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Initial State Dependence of Nonlinear Kinetic Equations: The Classical Electron Gas

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The method of nonequilibrium cluster expansion is used to study the decay to equilibrium of a weakly coupled inhomogeneous electron gas prepared in a local equilibrium state at the initial time, $t = 0$. A nonlinear kinetic equation describing the long time behavior of the one-particle distribution function is obtained. For consistency, initial correlations have to be taken into account. The resulting kinetic equation differs from that obtained when the initial state of the system is assumed to be factorized in a product of one-particle functions. The question of to what extent correlations in the initial state play an essential role in determining the form of the kinetic equation at long times is discussed. To that end, the present calculations are compared with results obtained before for hard sphere gases and in general gases with strong short-range forces. A partial answer is proposed and some open questions are indicated.

KEY WORDS: Kinetic equation; initial correlations; electron gas; nonequilibrium cluster expansion.

1. INTRODUCTION

A few years ago two of us$^{(1)}$ derived a nonlinear kinetic equation for the single-particle distribution function, $f_1(x_1, t)$, in a weakly coupled inhomogeneous electron gas by using the methods of nonequilibrium cluster expansions. The equation was argued to represent the generalization of the nonlinear Balescu–Guernsey–Lenard (BGL) equation$^{(2,3)}$ to a spatially inhomogeneous plasma.

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Recently,(4) a similar method was employed to obtain a linear kinetic equation for the two-time correlation function of the phase-space density fluctuations in an electron gas in thermal equilibrium. It was remarked there that when the nonlinear equation obtained in Ref. 1 is linearized around equilibrium, the resulting equation for $\delta f_1(x_1, t) = f_1(x_1, t) - f_{\mathrm{eq}}(x_1)$ differs from the linear equation obtained in Ref. 4 for the time correlation function of equilibrium fluctuations. The linearized equation for $\delta f_1(x_1, t)$ contains the correct generalized (i.e., inhomogeneous and non-Markovian) BGL collision operator, but it contains in addition a term that has the structure of a dynamical correction to the Vlasov operator and is as singular as the Vlasov operator itself at large distances. The kinetic equation that contains this singular operator, here referred to as a singular Vlasov correction, leads to unphysical results. For instance, it does not predict the correct hydrodynamic equations for the electron gas.(5)

The objective of this paper is to investigate and clarify the origin of the discrepancy between the two derivations.

Both derivations of Ref. 1 and Ref. 4 were carried out by analyzing the cluster expansion for the one- and two-particle functions of interest.(6-9) Divergences appear in such expansions in the long time limit. A well defined collision operator was then obtained by resumming the most divergent terms in each order in the density. In Ref. 1, it was assumed that at the initial time, $t = 0$, the N-particle distribution function of the system factorizes into the product of one-particle functions, or, equivalently, initial correlations were neglected. This assumption was motivated by the fact that for gases interacting via strong short-range forces it was shown some time ago(9) that initial correlations only contribute to less divergent terms in each order in the density. This is, however, not true for gases with long-range forces. In particular, we showed explicitly, when deriving the linear equation for the correlation function that terms containing equilibrium statistical correlations are among the most divergent ones in each order in the density.(4)

To study the effect of the initial correlations when deriving a nonlinear kinetic equation for the electron gas, we have used in this paper the same procedure as in Ref. 1, but we have assumed that the gas is in a local equilibrium state at $t = 0$. The initial correlations are then known explicitly and their consequences can be analyzed in detail. We have found that terms containing initial static correlations are as important as purely dynamical ones and cannot be neglected.

By summing again the most divergent terms in each order in the density, we have obtained a nonlinear kinetic equation for the one-particle distribution function. The collision operator differs from that obtained in Ref. 1 in that it contains explicitly statistical correlations in the form of a "local" Debye–Hückel pair correlation function. When linearized around equilibrium, this nonlinear equation does reduce to the linear equation for the equilibrium two-time correlation function obtained elsewhere.(4)

We are here in the situation where two different kinetic equations are obtained from two different initial states of the system. Our calculation raises an old and fundamental question: when and to what extent are the details of the initial nonequilibrium state of a many-body system forgotten in time and does a kinetic equation for $f_1(x_1, t)$ exist?(9–12) We cannot provide a general answer to such a question. However, through an analysis of the results given here for the electron gas as well as of results obtained before in the literature for a gas of hard spheres,(13,14) we have tried to draw a few conclusions for the two specific systems mentioned and to formulate more precisely some open questions.

In Section 2, we sketch the nonequilibrium cluster expansion of the one- and two-particle distribution functions for a system in local equilibrium at $t=0$. In Section 3, the divergences appearing in each term of such expansions in the long time limit are discussed and resummed. A nonlinear kinetic equation for $f_1(x_1, t)$ is obtained and compared to that given in Ref. 1. In Section 4, we discuss our work in relationship to previous results for a hard sphere gas and propose an interpretation for the initial state dependence of the kinetic equation.

2. NONEQUILIBRIUM CLUSTER EXPANSION: BASIC EQUATIONS

We consider a gas of N electrons contained in a volume Ω and immersed in a uniform neutralizing background of opposite charge. The nonequilibrium N-particle distribution function, $\rho_N(x_1,..., x_N, t)$, satisfies the Liouville equation

$$\frac{\partial}{\partial t}\rho_N + L_N\rho_N = 0 \tag{2.1}$$

where $x_i = (\mathbf{r}_i, \mathbf{v}_i)$ denotes the phase of the ith electron. For a system of particles interacting via a pairwise additive, central potential, $V(r_{ij})$, with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, the Liouville operator L_N is given by

$$L_N = \sum_{i=1}^{N} L_0(i) - \sum_{i<j=1}^{N} \theta_{ij} \tag{2.2a}$$

where

$$L_0(i) = \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \tag{2.2b}$$

and

$$\theta_{ij} = \frac{1}{m} \frac{\partial V(r_{ij})}{\partial \mathbf{r}_i} \cdot \left(\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j} \right) \tag{2.2c}$$

