x = x'$ deleted (the self-force contribution). Each equation of (2.20) has its advantages and disadvantages. The first is linear but has $6N$ independent variables; the second equation has only six variables but is nonlinear. Since the Klimontovich equation involves the same variables as the kinetic equation for $\psi(x,t)$ it is sometimes referred to also by that terminology. The crucial difference, however, is that the initial condition for the Klimontovich equation still depends on all phase points $\{x_i\}$, while these variables have been averaged over in $\psi(x,0)$.

It is somewhat surprising to recognize that the *exact* Klimontovich equation has the same form as the nonlinear Vlasov equation, an *approximate* equation for the reduced distribution function of a nonequilibrium state. This was apparently first noted by Vlasov.(13) More recently, it has been shown that the Klimontovich equation for a fluid of hard spheres has the form of the nonlinear Boltzmann equation(14) (this result is also implicit in the earlier discussions of binary collision dynamics for hard spheres(15)). The Klimontovich equation in this case is (see Appendix A for a brief derivation)

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right) f(x,t) = J[f,f] \tag{2.22}$$

with

$$J[f,f] = \int dx'\, \bar{T}_-(x,x') f(x,t) f(x',t) \tag{2.23}$$

and $\bar{T}_-(x,x')$ is a binary collision operator, defined by Eq. (A10), (the notation here and below is chosen to agree with that of Ref. 16). The binary collision operator contains two δ functions in the positions of the colliding pair, corresponding to a separation of the pair by the hard sphere diameter. This spatial delocalization is neglected in the usual nonlinear Boltzmann equation, so the operator $J[f,f]$ differs from the Boltzmann operator in this one respect. The equation for $\phi(x,t)$ in Eq. (2.10) follows directly from Eq. (2.22):

$$\left(\frac{\partial}{\partial t} + L\right)\phi = \tilde{J}[\phi,\phi] \tag{2.24}$$

where

$$\begin{aligned} \tilde{J}[\phi,\phi] &= F_0^{-1} J[F_0\phi, F_0\phi] \\ L[\phi] &= \mathbf{v}\cdot\mathbf{v}_{\phi} - \tilde{J}[1,\phi] - \tilde{J}[\phi,1] \end{aligned} \tag{2.25}$$

The operator, L, is identified as the generator for the solution to the inhomogeneous linear Boltzmann equation. For the rest of the section and the following two sections attention will be restricted to the hard sphere fluid. Some comments on the relevance of these calculations for more general potentials are given in the last section.

Let T_t denote the nonlinear solution operator for the Klimontovich equation for ϕ. Then $G(x,t;x',0)$ can be expressed in terms of T_t as

$$G(x,t;x',0) = \langle [T_t\phi(x)]\phi(x')\rangle \tag{2.26}$$

This suggests an alternative means to calculate $G(x,t;x',0)$: Look for approximations to the Klimontovich equation at the microscopic level, to use in the average on the right side of (2.26). Since the Klimontovich equation is nonlinear this procedure defines a nonlinear formulation for time correlation functions. It should be noted that although T_t is the solution operator for the nonlinear Boltzmann equation, usually associated with gases, there is no limitation to low density in the present context. As indicated in Section 4, the additional density effects in $G(x,t;x',0)$ are generated by the final average in (2.26); the latter is quite complex due to the nonlinearity of T_t.

It is appropriate at this point to compare and contrast the Klimontovich formulation and the linear kinetic theory. The operators in the Klimontovich equation are structurally simple, have explicit dependence on the density, are local in time, and approximately local in space. The solution to this equation is complicated, however, owing to the nonlinearity. The kinetic equation (2.14) is linear in time and therefore easy to solve, but it is nonlocal in both space and time, and the operator $K(t)$ is difficult to determine as a function of the density. The relationship of these two formulations is seen from Eqs. (2.8), (2.13), and (2.26) to be

$$\overline{U}_t\langle\phi(x)\phi(x')\rangle = \langle [T_t\phi(x)]\phi(x')\rangle \tag{2.27}$$

The linear operator, $\overline{U}_t$, is related to U_t simply by $U_t = \overline{U}_t U_0$. Equation (2.27) expresses most concisely the difference between linear and nonlinear equations for equilibrium correlation functions. Such functions may be calculated either from the linear kinetic equation on the left side or from the Klimontovich equation on the right side. However, the variables obeying these equations are different in the two cases, depending on whether the average is performed before or after solving the corresponding equation. In particular, although T_t is independent of the variables being averaged, it does not commute with the average,

$$\langle [T_t\phi(x)]\phi(x')\rangle \neq T_t\langle\phi(x)\phi(x')\rangle \tag{2.28}$$

because T_t is a nonlinear operator.

The linear kinetic theory for time correlation functions has been discussed extensively. In the remainder of this discussion attention will be limited to the nonlinear Klimontovich formulation in an attempt to answer the questions raised in the Introduction. The first question—In what sense can the nonlinear Boltzmann equation apply?—has been answered: $\psi(x,t)$ does *not* obey the nonlinear Boltzmann equation because of the inequality in Eq. (2.28) and the properties (2.5); however, $\phi(x,t)$ obeys the Klimontovich equation which is formally equivalent to the nonlinear Boltzmann equation, and determines the correlation functions through the right side of (2.27). In the following section it is verified that the approach of Ref. 5, reformulated as applying to the microscopic phase space density, does indeed give the correct mode-coupling result for the long-time behavior of $C(t)$.

3. MODE COUPLING FROM THE KLIMONTOVICH EQUATION

In this section the low-density mode-coupling contribution to the correlation functions is shown to result from a simple approximate solution to the Klimontovich equation. The solution is represented in terms of a sequence of approximations that is expected to converge in the weak sense,

$$\left\langle \phi\left\{\phi(t) - \left[\phi^{(0)}(t) + \phi^{(1)}(t) + \cdots\right]\right\}\right\rangle \to 0 \tag{3.1}$$

To allow the closest comparison with the results of Ref. 5, the approximation will be generated by treating the nonlinear part of the Klimontovich equation as a perturbation. Qualitatively, this is based on the fact that for long times $\phi(x,t)$ approaches zero [in the sense of (3.1)] so that the quadratic term is smaller than the linear term. In the next solution an improved perturbation expansion is described.