In the following, we will consider specifically the case of electrons interacting via the Coulomb potential, $V(r_{ij}) = e^2/r_{ij}$. The formal solution of Eq. (2.1) is given in terms of the initial value $\rho_N(x^N, 0) = \rho_N(x^N, t=0)$ by

$$\rho_N(x^N, t) = S_{-t}(x^N)\, \rho_N(x^N, 0) \tag{2.3}$$

where $x^N = x_1, x_2,..., x_N$, and $S_{-t}(x^s) = e^{-tL_s}$ is the s-particle streaming operator that transforms the phases of particle 1 through s at time $t=0$ into their values at time $-t$. The nonequilibrium s-particle distribution function, $f_s(x_1,..., x_s, t)$, is defined in terms of $\rho_N(x^N, t)$ by

$$n^s f_s(x_1,..., x_s, t) = \frac{N!}{(N-s)!} \int dx_{s+1} \cdots dx_N\, S_{-t}(x^N)\, \rho_N(x^N, 0) \tag{2.4}$$

for $s = 1, 2,...$, where here and in the following the thermodynamic limit is intended. In Eq. (2.4) it is indicated explicitly that $n^s f_s$ is of order n^s, provided ρ_N has been normalized to unity.$^{(8)}$

Our objective is to obtain a kinetic equation describing the time evolution of the one-particle distribution function, $f_1(x_1, t)$, given by Eq. (2.4) for $s = 1$, at long times. This will be done by using the methods of nonequilibrium cluster expansions, following closely the theory of gases with strong short-range forces.$^{(6-9)}$ The derivation is analogous to that given in Ref. 4 for the linearized BGL equation for the two-time correlation function of equilibrium phase space fluctuations. Owing, however, to the nonlinearity of the equation considered here we will work in time language.$^{(7)}$ The time dependence of the one-particle distribution function is related to the two-particle distribution function, $f_2(x_1, x_2, t)$, through the first equation of the BBGKY hierarchy,

$$\frac{\partial}{\partial t} f_1(x_1, t) + L_0(1) f_1(x_1, t) = n \int dx_2\, \theta_{12} f_2(x_1, x_2, t) \tag{2.5}$$

which can be obtained by integrating the Liouville equation, assuming that all distribution functions vanish as $\mathbf{r}_i, \mathbf{v}_i \to \infty^{(8)}$ and going to the bulk limit.

We now proceed to derive a generalized kinetic equation for $f_1(x_1, t)$ by performing a density expansion of the right-hand side of Eq. (2.5). The first step consists in making a cluster expansion of the streaming operator

$S_{-t}(x^N)$ in Eq. (2.4) for $s = 1, 2$. To obtain the cluster expansion of f_1 we write

$$S_{-t}(x^N) = U_t(x_1)\, S_{-t}(x^{N-1}) + \sum_{i=2}^{N} U_t(x_1 \mid x_i)\, S_{-t}(x^{N-2}) + \cdots \tag{2.6a}$$

and for the cluster expansion of $f_2(x_1, x_2, t)$,

$$S_{-t}(x^N) = U_t(x_1, x_2)\, S_{-t}(x^{N-2}) + \sum_{i=3}^{N} U_t(x_1, x_2 \mid x_i)\, S_{-t}(x^{N-3}) + \cdots \tag{2.6b}$$

where the cluster functions $U_t(x_1 \mid x_2,..., x_s)$ and $U_t(x_1, x_2 \mid x_3,..., x_s)$ have been given elsewhere.[(6)] Inserting the cluster expansion (2.6a) and (2.6b) into Eq. (2.4) for $s = 1$ and $s = 2$, respectively, and using Liouville's theorem, we obtain cluster expansions for f_1 and f_2 in the form

$$\begin{aligned} nf_1(x_1, t) &= nS_{-t}(x_1)\, f_1(x_1, 0) \\ &\quad + n^2 \int dx_2\, U_{-t}(x_1 \mid x_2)\, f_2(x_1, x_2, 0) + \cdots \end{aligned} \tag{2.7a}$$

and

$$\begin{aligned} n^2 f_2(x_1, x_2, t) &= n^2 S_{-t}(x_1, x_2)\, f_2(x_1, x_2, 0) \\ &\quad + n^3 \int dx_3\, U_t(x_1, x_2 \mid x_3)\, f_3(x_1, x_2, x_3, 0) + \cdots \end{aligned} \tag{2.7b}$$

respectively, where

$$f_s(x_1,..., x_s, 0) = f_s(x_1,..., x_s, t = 0) \tag{2.7c}$$

is the initial value of the s-particle distribution function. To proceed, we have to specify the initial state of the system. First, we write the initial values $f_s(x_1,..., x_s, 0)$, in the form

$$f_s(x_1,..., x_s, 0) = a_s(x_1,..., x_s, 0) \prod_{i=1}^{s} f_1(x_i, 0) \tag{2.8}$$

where the a_s represent initial correlations between the particles. At this point of the derivation it was assumed in Ref. 1 that the initial state is such that the a_s are all equal to unity. This assumption has been justified for a dilute gas of particles interacting through a short-range interparticle potential. For that case, it has been shown[(9)] that terms containing initial correlations are not among the most divergent terms in the density expansion of $f_1(x_1, t)$ for long times. As a consequence, such terms are not important for the long-time behavior of the distribution function in a dilute gas with short-range intermolecular forces. This is, however, not true for a Coulomb gas. On the contrary, in our derivation of the linearized BGL equation we showed explicitly that terms in the density expansion that contain static correlations between the electrons can be among the most divergent ones at long times in each order in the density.(4) To analyze the effect of the initial correlations, we have to specify the form of the initial state. We assume that at $t=0$ the gas can be described by an ensemble density of the form(14)

$$\rho(x^N, t=0) = \frac{1}{N!\,Z} W_N(x^N) \prod_{i=1}^{N} D(x_i) \tag{2.9a}$$

where Z is the normalization factor and $D(x_i)$ is a nonnegative function of x_i. In Eq. (2.9a) $W_N(x^N)$ is the potential part of the phase space local equilibrium distribution,

$$W_N(x^N) = \prod_{i<j=1}^{N} (1 + f_{ij}^L) \tag{2.9b}$$

where f_{ij}^L is a local Mayer function, given by

$$f_{ij}^L = \exp\{-\tfrac{1}{2}V(r_{ij})[\beta(\mathbf{r}_i, 0) + \beta(\mathbf{r}_j, 0)]\} - 1 \tag{2.9c}$$

The local temperature $T(\mathbf{r}, 0) = [k_B \beta(\mathbf{r}, 0)]^{-1}$ and the local flow velocity, $\mathbf{U}(\mathbf{r}, 0)$, at $\mathbf{r}$ at time $t=0$ are defined in terms of the one-particle distribution function, $f_1(x, 0)$, as

$$\tfrac{3}{2}n(\mathbf{r}, 0)\, k_B T(\mathbf{r}, 0) = \int d\mathbf{v}\, \tfrac{1}{2}m[\mathbf{v} - \mathbf{U}(\mathbf{r}, 0)]^2\, n f_1(x, 0) \tag{2.9d}$$

and

$$n(\mathbf{r}, 0)\, \mathbf{U}(\mathbf{r}, 0) = \int d\mathbf{v}\, \mathbf{v} n f_1(x, 0) \tag{2.9e}$$

with $n(\mathbf{r}, 0)$ the initial local density

$$n(\mathbf{r}, 0) = \int d\mathbf{v}\, n f_1(x, 0) \tag{2.9f}$$

In a general nonequilibrium fluid the temperature should be defined in terms of the total energy density by requiring thermodynamics to be locally valid.(15) Such a definition involves the two-particle as well as the one-particle distribution functions. For a dilute neutral gas as well as for a weakly interacting electron gas the definition given by Eq. (2.9d) can, however, be justified. One should also notice the difference between the overall density, $n = N/\Omega$, and the local density, $n(\mathbf{r}, t)$.

The density expansion of the a_s can be obtained in the same way as in the equilibrium case.(16,17) It is formally identical to the density expansion of the corresponding equilibrium quantities (i.e., the configurational part of the equilibrium distribution functions), with, however, the equilibrium temperature and density replaced by corresponding local quantities. For the specific initial state considered here the a_s are only functions of position. Their density expansion has the form

$$a_s(\mathbf{r}_1, ..., \mathbf{r}_s) = \sum_{l=0}^{\infty} \int dx_{s+1} \cdots dx_{s+l} a_s^{(l)}(\mathbf{r}_1, ..., \mathbf{r}_s \mid \mathbf{r}_{s+1}, ..., \mathbf{r}_{s+l}) \times \prod_{i=s+1}^{s+l} [nf_1(x_i, 0)] \tag{2.10}$$

For instance, for $s = 2$, we have

$$a_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = W_2(\mathbf{r}_1, \mathbf{r}_2) \tag{2.11a}$$

$$a_2^{(1)}(\mathbf{r}_1, \mathbf{r}_2 \mid \mathbf{r}_3) = W_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - (1 + P_{12})\, W_2(\mathbf{r}_1, \mathbf{r}_2)\, W_2(\mathbf{r}_1, \mathbf{r}_3) + W_2(\mathbf{r}_1, \mathbf{r}_2) \tag{2.11b}$$

etc., with W_s given by Eq. (2.9b). When Eqs. (2.8) and (2.11) are inserted in Eqs. (2.7a) and (2.7b), we obtain

$$nf_1(x_1, t) = nS_{-t}(x_1)\, f_1(x_1, 0) + n^2 \int dx_2\, U_t(x_1 \mid x_2)\, a_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \times f_1(x_1, 0)\, f_1(x_2, 0) + \cdots \tag{2.12a}$$

and

$$\begin{aligned} n^2 f_2(x_1, x_2, t) &= n^2 S_{-t}(x_1, x_2)\, a_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2)\, f_1(x_1, 0)\, f_1(x_2, 0) \\ &\quad + n^3 S_{-t}(x_1, x_2) \int dx_3\, a_2^{(1)}(\mathbf{r}_1, \mathbf{r}_2 \mid \mathbf{r}_3) \prod_{i=1}^{3} f_1(x_i, 0) \\ &\quad + n^3 \int dx_3\, U_t(x_1, x_2 \mid x_3)\, a_3^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \prod_{i=1}^{3} f_1(x_i, 0) \\ &\quad + \cdots \end{aligned} \tag{2.12b}$$

In Eqs. (2.12), $f_1(x_1, t)$ and $f_2(x_1, x_2, t)$ are expressed for all times t in terms of the initial values $f_1(x_i, t=0)$, both explicitly and implicitly through the $a_s^{(l)}$. It is, however, well known that, for both gases with short- and long-range forces, the series (2.12) can only be used to describe the time dependence of the distribution functions for times much less than the mean free time between collisions, since they diverge term by term in the long-time limit. They cannot, therefore, be used to determine the long-time behavior of the distribution functions. To circumvent this difficulty, one eliminates the initial values of the one-particle distribution function between Eqs. (2.12a) and (2.12b), to obtain an expression for $f_2(x_1, x_2, t)$ in terms of $f_1(x_1, t)$. The $a_s^{(l)}$ in Eqs. (2.12) depend implicitly on $f_1(x_1, 0)$ through the initial temperature, $\beta(\mathbf{r}, 0)$ and the initial flow velocity, $\mathbf{U}(\mathbf{r}, 0)$. We assume that the local density, temperature, and flow velocity are defined at all times by expressions of the form (2.9d–f). The elimination of the initial one-particle distribution function $f_1(x_1, 0)$ appearing implicity in the $a_s^{(l)}$ through $\beta(\mathbf{r}, 0)$ and $\mathbf{U}(\mathbf{r}, 0)$ [cf. Eqs. (2.9d,e)] in favor of $f_1(x_1, t)$ generates additional terms that are proportional to the gradients of the macroscopic variables. Such terms do not contribute to the hydrodynamic equations in the low-density limit and are therefore neglected here.