A formal solution to the Klimontovich equation is

$$\phi(x,t) = e^{-L(x)t}\phi(x) + \int_0^t dt'\, e^{-L(x)(t-t')}\tilde{J}\left[\phi(t'),\phi(t')\right] \tag{3.2}$$

and so $G(x,t;x',0)$ can be written

$$\begin{aligned} G(x,t;x',0) = e^{-L(x)t}G(x,0;x',0) + \int_0^t dt'\, e^{-L(x)(t-t')} \\ \times \tilde{J}\left[\phi(t'),\phi(t')\right]\phi(x') \end{aligned} \tag{3.3}$$

The argument of the operator, $L(x)$, indicates that its domain is functions of x. Further application of (3.2) in (3.3) produces a series in increasing powers of the nonlinear operator, $\tilde{J}$. Neglecting terms beyond first order gives the approximation

$$G(x,t;x'0) = G^{(0)}(x,t;x',0) + G^{(1)}(x,t;x',0) \tag{3.4}$$

with

$$\begin{aligned} G^{(0)}(x,t;x',0) &= e^{-L(x)t}G(x,0;x',0) \\ G^{(1)}(x,t;x',0) &= \int_0^t dt'\, e^{-L(x)(t-t')}\int dx_0\, F_0(x_0)\overline{T}_-(x,x_0) \\ &\qquad \times e^{-[L(x)+L(x_0)]t'}\langle\phi(x)\phi(x_0)\phi(x')\rangle \end{aligned} \tag{3.5}$$

where the definition of $\tilde{J}$, Eq. (2.25), has been used. Use of (3.5) in (2.11) gives the corresponding approximation for the correlation function,

$$C_t[a,b] = C_t^{(0)}[a,b] + C_t^{(1)}[a,b] \tag{3.6}$$

with

$$\begin{aligned} C_t^{(0)}[a,b] &= \int dx\, F_0(x) a^*(x) \int dx'\, F_0(x') G^{(0)}(x,t;x',0) b(x') \\ C_t^{(1)}[a,b] &= \int dx\, F_0(x) a^*(x) \int dx'\, F_0(x') G^{(1)}(x,t;x',0) b(x') \end{aligned} \tag{3.7}$$

The current–current correlation function in the form used by Ubbink and Hauge is obtained from the choice (2.15). It is convenient to represent the correlation function in terms of its Laplace transform,

$$\tilde{C}(z) = \int_0^\infty dt\, e^{-zt} C(t) \tag{3.8}$$

Substitution of (2.15) into (3.6) and (3.8) leads to the results

$$\begin{aligned} \tilde{C}^{(0)}(z) &= \int d\mathbf{v}\, F_0(v) j(v) R_0(v) j(v) \\ \tilde{C}^{(1)}(z) &= \int d\mathbf{v}\, F_0(v) j(v) R_0(v) \int \frac{d\mathbf{k}}{(2\pi)^3} \int d\mathbf{v}'\, F_0(v') T_k(v,v') \\ &\quad \times \left[z + L_k(v') + L_{-k}(v)\right]^{-1} A_k(v,v') \end{aligned} \tag{3.9}$$

The operators $T_k(v,v')$, $L_k(v)$, and $R_k(v)$ are defined by

$$\begin{aligned} T_k(v,v') &= \int d(\mathbf{r}-\mathbf{r}')\, e^{-ik\cdot(\mathbf{r}-\mathbf{r}')} \overline{T}_-(x,x') \\ L_k(v) &= e^{-i\mathbf{k}\cdot\mathbf{r}} L(x) e^{i\mathbf{k}\cdot\mathbf{r}} \\ R_k(v) &= \left[z + L_k(v)\right]^{-1} \end{aligned} \tag{3.10}$$

Equations (3.9) are identical to the corresponding results in Ref. 5 [Eqs. (2.12) and Eq. (2.14)], except for the definition of the function $A_k(v,v')$. Here the latter is defined by

$$A_k(v,v') = W_0 \left\{ \frac{\delta(v-v')}{F_0(v)} j(v) + nh(k)\left[j(v) + j(v')\right] \right\} \tag{3.11}$$

whereas the definition of Ref. 5 is

$$A_k^{\mathrm{UH}}(v,v') = W_k \left\{ \frac{\delta(\mathbf{v}-\mathbf{v}')}{F_0(v)} j(v) W_k + nh(k)\left[j(v) + j(v')\right] \right\} \tag{3.12}$$

In (3.11) and (3.12) $h(k)$ is the Fourier transform of $g(r) - 1$, where $g(r)$ is the radial distribution function, and W_k is the Fourier transform of the function, $W(r)$, in Eq. (2.15). Although the results (3.11) and (3.12) are similar, their differences are significant. The Klimontovich form is linear in W_k, as required by Eq. (2.5), while the nonlinear Boltzmann kinetic equation predicts a quadratic dependence on W. Imposing the normalization (2.17) also requires that $\tilde{C}(z)$ be independent of the arbitrary function, W. This is exactly true from the Klimontovich formulation (since $W_0 = 1$ in this case), but the nonlinear Boltzmann kinetic model predicts an inherent dependence on W_k.

The mode-coupling contribution for the long-time behavior of the correlation function is obtained from the hydrodynamic eigenvalues of $L_k(v') + L_{-k}(v)$ in Eq. (3.9), which exists for sufficiently small k. The dominant part of the residues of these poles is determined from A_k at $k = 0$. It is clear from Eqs. (3.11) and (3.12) that the Klimontovich and nonlinear Boltzmann model results are the same in this approximation. Consequently, the mode coupling from the Klimontovich formulation is the same as that obtained in Ref. 5. As mentioned in the Introduction this result is in agreement with that obtained by other methods (e.g., the ring kinetic theory). The details of the calculation from Eq. (3.9) follow closely those of Ref. 5 and will not be repeated here.

The nonlinear Boltzmann equation method, when applied to the *microscopic* phase dynamics instead of the average phase space dynamics, is seen to predict the correct asymptotic behavior for the correlation functions without violating the bilinearity of such functions. Nevertheless, the connection with the results from linear kinetic theory (in particular the ring approximation) is still not clear. The linear ring approximation yields a mode-coupling result of the form (3.9), but with an entirely different expression for the function $A_k(v, v')$. Its equivalence with the above expressions is again established only in the mode-coupling limit of $k \to 0$. In the following section it is shown how an improved solution to the Klimontovich equation leads to full equivalence with the ring approximation, even outside the mode-coupling limit.