To stress the relationship of our calculation with that of Dorfman and Cohen,$^{(1)}$ it is also convenient to write the a_s in terms of cluster functions h_s defined in the usual way:

$$a_2(\mathbf{r}_1, \mathbf{r}_2, 0) = 1 + h_2(\mathbf{r}_1, \mathbf{r}_2, 0) \tag{2.13a}$$

$$\begin{aligned} a_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, 0) = 1 &+ h_2(\mathbf{r}_1, \mathbf{r}_2, 0) + h_2(\mathbf{r}_1, \mathbf{r}_2, 0) + h_2(\mathbf{r}_1, \mathbf{r}_3, 0) \\ &+ h_2(\mathbf{r}_2, \mathbf{r}_3, 0) + h_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, 0) \end{aligned} \tag{2.13b}$$

etc. The virial expansion for the h_s is immediately obtained from that for the h_s as

$$\begin{aligned} h_s(\mathbf{r}_1,\ldots, \mathbf{r}_s, 0) = \sum_{l=0}^{\infty} n^l \int dx_{s+1} \cdots dx_{s+l} h_s^{(l)}(\mathbf{r}_1,\ldots, \mathbf{r}_s \mid \mathbf{r}_{s+1},\ldots, \mathbf{r}_{s+l}) \\ \times \prod_{i=s+1}^{s+l} f_1(x_i, 0) \end{aligned} \tag{2.14}$$

Again, the density expansion of h_s is formally identical to that of the corresponding equilibrium cluster function, with the equilibrium density and temperature replaced by the corresponding local quantities. After carrying out the elimination and introducing the cluster functions h_s, $f_2(x_1, x_2, t)$ can be written in a virial-like series in terms of products of $f_1(x_1, t)$,

$$n^2 f_2(x_1, x_2, t) = n^2 f_2^{(d)}(x_1, x_2, t) + n^2 f_2^{(s)}(x_1, x_2, t) \tag{2.15a}$$

where we have separated the part of f_2 that only contains purely dynamical collision sequences and does not depend on initial correlations, denoted with $f_2^{(d)}$, from the part of f_2 that explicitly contains the initial static correlations, $f_2^{(s)}$. They are given by

$$\begin{aligned} n^2 f_2^{(d)}(x_1, x_2, t) &= n^2 \mathscr{S}_t(x_1, x_2)\, f_1(x_1, t)\, f(x_2, t) \\ &\quad + n^3 \int dx_3\, \tau_t(x_1, x_2 \mid x_3) \prod_{i=1}^{3} f_1(x_i, t) + O(n^4) \end{aligned} \tag{2.15b}$$

and

$$\begin{aligned} n^2 f_2^{(s)}(x_1, x_2, t) &= n^2 S_{-t}(x_1, x_2)\, h_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2)\, S_t^0(x_1, x_2)\, f_1(x_1, t)\, f_1(x_2, t) \\ &\quad + n^3 S_{-t}(x_1, x_2) \int dx_3\, h_2^{(1)}(\mathbf{r}_1, \mathbf{r}_2 \mid \mathbf{r}_3)\, S_t^0(x_1, x_2, x_3) \\ &\quad \times \prod_{i=1}^{3} f_1(x_i, t) + n^3 \int dx_3 \{ U_t(x_1, x_2 \mid x_3) [h_3^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &\quad + (1 + P_{12} + P_{13})\, h_2^{(0)}(\mathbf{r}_2, \mathbf{r}_3)]\, S_t^0(x_1, x_2, x_3) \\ &\quad - (1 + P_{12})\, \mathscr{S}_t(x_1, x_2)\, U_t(x_1 \mid x_3)\, h_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2)\, S_t^0(x_1, x_3) \\ &\quad - (1 + P_{12})\, S_{-t}(x_1, x_2)\, h_2^{(0)}(\mathbf{r}_1, \mathbf{r}_2)\, S_t^0(x_1, x_2) \\ &\quad \times U_t(x_1 \mid x_3)\, a_2^{(0)}(\mathbf{r}_1, \mathbf{r}_3)\, S_t^0(x_1, x_3) \} \\ &\quad \times \prod_{i=1}^{3} f_1(x_i, t) + O(n^4) \end{aligned} \tag{2.15c}$$

where

$$S_{-t}^0(x_1, \dots, x_s) = \prod_{i=1}^{s} S_{-t}(x_i) \tag{2.15d}$$

and

$$\mathscr{S}_t(x_1, \dots, x_s) = S_{-t}(x_1, \dots, x_s)\, S_t^0(x_1, \dots, x_s) \tag{2.15e}$$

$$\begin{aligned} \tau_t(x_1, x_2 \mid x_3) &= \mathscr{S}_t(x_1, x_2, x_3) - (1 + P_{12})\, \mathscr{S}_t(x_1, x_2)\, \mathscr{S}_t(x_1, x_3) \\ &\quad + \mathscr{S}_t(x_1, x_2) \end{aligned} \tag{2.15f}$$

Finally, P_{ij} is a permutation operator that interchanges the labels of particles i and j.

In Ref. 1 the choice $a_s = 1$ for all s, implies that $f_2^{(s)}$ vanishes. We remark that all the manipulations carried out to this point apply for any pairwise additive central potential. To proceed further, one has to study the various terms in the series (2.15b) and (2.15c) to see to what extent they are useful representations of the right-hand side of Eq. (2.5) for long times. This analysis depends on the form of the intermolecular potential and will be carried out in the next section for the case of a Coulomb potential.