4. CONNECTION WITH LINEAR KINETIC THEORY

To clarify the connection between the two different descriptions of time correlation functions, it is useful to understand how the density dependence of the linear theory is generated by the Klimontovich equation. In the linear case the formal equation (2.14) applies:

$$\left(\frac{\partial}{\partial t} + \Omega\right)G(t) = -\int_0^t dt' \, K(t - t')G(t') \tag{4.1}$$

while the Klimontovich equation gives

$$\left(\frac{\partial}{\partial t}+L\right)G(t)=\langle J[\phi(t),\phi(t)]\phi\rangle \tag{4.2}$$

It is clear from comparison of these two exact equations that *all* of the density corrections to the linear Boltzmann operator, L, that are contained in the operators Ω and $K(t)$ arise in the Klimontovich formulation from the nonlinear part. This shows how it is possible for the Klimontovich equation, formally the same as the Boltzmann equation, to describe density effects beyond those associated with a Boltzmann gas: the variable in the Klimontovich equation is stochastic in that a final average over the phase variables is to be taken, and the interference of the nonlinearity with this average generates the density corrections. Viewed in this fashion, the operators Ω and $K(t)$ result from a "fluctuation renormalization" of the operator, L. There are several types of density effects that originate in this way. One of these is due entirely to initial (static) correlations in the equilibrium ensemble and is required to upgrade the linear Boltzmann operator to the Enskog operator, Ω [this is apparent from comparison of (4.1) and (4.2) at $t=0$]. A second class of density corrections is associated with dynamical correlations such as those included in the ring approximation to describe collective behavior at long times, even for gases. These appear in the operator, $K(t)$.

The Klimontovich calculation of the last section provides only the low-density form of the mode-coupling contribution (the hydrodynamic modes are those of the linear Boltzmann operator). The reason for this is evident from the above comments. That calculation treats $J[\phi,\phi]$ as a small perturbation, but since this operator is responsible for the density corrections to the Boltzmann approximation to $G(t)$, the expansion can only be meaningful at low density. Furthermore, the expansion is not systematic in the density as a small parameter, since the latter does not control the size of $J[\phi,\phi]$ relative to the linear term $L[\phi]$. The nonlinear term is apparently small only at low density *and* asymptotically long times, when ϕ^2 is small compared to ϕ. It is precisely in this limit that the method of the last section yields the correct prediction for $G(t)$. To describe shorter times and/or higher densities, a better solution to the Klimontovich equation is required. One possibility is to extract from the nonlinear term its component in the subspace spanned by the set, $\{\phi(x,t)\}$. The remainder is then expected to be small in the sense that it is orthogonal to the desired solution. This may be accomplished using the projection operator, P, defined in Appendix B:

$$J[\phi(t),\phi(t)]=P_tJ[\phi(t),\phi(t)]+(1-P_t)J[\phi(t),\phi(t)] \tag{4.3}$$

The first term on the right side of Eq. (4.3) is linear in $\phi(x,t)$ and may be combined with the linear operator, L, in Eq. (4.2). The Klimontovich equation then takes the equivalent form,

$$\left(\frac{\partial}{\partial t} + \Omega\right)\phi = B[\phi,\phi] \tag{4.4}$$

where Ω is the same Enskog operator as occurs in the linear theory (4.1). The new nonlinear term, $B[\phi,\phi]$, is defined by

$$B[\phi(t),\phi(t)] = \int dx'\, F_0(x')\bar{T}_-(x,x')(1-P_t)\phi(x,t)\phi(x',t) \tag{4.5}$$

The derivation of Eq. (4.4) is sketched in Appendix C. The equation for $G(x,t;x',0)$ obtained from this new form of the Klimontovich equation is

$$\left(\frac{\partial}{\partial t} + \Omega\right)G(t) = \langle B[\phi(t),\phi(t)]\phi\rangle \tag{4.6}$$

Comparison with the linear kinetic theory shows that $B[\phi,\phi]$ now generates only the dynamical effects associated with $K(t)$.

The stationarity of the correlation function is expressed by

$$\langle \phi(x,t)\phi(x')\rangle = \langle \phi(x)\phi(x',-t)\rangle \tag{4.7}$$

Consequently, the correlation function can be calculated from either the Klimontovich equation for $\phi(x,t)$ or that for $\phi(x',-t)$. However, it is found that the approximation (3.4) is not equivalent to the corresponding approximation obtained from $\phi(x',-t)$, except in the mode-coupling limit. The reason for this is that the approximation to the dynamics is made without any reference to the stationary state. A proper expansion should explicitly combine the stationarity with the dynamical approximation for self-consistency. Here, the stationarity will be used only as a constraint to improve the method of the last section and show how the ring approximation of the linear kinetic theory may be obtained from the Klimontovich equation. In this spirit the formal solution to Eq. (4.4) may be used to write an expression for $G(x,t;x',0)$ analogous to Eq. (3.3):

$$\begin{aligned} G(x,t;x',0) = e^{-\Omega(x)t}G(x,0;x',0) + \int_0^t dt'\, e^{-\Omega(x)(t-t')} \\ \times \langle B[\phi(t'),\phi(t')]\phi(x')\rangle \end{aligned} \tag{4.8}$$

Truncation of (4.8) to first order, as in the last section, leads to a vanishing contribution from the perturbation, B. This is due to the presence of the factor $1-P_t$ in the definition of B. Before iterating (4.8) to second order, the stationarity may be introduced through the condition

$$\langle B[\phi(t'),\phi(t')]\phi(x')\rangle = \langle B[\phi,\phi]\phi(x',-t)\rangle \tag{4.9}$$

The Klimontovich equation for $\phi(x',-t)$, in the form analogous to Eq.

(4.4), is given in Appendix C:

$$\left(\frac{\partial}{\partial t}+\bar{\Omega}\right)\phi(-t)=\bar{B}\left[\phi(-t),\phi(-t)\right] \tag{4.10}$$

The operator, $\bar{B}$, is given by Eq. (4.5) with $\bar{T}_-(x,x')$ replaced by a related binary collision operator, $\bar{T}_+(x,x')$, and the operator, $\bar{\Omega}$, is related to Ω by

$$\bar{\Omega}(x')G(x,0;x',0)=\Omega(x)G(x,0;x',0) \tag{4.11}$$

The simplest approximation to $G(x,t;x',0)$ in this context is obtained by substituting the formal solution to (4.10) in (4.9) and (4.8) and retaining only terms up to second order in the perturbation, B and $\bar{B}$. The result is (see Appendix D for more detail)

$$G(x,t;x',0)=G^{(0)}(x,t;x',0)+G^{(1)}(x,t;x'0)+G^{(2)}(x,t;x',0) \tag{4.12}$$

with

$$\begin{aligned}
G^{(0)}(x,t;x',0)&=e^{-\Omega(x)t}G(x,0;x',0)\\
G^{(1)}(x,t;x',0)&=0\\
G^{(2)}(x,t;x',0)&=-\int_0^t dt'\int_0^t dt'\int dx_1\,dx_2\,G^{(0)}(x,t-t';x_1,0)\\
&\qquad\times\Gamma(x_1,x_2;t'-t'')G^{(0)}(x_2,t'';x',0)
\end{aligned} \tag{4.13}$$

and

$$\begin{aligned}
\Gamma(x,x';t)&=\int dx_1\,dx_2\,dx_3\,F_0(x_1)F_0(x_2)F_0(x_3)\bar{T}_-(x,x_1)\\
&\qquad\times C(x,x_1,0;x_2,x_3,-t)T_-(x_2,x_3)\delta(x_3-x')\\
C(x,&x_1,0;x_2,x_3,-t)\\
&=e^{-[\bar{\Omega}(x_2)+\bar{\Omega}(x_3)]t}\langle\phi(x)\phi(x_1)(1-P)\phi(x_2)\phi(x_3)\rangle^{(0)}
\end{aligned} \tag{4.14}$$