3. NONLINEAR KINETIC EQUATION FOR AN INHOMOGENEOUS ELECTRON GAS

As discussed elsewhere,(1,7,8) in the long-time limit, Eqs. (2.15a) and (2.15c) contain divergences associated with both the long range of the potential and with dynamical processes. An appropriate resummation is necessary to remove both these divergences and properly incorporate the collective effects. To analyze the case of the weak, long-ranged Coulomb potential, we expand both the streaming operator and the correlation functions h_s in powers of the potential, in analogy to the Mayer expansion of the f functions in the equilibrium case.(17) The streaming operators are expanded in powers of the θ_{ij} operators by making repeated use of the identity

$$S_{-t}(x_1,..., x_s) = S^0_{-t}(x_1,..., x_s) + \sum_{i \leqslant i < j \leqslant s} \alpha \int_0^t dt_1\, S_{-(t-t_1)}(x_1,..., x_s)\, \tilde{\theta}_{ij} \times S^0_{-t_1}(x_1,..., x_s) \tag{3.1}$$

where $\alpha\tilde{\theta}_{ij} = \theta_{ij}$. The parameter α has been introduced to keep track of the ordering in the expansion in the strength of the potential. It is related to the square of the electron charge, e^2. The expansion of the h_s is formally identical to Mayer's equilibrium expansion and reads

$$h_s^{(l)}(\mathbf{r}_1,..., \mathbf{r}_s \mid \mathbf{r}_{s+1},..., \mathbf{r}_{s+l}) = \sum_{k=s-1}^{\infty} \alpha^k U_s^{(k)}(\mathbf{r}_1,..., \mathbf{r}_s \mid \mathbf{r}_{s+1},..., \mathbf{r}_{s+l}) \tag{3.2a}$$

where we have indicated that the first nonvanishing term in the expansion of $h_s^{(l)}$ is of the order α^{s-1}. For instance,

$$U_2^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = -\tfrac{1}{2}[\beta(\mathbf{r}_1, 0) + \beta(\mathbf{r}_2, 0)]\, \tilde{V}(r_{12}) \tag{3.2b}$$

with $\alpha\tilde{V}(r) = V(r)$.

We remark that the θ expansion is only suitable for the description of small angle scattering at large interparticle separation, since it does not properly describe the strong short-ranged interactions that lead to large angle scattering. Here we shall discuss only divergences associated with the long range of the potential and small angle scattering. When the expansion in the strength of the potential is carried out in Eqs. (2.15a,b) and the resulting expression for $f_2(x_1, x_2, t)$ is substituted in the first hierarchy equation, Eq. (2.5), one finds the following equation for $f_1(x_1, t)$:

$$\begin{aligned}\frac{\partial}{\partial t} f_1(x_1, t) + L_0(1)\, f_1(x_1, t) \\ = \sum_{v=s,d} \{n\Gamma_2^{(v)}(f_1, f_1) + n^2\Gamma_3^{(v)}(f_1, f_1, f_1) + \cdots\}\end{aligned} \tag{3.3}$$

The right-hand side of Eq. (3.2a) has the form of an expansion in powers of f_1, with

$$\begin{aligned} n\Gamma_2^{(d)}(f_1, f_1) = {}& n\alpha \int dx_2\, \tilde{\theta}_{12} f_1(x_1, t)\, f_1(x_2, t) \\ & + n\alpha^2 \int dx_2 \int_0^t dt_1\, \tilde{\theta}_{12} S^0_{-(t-t_1)}(x_1, x_2)\, \tilde{\theta}_{12} \\ & \times f_1(x_1, t_1)\, f_1(x_2, t_1) + \cdots \end{aligned} \tag{3.4a}$$

$$\begin{aligned} n^2\Gamma_3^{(d)}(f_1, f_1) = {}& n^2\alpha^3 \int dx_2\, dx_3 \int_0^t dt_1 \int_0^{t_1} dt_2\, \tilde{\theta}_{12} S^0_{-(t-t_1)}(x_1, x_2)\, \tilde{\lambda}_3(x_1, x_2) \\ & \times f_1(x_3, t_1)\, S^0_{-(t_1-t_2)}(x_1, x_2)\, \tilde{\theta}_{12} \\ & \times f_1(x_1, t_2)\, f_1(x_2, t_2) + \cdots \end{aligned} \tag{3.4b}$$

and

$$\begin{aligned} n\Gamma_2^{(s)}(f_1, f_1) = {}& n\alpha^2 \int dx_2\, \tilde{\theta}_{12} U_2^{(1)}(\mathbf{r}_1, \mathbf{r}_2)\, f_1(x_1, t)\, f_1(x_2, t) \\ & + n\alpha^2 \int dx_2 \int_0^t dt_1\, \tilde{\theta}_{12} S^0_{-(t-t_1)}(x_1, x_2) \\ & \times [-L_0(x_1, x_2)\, U_2^{(1)}(\mathbf{r}_1, \mathbf{r}_2)]\, f_1(x_1, t_1)\, f_1(x_2, t_1) + \cdots \end{aligned} \tag{3.5a}$$

$$\begin{aligned} n^2\Gamma_3^{(s)}(f_1, f_1, f_1) = {}& n^2\alpha^3 \int dx_2\, dx_3\, \tilde{\theta}_{12} U_2^{(2)}(\mathbf{r}_1, \mathbf{r}_2 \mid \mathbf{r}_3) \prod_{i=1}^{3} f_1(x_i, t) \\ & + n^2\alpha^3 \int dx_2\, dx_3 \int_0^t dt_1\, \tilde{\theta}_{12} S^0_{-(t-t_1)}(x_1, x_2) \\ & \times [-L_0(x_1, x_2, x_3)\, U_3^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)] \prod_{i=1}^{3} f_1(x_1, t_1) \\ & + n^2\alpha^3 \int dx_2\, dx_3 \int_0^t dt_1 \int_0^{t_1} dt_2\, \tilde{\theta}_{12} S^0_{-(t-t_1)}(x_1, x_2) \\ & \times \tilde{\lambda}_3(x_1, x_2)\, f_1(x_3, t_1)\, S^0_{-(t_1-t_2)}(x_1, x_2) \\ & \times [-L_0(x_1, x_2)\, U_2^{(1)}(\mathbf{r}_1, \mathbf{r}_2)]\, f_1(x_1, t_2)\, f_1(x_2, t_2) + \cdots \end{aligned} \tag{3.5b}$$