The binary collision operator, $T_-(x,x')$ is the adjoint of $\bar{T}_-(x,x')$ [see Eq. (A9)]. The superscript on the brackets $\langle\ \rangle^{(0)}$ indicates that this time-independent correlation function is to be evaluated in an approximation consistent with the stationarity condition (4.7). Repeating the analysis leading to (4.13) starting with $\langle\phi(x)\phi(x',-t)\rangle$ instead, it is found that this condition requires

$$\left[\bar{\Omega}(x_2)+\bar{\Omega}(x_3)-\Omega(x)-\Omega(x_1)\right]\langle\phi(x)\phi(x_1)(1-P)\phi(x_2)\phi(x_3)\rangle^{(0)}=0 \tag{4.15}$$

The solution to this equation is

$$\begin{aligned}\langle\phi(x)\phi(x_1)(1-P)\phi(x_2)\phi(x_3)\rangle^{(0)} &\\ = G(x,0;x_1,0)G(x_2,0;x_3,0) &\\ +\left[1+P(x,x_1)\right]G(x,0;x_2,0)G(x_1,0;x_3,0) &\end{aligned} \tag{4.16}$$

Here, $P(x,x_1)$ is the permutation operator that exchanges the labels, x and x_1. Substitution of (4.16) into (4.14) gives the desired self-consistent approximation:

$$\begin{aligned}\Gamma(x,x';t) = \int dx_1\,dx_2\,dx_3\,F_0(x_1)F_0(x_2)F_0(x_3)\bar{\bar{T}}_-(x,x_1)\left[1+P(x,x_1)\right] &\\ \times G^{(0)}(x,t;x_2,0)G^{(0)}(x_1,t;x_3,0)T_-(x_2,x_3)\delta(x_3-x') &\end{aligned} \tag{4.17}$$

The right side of (4.16) is an exact representation for $\langle\phi(x)\phi(x_1)(1-P)\phi(x_2)\phi(x_3)\rangle$ only at low density. Therefore the factors $G^{(0)}$ in Eqs. (4.17) and (4.13) should also be evaluated at low density. The result (4.13) is then indeed equivalent to the ring approximation of linear kinetic theory.[1]

The mode-coupling contributions to the current–current correlation functions from the ring approximation have been discussed in detail elsewhere and will not be repeated here. As noted above they agree with the results of Section 3. The primary conclusion to be drawn here is that an improved solution to the Klimontovich equation describes these mode coupling effects in the *same* form as the linear kinetic theory. This point could be emphasized by a direct determination of $K(x,x';t)$ in Eq. (4.1) from the Klimontovich equation, rather than $G(x,t;x'0)$ as above. This is accomplished using the relation

$$\int_0^t dt' \int dx_1\,K(x,x_1;t-t')G(x_1,t';x',0) = -\langle B[\phi(t),\phi(t)]\phi(x')\rangle \tag{4.18}$$

The result to second order in the perturbation, B, is simply

$$K(x_1,x_2;t) = \Gamma(x_1,x_2;t) \tag{4.19}$$

with $\Gamma(x_1,x_2;t)$ given by (4.17). Thus the complete linear ring kinetic equation is obtained from the Klimontovich equation.

5. DISCUSSION

The questions raised in the Introduction have been answered in the following way. The analysis of Section 2 shows that the kinetic theory for $\psi(x,t)$ in Eq. (2.7) should be linear, and therefore is not governed by the nonlinear Boltzmann equation as a low-density approximation. However,

$\psi(x,t)$ is closely related to the microscopic phase space variable $\phi(x,t)$, Eq. (2.10), that *does* obey a "nonlinear Boltzmann equation," the Klimontovich equation for hard spheres. It was shown in Section 3 that if the calculations of Hauge are reinterpreted as applying to $\phi(x,t)$ instead of $\psi(x,t)$, then the correct mode-coupling results are obtained in the *same* form as given by Hauge. However, the method of solving the nonlinear equation by treating the nonlinear Boltzmann operator as a small perturbation, is limited to low density and asymptotically long times (as noted above, stationarity of the approximation is violated outside this limit). In Section 4, the Klimontovich equation was written in a form more suitable for a perturbation expansion, and the stationarity of $G(x,t;x')$ was imposed. The resulting approximation to first nonvanishing order (second) in the perturbation was found to be the ring approximation of linear kinetic theory. Alternatively, Eq. (4.19) shows that the ring collision operator can be obtained from a second-order perturbation expansion of the Klimontovich equation.

To clarify and elaborate on some of these points the following comments may be useful.

(1) Although Eqs. (3.11) and (3.12) show how the calculation based on the Klimontovich equation is related to that from the nonlinear Boltzmann equation, still it may be asked why the latter method works at all. This can be understood by considering the inequality (2.28)

$$\langle [T_t\phi(x)]\phi(x')\rangle \neq T_t\langle \phi(x)\phi(x')\rangle \tag{5.1}$$

which expresses most concisely the difference between the two methods. The inequality arises from the fact that T_t is nonlinear and hence generates higher-order fluctuations in ϕ, whereas the right side does not. If the left and right sides of (5.1) are each calculated to first-order perturbation theory as in Section 2, the results are seen to differ only by the time-independent fluctuations

$$\langle \phi(x)\phi(x')\phi(x'')\rangle \neq \langle \phi(x)\phi(x')\rangle\langle \phi(x'')\phi(x')\rangle \tag{5.2}$$

However, in the low-density limit it is seen that the left and right sides of (5.2) are indeed the same. Therefore, to first-order perturbation of T_t, and to lowest order in the density, the left and right sides of (5.1) are equal.

(2) The test function, $W(r)$, of Eq. (2.16), was introduced in Ref. 5 in order to apply the inhomogeneous nonlinear Boltzmann equation; without the latter, the hydrodynamic modes would not appear. However, $W(r)$ clearly should not appear in any approximation to the correlation function and, as indicated in Ref. 5, this is a difficulty in the nonlinear kinetic theory outside the mode-coupling limit. In the Klimontovich equation the function $W(r)$ is extraneous, since the variable $\phi(x,t)$ that obeys this equation is defined at the microscopic level; the Klimontovich equation is *always*

inhomogeneous. The function $W(r)$ simply cancels out identically as it should from Eq. (2.16).

(3) The application of the Klimontovich equation in Sections 3 and 4 are quite different. In Section 3 the nonlinear Boltzmann operator $\tilde{J}[\phi, \phi]$ is treated as a small parameter. Such an expansion is limited to *both*, low density and long times. In Section 4 two changes were introduced: The Klimontovich equation was restructured in such a way that the new nonlinear term, $B[\phi, \phi]$, should be small (in the sense that it is orthogonal to the exact solution), and the stationarity of $G(x, t; x', 0)$ was required to hold. These constraints compromise severely the simplicity of the mode-coupling derivation of Section 3. Consequently, it appears that if one wants more than the mode-coupling limit (e.g., the complete ring kinetic theory), application of the Klimontovich is as complex as the many-body analysis of the linear kinetic theory.

(4) The nonlinear Boltzmann equation, which is based on the assumption of only binary collisions, cannot be equivalent to the ring approximation which includes many-body effects. In contrast the dependent variable, $\phi(x, t)$, of the Klimontovich formalism depends on the microscopic state of the system and contains the complete many-body dynamics, as the derivation in Appendix A indicates [e.g., compare left and right sides of Eq. (A10)].

(5) The attempt to extend the mode-coupling calculations to higher densities in Ref. 3 is not correct. This authors calculate the hydrodynamic modes from the eigenvalues of the linear Boltzmann operator, L_k in Eq. (3.10), retaining the delocalization effects on the binary collision operator [the k-dependence of $T_k(v, v')$ in Eq. (3.10)]. This gives some of the first Enskog density corrections to the Boltzmann eigenvalues, but not all of them. Instead, the correct eigenvalues are obtained from the low-density limit of the operator Ω, given explicitly by Eq. (B11). This differs from L by the terms depending on the direct correlation function in (B11). It may be noted that the ring approximation of Section 4 is correctly described in terms of the low-density limit of Ω, rather than L.

(6) The relationship of the Klimontovich equation to the Boltzmann equation is close only for the special case of hard spheres. The reason for this is that the usual Boltzmann equation results only for times large compared to a collision time whereas the Klimontovich equation is exact for all times. However, for hard spheres the collision time is arbitrarily small and the two equations are formally the same. To apply the Klimontovich equation for continuous potentials therefore requires a rearrangement analogous to that of Section 4 to include the description of a complete binary collision. While this is possible to do, the result is considerably more complex and cumbersome than the hard sphere case.

(7) The discussion at the end of Appendix A shows that the terminology Klimontovich "equation" is misleading. It is actually an identity satisfied by the unique function, $f(x,t)$, defined by Eq. (2.9). This is in contrast to the Hamilton's equations or Liouville's equation that apply to all phase functions. Consequently, certain paradoxes can arise if the distinction is not made. For example, a scale change in the initial conditions, $f(x,0) \to \alpha f(x,0)$, implies a corresponding change in the microscopic phase density at time t, $f(x,t) \to \alpha f(x,t)$. While Liouville's equation is invariant under this transformation, as might be expected, the Klimontovich equation is not. It is transformed, instead, to the bilinear form (A12).

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APPENDIX A: HARD SPHERE DYNAMICS

The force of interaction between two particles is singular for hard spheres, and the usual formulation of dynamics in terms of the Liouville operator as the generator of time translations must be extended. This problem has been discussed in detail elsewhere$^{(16)}$ so only the relevant results will be quoted here. The pseudo-Liouville operator for hard spheres is defined for positive times by

$$\langle AB(t)\rangle = \langle A e^{\mathscr{L}_+ t} B\rangle \tag{A1}$$

The corresponding result for negative times is determined from time translational invariance,

$$\langle AB(t)\rangle = \langle A(-t)B\rangle = \langle (e^{-\mathscr{L}_- t} A) B\rangle \tag{A2}$$

An explicit representation of these operators is

$$\mathscr{L}_\pm(x^N) = \sum_{i=1}^{N} \mathscr{L}_0(x_i) \pm \frac{1}{2} \sum_{i\neq j}\sum T_\pm(x_i x_j) \tag{A3}$$

with

$$\begin{aligned} \mathscr{L}_0(x_i) &= \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \\ T_\pm(x_1, x_2) &= \sigma^2 \int d\sigma \, |\mathbf{g}\cdot\hat{\sigma}| \theta(\mp \mathbf{g}\cdot\hat{\sigma}) \delta(\mathbf{r}_1 - \mathbf{r}_2 - \boldsymbol{\sigma})(b_\sigma - 1) \end{aligned} \tag{A4}$$

In this equation $\mathbf{g}$ is the relative velocity, $\mathbf{g} = \mathbf{v}_1 - \mathbf{v}_2$, and θ is the Heaviside step function restricting the integration to either the forward or backward hemisphere. Also, σ is the hard sphere diameter and the operator, b_σ, changes the velocities of the pair x_1, x_2 to their scattered velocities,

$$b_\sigma \mathbf{v}_1 = \mathbf{v}_1 - \hat{\sigma}(\hat{\sigma} \cdot \mathbf{g}), \qquad b_\sigma \mathbf{v}_2 = \mathbf{v}_2 + \hat{\sigma}(\hat{\sigma} \cdot \mathbf{g}) \tag{A5}$$

The Klimontovich equation for hard spheres now follows by considering the time dependence of the phase space density, $f(x,t)$ defined by Eq. (2.9),

$$\frac{\partial}{\partial t} f(x,t) = \mathscr{L}_\pm f(x,t) \tag{A6}$$

for positive ($\mathscr{L}_+$) and negative ($\mathscr{L}_-$) times. The operators $\mathscr{L}_\pm$ act on the implicit dependence of $f(x,t)$ on the positions and momenta of all the particles of the fluid. However, since this dependence occurs through δ functions at the point x, it is possible to express $\mathscr{L}_\pm$ in this case as operators on the variables x. This may be accomplished using the identities(16)

$$T_\pm(x_1, x_2)\delta(x - x_1)\delta(x' - x_2) = \overline{T}_\mp(x, x')\delta(x - x_1)\delta(x' - x_2) \tag{A7}$$

$$\mathscr{L}_0(x_i) f(x,t) = \mathbf{v} \cdot \boldsymbol{\nabla} f(x,t) \tag{A8}$$