where

$$\tilde{\lambda}_3(x_1, x_2) = \tilde{\theta}_{13}(1 + P_{13}) + \tilde{\theta}_{23}(1 + P_{23}) \tag{3.5c}$$

and

$$L_0(x_1, ..., x_s) = \sum_{i=1}^{s} L_0(i) \tag{3.5d}$$

The s-body collision integrals $\Gamma_s^{(d)}$ were already obtained in Ref. 1. The first term on the right-hand side of Eq. (3.4a) is the Vlasov term, which incorporates the action of an effective mean field. The second term on the right-hand side of Eq. (3.4a) is the Landau collision integral that is logarithmically divergent for long times. The triple collision integral $\Gamma_3^{(d)}$ and all the higher-order integrals also diverge at long times.

The s-body collision integrals $\Gamma_s^{(s)}$ contain the effect of initial correlations and were not obtained in Ref. 1. The first term on the right-hand side of Eq. (3.5a) is instantaneous and therefore does not contain any long-time divergence. It contributes plasma parameter corrections to the Vlasov term. Such corrections are neglected in our calculation. The second term on the right-hand side of Eq. (3.5a) diverges logarithmically at long times. Similarly, all the noninstantaneous terms in $\Gamma_s^{(s)}$, for $s \geqslant 3$, diverge. In each order in the density, one finds that both $\Gamma_s^{(d)}$ and $\Gamma_s^{(s)}$ contain terms that are most divergent at long times. To obtain a convergent expression for the collision integral to lowest order in the plasma parameter, one must resum the most divergent terms in the density expansion on the right-hand side of Eq. (3.3). This leads to a nonlinear kinetic equation for $f_1(x_1, t)$, given by

$$\begin{aligned}
&\left[\frac{\partial}{\partial t} + L_0(1)\right] nf_1(x_1, t) \\
&\quad = \int dx_2\, \theta_{12} nf_1(x_2, t)\, nf_1(x_1, t) \\
&\qquad + \int dx_2\, \theta_{12} \int_0^t d\tau\, U_{12}(t \mid \tau)[\theta_{12} + \bar{\theta}_{12}(\tau)]\, nf_1(x_1, \tau)\, nf_2(x_2, \tau) \\
&\qquad + \int dx_2\, \theta_{12} \int_0^t d\tau\, U_{12}(t \mid \tau)(1 + P_{12}) \int dx_3 [\theta_{13} + \bar{\theta}_{13}(\tau)]\, \tilde{h}_2(\mathbf{r}_2, \mathbf{r}_3, \tau) \\
&\qquad \times \prod_{i=1}^{3} [nf_1(x_i, \tau)]
\end{aligned} \tag{3.6a}$$

Here

$$U_{12}(t \mid \tau) = T_+ \exp\left\{ - \int_\tau^t d\tau' [L_0(x_1, x_2) - \lambda_p(x_1, x_2, \tau')] \right\} \tag{3.6b}$$

with

$$\lambda_p(x_1, x_2, \tau) = \int dx_3[\theta_{13}(1+P_{13}) + \theta_{23}(1+P_{23})]\, nf_1(x_3, \tau) \tag{3.6c}$$

and $\bar{\theta}_{ij}$ is a function, defined by

$$\bar{\theta}_{ij}(t) = -L_0(x_i, x_j)\{-\tfrac{1}{2}V(r_{ij})[\beta(\mathbf{r}_i, t) + \beta(\mathbf{r}_j, t)]\} \tag{3.6d}$$

Finally, in Eq. (3.6a), $\tilde{h}_2(x_2, x_3, \tau)$ is a local Debye–Hückel pair correlation function, defined by the expansion

$$\tilde{h}_2(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{l=3}^{\infty} \frac{1}{(l-2)!} \int d\mathbf{r}_3 \cdots d\mathbf{r}_l\, V(\mathbf{r}_1, \mathbf{r}_2 \mid \mathbf{r}_3, \ldots, \mathbf{r}_l; t) \times \prod_{i=3}^{l} n(\mathbf{r}_i, t) \tag{3.7}$$

where the functions $V(\mathbf{r}_1, \mathbf{r}_2 \mid \mathbf{r}_3, \ldots, \mathbf{r}_l)$ are represented by the set of all linked l-particle Mayer-like graphs—where the Mayer functions are replaced by factors of the potential times the local inverse temperature $\beta(\mathbf{r}, t)$—with two root points and no articulation points.(16) Here $n(\mathbf{r}, t)$ and $\beta(\mathbf{r}, t)$ are the local density and temperature at time t, given by Eqs. (2.9d) and (2.9f) with $f_1(x, 0)$ replaced by $f_1(x, t)$. When the local thermodynamic variables in Eq. (3.7) are replaced by their equilibrium values, the usual Debye–Hückel equilibrium pair correlation function is obtained. We refer to $\tilde{h}_2(\mathbf{r}_1, \mathbf{r}_2, t)$ as to a local Debye–Hückel pair correlation function. The nonlinear equation (3.6a) can be linearized around equilibrium by letting

$$f_1(x_1, t) = \phi(v_1) + \delta f_1(x_1, t) \tag{3.8}$$

with $\phi(v_1)$ a Maxwell velocity distribution. The resulting linear equation for $\delta f_1(x_1, t)$ is given by

$$\begin{aligned}
&\left[\frac{\partial}{\partial t} + L_0(1)\right] \delta f_1(x_1, t) \\
&\quad = n \int dx_2\, \theta_{12}(1+P_{12})\, \phi(v_2)\, \delta f_1(x_1, t) \\
&\qquad + n \int dx_2\, \theta_{12} \int_0^t d\tau\, e^{-L_v(x_1,x_2)(t-\tau)}(1+P_{12}) \\
&\qquad \times \left[\theta_{12} + n \int dx_3\, \theta_{13} h_{\mathrm{DH}}(r_{23})\, \phi(v_3)\right] \phi(v_2)\, \delta f_1(x_1, \tau)
\end{aligned} \tag{3.9a}$$

with $h_{\mathrm{DH}}(r)$ the Debye–Hückel pair correlation function and

$$L_v(x_1, x_2) = (1 + P_{12})\left[L_0(1) - n \int dx_3\, \theta_{13}(1 + P_{13})\, \phi(v_3)\right] \tag{3.9b}$$