The binary collision operators, $\overline{T}_\pm(x,x')$, are defined by

$$\overline{T}_\pm(x_1, x_2) = \sigma^2 \int d\hat{\boldsymbol{\sigma}}\, |g \cdot \hat{\boldsymbol{\sigma}}| \theta(\mp \mathbf{g} \cdot \hat{\boldsymbol{\sigma}}) \left[\delta(\mathbf{r}_1 - \mathbf{r}_2 - \boldsymbol{\sigma}) b_\sigma - \sigma(\mathbf{r}_1 - \mathbf{r}_2 + \boldsymbol{\sigma}) \right] \tag{A9}$$

and the notation is the same as that of Eq. (A4). The action of $\mathscr{L}_\pm$ on $f(x)$ is then

$$\mathscr{L}_\pm f(x) = -\mathbf{v} \cdot \boldsymbol{\nabla} f(x) \pm \tfrac{1}{2} \sum_{i \neq j} T_\pm(x_i, x_j) \left[\delta(x - x_i) + \delta(x - x_j) \right]$$

where use has been made of the fact that $T_\pm(x_i, x_j)$ vanishes when operating on a phase function independent of x_i or x_j. Introducing a second δ function and application of (A7) gives

$$\mathscr{L}_\pm f(x) = -\mathbf{v} \cdot \boldsymbol{\nabla} f(x) \pm \int dx'\, \overline{T}_\mp(x, x') \left[f(x) f(x') - \delta(x - x') f(x) \right] \tag{A10}$$

The last term in the integrand proportional to a δ function vanishes owing to the δ functions in the definition of $\overline{T}_\pm(x,x')$. The Klimontovich equation now follows directly from Eqs. (A6) and (A10):

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla} \right) f(x,t) = \pm \int dx'\, \overline{T}_\mp(x, x') f(x', t) f(x, t) \tag{A11}$$

The upper signs on the right side refer to positive times, while the lower signs are for negative times.

There are some important distinctions between the Liouville form, (A6), and the Klimontovich form, (A11). The former is an *equation* in the sense that it defines a wide class of solutions, one of which is $f(x,t)$, and uniqueness is obtained by supplementing the equation with initial conditions. In contrast, the Klimontovich form applies only for the particular phase function, $f(x,t)$, defined by Eq. (2.9); the initial conditions are already implicit in (A11). The Klimontovich equation should therefore be viewed more properly as an *identity* for the particular $f(x,t)$ considered. This distinction is illustrated by repeating the above derivation for the function, $y(x,t) = \alpha f(x,t)$, where α is an arbitrary constant. The result is

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right)y(x,t) = \pm\int dx'\,\overline{T}_{\mp}(x,x')f(x',t)y(x,t) \qquad \text{(A12)}$$

This is now an equation in the sense that many solutions exist (for different α), but it no longer has the Klimontovich form (A11). Instead, a bilinear equation is obtained. It is this difference between (A11) and (A12) that allows consistency between the seemingly nonlinear Klimontovich "equation" and the bilinearity of the correlation functions.

APPENDIX B: LINEAR KINETIC EQUATION

A brief derivation of the exact linear kinetic equation for $G(x,t;x',0)$, Eq. (2.14), is given in this appendix using the Zwanzig–Mori projection operator formalism.(17) For backward streaming in time Eq. (A6) may be used in the definition (2.10) to give

$$\left(\frac{\partial}{\partial t} + \mathscr{L}_-\right)\phi(x,-t) = 0, \qquad t > 0 \qquad \text{(B1)}$$

Define a projection operator onto the set of functions $\{\phi(x)\}$, by

$$PA = \int dx\,\phi(x)\int dx'\,g^{-1}(x,x')\langle\phi(x')A\rangle \qquad \text{(B2)}$$

Here $\langle\cdots\rangle$ denotes an equilibrium average, A is an arbitrary phase function, and $g(x,x')$ is the initial value for $G(x,t;x',0)$, defined by Eq. (2.12). The inverse function, $g^{-1}(x,x')$, is defined by

$$\int dx''\,g(x,x'')g^{-1}(x'',x') = \delta(x-x') \qquad \text{(B3)}$$

The time correlation function $G(x,t;x',0)$ can then be expressed as

$$G(x,t;x',0) = \langle\phi(x)P\phi(x',-t)\rangle \qquad \text{(B4)}$$

where use has been made of the time translation invariance of $G(x,t;x',0)$. Operating on Eq. (B1) with P and $1-P$ provides a closed equation for $P\phi(x,-t)$,

$$\left(\frac{\partial}{\partial t}+P\mathscr{L}_{-}P\right)P\phi(x',-t)$$
$$-\int_0^t d\tau\, P\mathscr{L}_{-}\, V(t-\tau)(1-P)\mathscr{L}_{-}\, P\phi(x',-\tau)=0 \qquad \text{(B5)}$$

with

$$V(t)\equiv\exp\left[-(1-P)\mathscr{L}_{-}(1-P)t\right] \qquad \text{(B6)}$$

Differentiation of Eq. (B4) and use of (B5) gives the desired exact equation for $G(x,t;x',0)$,

$$\frac{\partial}{\partial t}G(x,t;x'0)+\int dx''\,\Omega(x,x'')G(x'',t;x'0)$$
$$+\int_0^t d\tau\int dx''\,K(x,t-\tau;x'')G(x''\tau;x',0)=0 \qquad \text{(B7)}$$

where the functions $\Omega(x,x')$ and $K(x,t;x')$ are defined by

$$\Omega(x,x')=\int dx''\,\langle\phi(x)\mathscr{L}_{-}\phi(x'')\rangle g^{-1}(x'',x') \qquad \text{(B8)}$$

$$K(x,t;x')=\int dx''\,\langle\phi(x)\mathscr{L}_{-}\,V(t)(1-P)\mathscr{L}_{-}\phi(x'')\rangle g^{-1}(x'',x') \qquad \text{(B9)}$$

For notational purposes it is convenient to consider $\Omega(x,x')$ and $K(x,t;x')$ as the kernels for two operators Ω and $K(t)$ defined on the Hilbert space of single-particle functions. Then Eq. (B7) becomes

$$\left(\frac{\partial}{\partial t}+\Omega\right)G(x,t;x',0)+\int_0^t d\tau\,K(t-\tau)G(x,\tau;x',0)=0 \qquad \text{(B10)}$$

where $G(x,t;x',0)$ is taken as a function of x, parameterized by x'.

In general the operator $K(t)$ cannot be expressed in any simple form without introduction of suitable approximations. In contrast, the operator Ω depends only on the static equilibrium properties of the fluid and may be determined more explicitly. This operator, Ω, the function $g(x,x')$ and its inverse are evaluated in Ref. 11 with the results

$$\Omega(x,x')=\mathbf{v}\cdot\nabla\left\{\delta(x-x')F_0^{-1}(x)-\left[C(\mathbf{r}-\mathbf{r}')-g(\sigma)C^{(0)}(\mathbf{r}-\mathbf{r}')\right]\right\}$$
$$-g(\sigma)\int dx''\,F_0(x'')\bar{T}_{-}(x,x'')\left[\delta(x-x')+\delta(x''-x')\right]$$
$$\text{(B11)}$$

$$g(x,x')=\delta(x-x')F_0^{-1}(x)+h(\mathbf{r}-\mathbf{r}') \qquad \text{(B12)}$$

$$g^{-1}(x,x')=\delta(x-x')F_0(x)-F_0(x)F_0(x')C(\mathbf{r}-\mathbf{r}') \qquad \text{(B13)}$$

Here $h(\mathbf{r}) = g(\mathbf{r}) - 1$, and $g(\mathbf{r})$ is the radial distribution function. Also, $C(\mathbf{r})$ is the direct correlation function and $C^{(0)}(\mathbf{r})$ is its low-density limit.

APPENDIX C: DERIVATION OF EQ. (4.4)

In this appendix the Klimontovich equation is obtained in the form of Eq. (4.4) and it is shown that the operator Ω in this equation is the same as that occurring in the linear kinetic theory. Equation (2.24) is first rewritten as

$$\left(\frac{\partial}{\partial t} + L\right)\phi + P_t\tilde{J}[\phi,\phi] = (1 - P_t)\tilde{J}[\phi,\phi] \tag{C1}$$

where L and $\tilde{J}$ are defined by Eq. (2.25) and P_t is given by Eq. (B2) with $\phi(x)$ replaced by $\phi(x,t)$. The free streaming part of the operator L is represented by the identity

$$\mathbf{v}\cdot\nabla\phi(x,t) = \mathbf{v}\cdot\nabla\int dx'\,\delta(x - x')\phi(x',t) \tag{C2}$$

and, substituting Eq. (B3) in (C2), the Klimontovich equation (C1) becomes

$$\begin{aligned}\frac{\partial}{\partial t}\phi(x,t) &+ \int dx'\,dx''\,\langle[v\cdot\nabla\phi(x)]\phi(x'')\rangle g^{-1}(x'',x')\phi(x',t)\\ &-\tilde{J}[\phi,1] - \tilde{J}[1,\phi] - P_t\tilde{J}[\phi,\phi] = (1 - P_t)\tilde{J}[\phi,\phi]\end{aligned} \tag{C3}$$

The last term on the left side of (C3) is, explicitly,

$$\begin{aligned}-P_t\tilde{J}[\phi,\phi] = -\int dx'\,dx''\,dx'''\,F_0(x''')\overline{T}_-(x,x''')\phi(x',t)\\ \times g^{-1}(x',x'')\langle\phi(x'')\phi(x)\phi(x''')\rangle\end{aligned} \tag{C4}$$

But the correlation function in Eq. (C4) is also given by

$$\begin{aligned}\langle\phi(x'')\phi(x)\phi(x''')\rangle = F_0^{-1}(x)F_0^{-1}(x''')\langle\phi(x'')f(x)f(x''')\rangle\\ -g(x'',x) - g(x'',x''')\end{aligned} \tag{C5}$$

and therefore

$$\begin{aligned}-P_t\tilde{J}[\phi,\phi] = -\int dx'\,dx''\,\phi(x')g^{-1}(x',x'')F_0^{-1}(x)\int dx'''\,\overline{T}_-(x,x''')\\ \times\langle\phi(x'')f(x)f(x''')\rangle + \tilde{J}[\phi,1] + \tilde{J}[1,\phi]\end{aligned} \tag{C6}$$

The last two terms in this equation are due to the last two terms in Eq.

(C5). Substitution of (C6) in (C3) then gives

$$\begin{aligned}&\frac{\partial}{\partial t}\phi(x,t)\\&\quad+\int dx'\,dx''\left\langle\left[\mathbf{v}\cdot\nabla\phi(x)-F_0^{-1}(x)\int dx'''\,\overline{T}_-(x,x''')f(x)f(x''')\right]\phi(x'')\right\rangle\\&\quad\times g^{-1}(x'',x')\phi(x',t)=(1-P_t)\tilde{J}[\phi,\phi]\end{aligned}\tag{C7}$$

The second term on the left can be transformed further by using Eq. (A10), so the Klimontovich equation becomes

$$\frac{\partial}{\partial t}\phi(x,t)+\int dx'\,dx''\,\langle\phi(x)\mathscr{L}_-\phi(x'')\rangle g^{-1}(x'',x')\phi(x',t)=(1-P_t)\tilde{J}[\phi,\phi]$$

or finally,

$$\frac{\partial}{\partial t}\phi(x,t)+\int dx'\,\Omega(x,x')\phi(x',t)=B[\phi(t),\phi(t)]\tag{C8}$$

with

$$B[\phi(t),\phi(t)]=(1-P_t)\tilde{J}[\phi,\phi]\tag{C9}$$

$$\Omega(x,x')=\int dx''\,\langle\phi(x)\mathscr{L}_-\phi(x'')\rangle g^{-1}(x'',x')\tag{C10}$$

This is the desired result, Eq. (4.4), and also confirms that the operator Ω is the same as that occurring in the linear kinetic theory, Eq. (B10).

Equation (C8) is valid for the time domain $t > 0$. For negative times the corresponding equation is obtained from the Klimontovich equation (A11), with $t < 0$:

$$\frac{\partial}{\partial t}\phi(x,-t)+\int dx'\,\overline{\Omega}(x,x')\phi(x',-t)=\overline{B}[\phi(-t),\phi(-t)]\tag{C11}$$

Here $\overline{B}$ is obtained from Eq. (4.5) by changing t to $-t$ and replacing $\overline{T}_-(x,x')$ by the operator $\overline{T}_+(x,x')$. The operator $\overline{\Omega}$ is given by

$$\overline{\Omega}(x,x')=-\int dx''\,\langle\phi(x)\mathscr{L}_+\phi(x'')\rangle g^{-1}(x'',x')\tag{C12}$$