The first term on the right-hand side of Eq. (3.9a) is the linearized Vlasov operator; the second term is the linearized BGL operator for an inhomogeneous electron gas. The Laplace transform of Eq. (3.9a) is identical to Eq. (3.15) obtained in Ref. 4 for the Laplace transform of the two-time equilibrium correlation function. The nonlinear equation obtained in Ref. 1 by neglecting all correlations in the initial state is given by

$$\begin{aligned}\left[\frac{\partial}{\partial t} + L_0(1)\right] n f_1(x_1, t) &= \int dx_2\, \theta_{12} n f_1(x_1, t)\, n f_1(x_2, t) \\ &\quad + \int dx_2\, \theta_{12} \int_0^t dt_1\, U_{12}(t \mid \tau)\, \theta_{12} n f_1(x_1, \tau)\, n f_1(x_2, \tau)\end{aligned} \tag{3.10}$$

All the terms present on the right-hand side of Eq. (3.6a) and that are not in Eq. (3.10) arise from the initial correlations. The latter, however, do not appear explicitly in Eq. (3.6a). Our choice of an initial state, where the distribution functions can be written as functionals of the one-particle distribution function, has allowed us to eliminate everywhere the initial distribution $\mathrm{f}_1(x_1, 0)$ in terms of its value at a later time. Equation (3.6a) is then a closed, highly nonlinear equation for $f_1(x_1, t)$. The linearization around equilibrium of Eq. (3.10) leads to a kinetic equation that contains the correct linearized BGL operator, but it contains in addition an extra term given by

$$\begin{aligned}\delta\mathscr{V}_s(x_1, t) * \delta f_1(x_1, t) = n^2 \int dx_2\, \theta_{12} \int_0^t dt\, e^{-L_v(x_1, x_2)(t-\tau)}(1 + P_{12}) \\ \times \int dx_3\, \theta_{13} h_{\mathrm{DH}}(r_{12})\, \phi(v_1)\, \phi(v_2)\, \delta f_1(x_3, \tau)\end{aligned} \tag{3.11}$$

where the star denotes the time convolution. The operator $\delta\mathscr{V}_s$ has the structure of a correction to the Vlasov operator since, like the Vlasov operator itself, it is directly related to density fluctuations and is singular at large distances. Its presence in the kinetic equation leads to unphysical features. For instance, the linearized kinetic equation containing $\delta\mathscr{V}_s$ leads to a set of five hydrodynamic equations that are qualitatively different from the usual phenomenological hydrodynamic equations for the electron gas and contain unphysical features.(5) On the other hand, Eq. (3.9a) leads to the correct hydrodynamic equations.

4. DISCUSSION

Our derivation suggests a number of remarks and questions.

1. Before discussing what conclusions one can draw from our work, we wish to emphasize a few aspects of the derivation presented here.

a. We have chosen a special initial state where all the distribution functions $f_s(x_1,..., x_s, 0)$ can be expressed as functionals of the initial value of the one-particle function, $f_1(x_1, 0)$. The basic idea was then to eliminate everywhere $f_1(x_1, 0)$ in favor of $f_1(x_1, t)$.(6)

In this way, the resulting kinetic equation does not contain any explicit reference to the initial state, but it depends on $f_1(x_1, \tau)$ at all previous times. It contains the quantity $\tilde{h}_2(x_1, x_2, t)$ that has the form of a local Debÿe–Hückel pair correlation function, where the density and temperature are evaluated at time t, i.e., it represents statistical correlations between the particles, evaluated at the instant at which the collision occurs in the kinetic operator. Clearly, $\tilde{h}_2(x_1, x_2, t)$ is not the full two-particle cluster function $h_2(x_1, x_2, t)$ at time t, as evolved from its initial value, $h_2(x_1, x_2, 0)$—the equation would then simply be the first equation of the BBGKY hierarchy—but it is that part of $h_2(x_1, x_2, t)$ that is "relevant" at time t in the order in the density and on the time and length scales of interest.

b. It is incorrect to argue that the singular Vlasov correction term can be neglected on the ground that it is of higher order in the plasma parameter than the Vlasov operator itself.(4) Firstly, it is of the same order in the plasma parameter as the BGL operator, which is kept. Secondly, and more importantly, its structure is not identical to that of the usual Vlasov term. As a consequence, the hydrodynamic equations that follow from the kinetic equation containing this singular Vlasov term are unphysical. For instance, such equations do not predict energy conservation.(5)

2. One of the basic ideas of kinetic theory, first introduced by Bogolubov,(10) is that after an initial short lived transient—i.e., for $t \gg t_c$, with t_c a characteristic collision time—the approach to equilibrium of a many-body system prepared in a nonequilibrium state at $t=0$ is adequately described by a closed kinetic equation for the one-particle distribution function, $f_1(x_1, t)$. For a large class of initial nonequilibrium states the form of the kinetic equation—in general explicitly time-depen-

dent and highly nonlinear—should be independent of the details of the initial state. Our calculation appears at first in contradiction with the above statement, since we have shown that two different initial states lead to two different kinetic equations. We believe, however, that the factorized initial state is an unphysical one for the electron gas, since it is not consistent with the condition of overall charge neutrality that manifests itself in the vanishing of the total density fluctuations. Only once those physical characteristics of the initial state that must be common to all physical initial conditions, as, for instance, charge neutrality for the electron gas and nonoverlap of particles for hard spheres, have been retained, the kinetic equation at long times can be independent on the details of the initial state. To make such statement with full confidence, it would, however, be necessary to modify our initial local ensemble and show that the same kinetic equation is recovered at long times for this modified initial state, which we have not done.

We will discuss again this point below for the case of hard spheres. There we will be able to make some more precise and firm statements.

3. Several years ago two of us(9) showed that for a gas with strong short-range forces initial correlations do not contribute to the most divergent terms in each order in the density in the expansion of $f_2(x_1, x_2, t)$ in powers of $f_1(x_1, t)$. As a consequence, in this case initial correlations could be neglected when deriving a kinetic operator to describe the leading long-time behavior of $f_1(x_1, t)$ to lowest order in the density. It is, however, dangerous to generalize this statement by saying that initial correlations are "forgotten" in the course of time. They simply do not contribute to the leading long-time low-density behavior of $f_1(x_1, t)$. When one, however, considers density corrections to the leading low-density behavior and is faced with the task of analyzing the less divergent terms in each order in the density in the cluster expansion, the initial correlations can no longer be neglected.(13,14) We will sharpen this point below by referring again to the case of a gas of hard spheres.

4. Concrete progress in kinetic theory has been mostly achieved for the specific case of a gas of hard spheres.(13,14) For this system the result discussed in point 3 above should certainly apply: indeed one finds that terms containing initial correlations are not among the most divergent contributions in each order in the density. The kinetic equation describing the leading long-time behavior of the function of interest—that is, the low-density ring kinetic equation—can be obtained neglecting initial correlations.(13) The essential physical feature contained in the spatial correlations of the hard sphere gas is that two hard spheres are never allowed to overlap. This requirement is preserved by the overlap function,

given by Eq. (2.9b) with the potential $V(r_{ij})$ replaced by the hard sphere interactions. Nonoverlap effects are density corrections to the leading low-density behavior. This is why they do not appear in the low-density Boltzmann kinetic equation. Spatial correlations between the particles are, however, explicitly in the kinetic equations that describe higher-order density effects: such as the Enskog equation(14) and the modified ring equation.(13) The question we want to address is to what extent these two equations can be derived by assuming a factorized initial state (when dealing with distribution functions) or by neglecting all correlations (when dealing with equilibrium two-time functions).

It is particularly instructive to compare two different derivations of the linearized Enskog equation. Van Beijeren and Ernst(14) obtained the Enskog equation by applying a diagrammatic technique to study a gas of hard spheres that is initially described by an N-particle distribution function very similar to that given in Eq. (2.9a). The Enskog operator was then given by the sum of all instantaneous diagrams. The presence of correlations in the initial state was essential for their derivation. If they had neglected the correlations in the initial state, (i.e., the overlap function) their method would have led only to a Boltzmann equation with the difference in position between the two colliding particles taken into account. An alternative way of extracting the Enskog operator from the cluster expansion of the one- and two-particle functions of interest was indicated some time ago.(13,18) This derivation was based on the observation that certain collision sequences that appear as purely dynamical (i.e., only contain free propagators and binary collision operators) contain static excluded volume corrections that are hidden in the product of $\bar{T}_{ij}$ collision operators. In other words, they were able to show that the static correlations in the Enskog operator can also be generated purely dynamically during the time evolution of the system through collisions. It is, however, important to remark that the introduction of pseudo-Liouville and $\bar{T}$ operator has essentially incorporated the condition of nonoverlapping into the dynamics. This is why one is in this case able to neglect the initial correlations and regenerate them dynamically. The basic physical constraint of nonoverlapping guaranteed by the initial correlations is preserved at all times by the $\bar{T}$ operators, even when the initial correlations are neglected. It appears then that there is an essential physical feature of the initial state, that is the condition of nonoverlapping, that cannot be neglected or "forgotten" when constructing a kinetic equation for a gas of hard spheres.

5. An interesting problem in kinetic theory is the derivation of an Enskog-type equation for a gas of particles interacting through a *continuous* strong short-range potential, i.e., an equation containing excluded

volume corrections to the low-density Boltzmann equation. The binary collision operator for hard spheres is time independent, since collisions are instantaneous. As a result, the nonlinear Enskog equation is always Markovian and the local pair correlation function that weighs the collision kernel is evaluated at the same time that is the argument of the unknown function.

In a gas with continuous strong short-range forces collisions have a finite duration. The binary collision operator is then time dependent and the generalized Boltzmann equation is non-Markovian. As a consequence, when attempting to construct an equation where the binary collision operator is weighed with correlations between the colliding particles, one is faced with the question of at what time should such correlations be evaluated.

The nonlinear kinetic equation obtained here is an example of a non-Markovian equation with a time-dependent effective binary collision kernel that contains explicitly local, and therefore, time-dependent correlations between the particles. Its structure could then be suggestive of the form of an Enskog-type equation for continuous potential and the derivation outlined in this paper could contain some indications on a possible route toward the generalization of the Enskog equation to gases with realistic intermolecular potential.

6. The question now is whether we can draw any general conclusions. Unfortunately, only two somewhat special systems have been considered in detail: the hard sphere gas and the electron gas. They both have some peculiar features. As a consequence, one must be cautious with generalizations. There are, however, some general questions one can ask.

Statistical correlations are in general both present in the initial nonequilibrium state of the system *and* generated dynamically through collisions. How does the interplay between the decay of the initial correlations and the generation of correlations through collisions proceed in time? When and to what extent can we neglect correlations in the initial state and still obtain, after several mean free times, a kinetic equation that incorporates all collective effects that should consistently be taken into account in the desired order in the density? Essentially, we are still left with the old problem of determining for a general interparticle potential the precise conditions under which a kinetic equation exists and its form at long times can be expected to be independent of the details of the initial state.

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