APPENDIX D: PERTURBATIVE APPROXIMATION FOR $G(x,t;x',0)$

The purpose of this appendix is to derive Eq. (4.12). Use of Eq. (4.9) in Eq. (4.8) leads to

$$G(x,t;x',0)=e^{-\Omega(x)t}G(x,0;x',0)+\int_0^t dt'\,e^{-\Omega(x)(t-t')}\langle B[\phi,\phi]\phi(x',-t')\rangle\tag{D1}$$

The formal solution to the backward Klimontovich equation, (4.10), may now be applied to obtain

$$
\begin{aligned}
G(x,t;x',0) &= G^{(0)}(x,t;x',0) + \int_0^t dt'\, e^{-\Omega(x)(t-t')} e^{-\overline{\Omega}(x')t'} \langle B[\phi,\phi]\phi(x')\rangle \\
&\quad + \int_0^t dt' \int_0^{t'} dt''\, e^{-\Omega(x)(t-t')} e^{-\overline{\Omega}(x')(t'-t'')} \\
&\quad \times \left\langle B[\phi,\phi]\overline{B}\left[\phi(-t''),\phi(-t'')\right]\right\rangle
\end{aligned}
\tag{D2}
$$

where

$$
G^{(0)}(x,t;x',0) = e^{-\Omega(x)t} G(x,0;x'0) \tag{D3}
$$

Also, by using definition (4.5), it can be seen that the first-order correction, is identically zero since

$$
\langle [(1-P)\phi(x)\phi(x_0)]\phi(x')\rangle = 0 \tag{D4}
$$

Using the explicit forms of B and $\overline{B}$, as given by Eq. (4.5), to second order in the perturbation we find

$$
\begin{aligned}
G^{(2)}(x,t;x',0) &= \int_0^t dt' \int_0^{t'} dt'' \int dx_2\, F_0(x_2) e^{-\Omega(x)(t-t')} \\
&\quad \times e^{-\overline{\Omega}(x')(t'-t'')} A(x,x',x_2)
\end{aligned}
\tag{D5}
$$

where

$$
\begin{aligned}
A(x,x',x_2) &= \int dx_1\, dx_3\, dx_4\, F_0(x_1) g(x,x_4) g^{-1}(x_4,x_3) \overline{T}_-(x_3,x_1) \overline{T}_+(x',x_2) \\
&\quad \times C(x_3,x_1,0;x',x_2,-t'')
\end{aligned}
\tag{D6}
$$

with

$$
\begin{aligned}
&C(x_3,x_1,0;x',x_2,-t'') \\
&\quad = \langle [(1-P)\phi(x_3)\phi(x_1)][(1-P_{-t''})\phi(x',-t'')\phi(x_2,-t'')]\rangle
\end{aligned}
\tag{D7}
$$

To second-order correction, $G^{(2)}$, C is evaluated using the lowest-order approximation, $\phi^{(1)}(x,-t) = e^{-\overline{\Omega}(x)t}\phi(x)$ in Eq. (D7). To this order it is possible to show that for an arbitrary function $\psi(x)$

$$
P\psi(x,t) = P_{-t}\psi(x,t) \tag{D8}
$$

and, thus, Eq. (D7) can be written as

$$
\begin{aligned}
&C(x_3,x_1,0;x',x_2,-t'') \\
&\quad = e^{-[\overline{\Omega}(x')+\overline{\Omega}(x_2)]t''} \langle \phi(x_3)\phi(x_1)(1-P)\phi(x')\phi(x_2)\rangle^{(0)}
\end{aligned}
\tag{D9}
$$

Here, as in Section 4, the superscript on the brackets indicates that this static correlation function must be evaluated in an approximation consistent with the stationary condition (4.7).

To transform the above expression for $G^{(2)}$ to the form given in (4.13), apply the identity

$$e^{-\Omega(x)t}\psi(x) = \int dx'\, dx''\, G^{(0)}(x,t;x'',0)g^{-1}(x',x'')\psi(x') \tag{D10}$$

to $A(x,x',x_2)$ and take the adjoint in the sense of Eq. (A7). This leads to

$$\begin{aligned} e^{-\Omega(x)(t-t')}A(x,x',x_2) = \int dx_1\, dx_3\, dx_4\, F_0(x_1)G^{(0)}(x,t-t';x_4,0)T_+(x_3,x_1) \\ \times g^{-1}(x_4,x_3)\bar{T}_+(x',x_2)C(x_3,x_1,0;x',x_2,-t'') \end{aligned} \tag{D11}$$

But from Eqs. (A5), (A7), and (B13) it follows that

$$T_+(x_3,x_1)g^{-1}(x_4,x_3) = T_+(x_3,x_1)F_0(x_4)\delta(x_4-x_3) \tag{D12}$$

so Eq. (D11) becomes

$$\begin{aligned} &e^{-\Omega(x)(t-t')}A(x,x',x_2) \\ &\quad = \int dx_1\, dx_3\, dx_4\, F_0(x_1)F_0(x_4)G^{(0)}(x,t-t'';x_4,0)\delta(x_4-x_3) \\ &\qquad \times \bar{T}_-(x_3,x_1)\bar{T}_+(x',x_2)C(x_3,x_1,0;x',x_2,-t'') \end{aligned} \tag{D13}$$

where the adjoint was taken again. In a similar calculation, it may be shown that

$$\begin{aligned} &e^{-\Omega(x)(t-t')}e^{-\bar{\Omega}(x')(t'-t'')}A(x,x',x_2) \\ &\quad = \int dx_1\, dx_3\, dx_4\, dx_5\, dx_6\, F_0(x_1)F_0(x_3)F_0(x_4) \\ &\qquad \times G^{(0)}(x_6,0;x',t'-t'')G^{(0)}(x,t-t';x_4,0) \\ &\qquad \times \delta(x_4-x_3)\bar{T}_-(x_3,x_1)C(x_3,x_1,0;x_5,x_2,-t'') \\ &\qquad \times T_-(x_5,x_2)F_0(x_6)\delta(x_6-x_5) \end{aligned} \tag{D14}$$

Substitution of this result into Eq. (D5) yields

$$\begin{aligned} G^{(2)}(x,t;x',0) = \int_0^t dt' \int_0^{t'} dt''\, dx_1\, dx_2\, G^{(0)}(x,t-t';x_1,0) \\ \times \Gamma(x_1,x_2;t'-t'')G^{(0)}(x_2,0;x',t'') \end{aligned} \tag{D15}$$

where we have defined

$$\Gamma(x_1, x_2; t) = \int dx_3\, dx_4\, dx_5\, F_0(x_3) F_0(x_4) F_0(x_5) \overline{T}_-(x_1, x_3) \\ \times C(x_3, x_1, 0; x_4, x_5, -t) T_-(x_4, x_5) \delta(x_5 - x_2) \quad \text{(D16)}$$

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