Kinetic-Equation Approach to Time-Dependent Correlation Functions

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We have developed and, to some extent, solved a number of kinetic equations for displaced correlation functions in a classical fluid. These functions, of which the Van Hove neutron scattering function is a special example, are one-particle distribution functions obtained from a Gibbs ensemble which is initially, at $t = 0$, in equilibrium except for one labeled particle whose distribution $W(\vec{r}, \vec{v})$ at $t = 0$ differs from its equilibrium value $\rho h_0(\vec{v})$, where ρ is the average fluid density, and $h_0(\vec{v})$ is the Maxwellian velocity distribution function. We investigate the time evolution of the (self-) distribution function of this labeled particle, $f_s(\vec{r}, \vec{v}, t)$, as well as the deviation from equilibrium, $\eta(\vec{r}, \vec{v}, t)$, of the total one-particle distribution function. The latter represents the density of fluid particles, labeled and unlabeled, at position $\vec{r}$ and velocity $\vec{v}$. Since both f_s and η are linear functionals of W, they will satisfy exactly a linear non-Markovian kinetic equation of the form $\dot{f} = \underline{B}f + \int_0^t dt'\, \underline{M}(t') f(t - t')$. $\underline{B}$ is a time-independent and $\underline{M}$ a time-dependent (memory) operator (nonsingular in t). Our kinetic equations (first- and higher-order) are based on neglecting or approximating $\underline{M}$ in such a way that the short-time behavior of f_s and η is described exactly. The rationale behind this scheme is that our choice of initial ensemble is precisely of the type generally assumed in the "derivation" of kinetic equations. The calculation of $\underline{B}$ is straightforward and depends in a very important way on whether the interparticle potential in the fluid is smooth or contains a hard core. In the former case, the first-order kinetic equation is of the Vlasov type with an effective potential given by the equilibrium direct correlation function, while in the latter case, $\underline{B}$ contains, in addition, a linear Enskog-type collision term. We show that this Vlasov equation (also derived previously by many authors) gives a damping linear in the wave number k for small k instead of the hydrodynamic k^2 dependence. The kinetic equation for systems with hard cores does not give correct hydrodynamic behavior. (For a one-dimensional system of hard rods, the first-order kinetic equation is exact.) We also obtain and solve a second-order kinetic equation, which is a generalized Vlasov-Fokker-Planck-type equation, for systems with continuous potentials.

I. INTRODUCTION

We have recently obtained and discussed the time evolution of the Van Hove self- and total correlation functions of a one-dimensional system of hard rods.[1-3] The reason for studying this system is that it is the only fluid with a true Hamiltonian for which these functions can be obtained exactly. We investigated, in particular, the relation between the exact result and that obtained from the solution of various approximate kinetic equations in the hope that the study of such a system would suggest viable approximations for real fluids. It is the purpose of this paper to discuss such approximate kinetic equations for these special time-dependent distributions in classical fluids.

The kinetic-equation approach to time-dependent phenomena in a fluid is on a level intermediate between that of hydrodynamics, where microstructure is totally ignored, and a full-scale attack on the N-body problem. It generally involves the derivation and solution of a trasnport equation for the one- (or a few) particle distribution function. It is thus somewhat analogous to the use of integral equations for the low-order configurational distribution functions in equilibrium fluids.[4] In the latter case, such methods have been found successful in yielding good approximations over a wide range of fluid temperatures and densities. This is particularly true in the case of the Percus-Yevick equation, which is exact for a one-dimensional system of hard rods.[5] It is our hope that we might be equally successful with some of our one-dimensional inspired kinetic equations, although the time-dependent problem is much more complicated.

In restricting our attention to the so-called time-displaced distribution functions of which the Van Hove functions are special cases, we have the advantage of having a well-posed strictly linear initial value problem. This, as we shall see, leads to kinetic equations which are not always identical, even within the same approximation scheme, to linearizations of the originally nonlinear kinetic equations, for example, the Boltzmann-Enskog equation.

We start by considering a classical system of N particles in a box (periodic) with average density ρ, interacting via a pair potential $\phi(\vec{r})$. At $t = 0$, the Γ-space ensemble density $\mu(\vec{x}_1, \ldots, \vec{x}_N; 0)$, where $\vec{x}_i = \vec{r}_i \, \vec{v}_i$ stands for the position and velocity vectors of the ith particle, corresponds to having one particle with a specified distribution $W(\vec{x})$ and the rest of the particles in equilibrium at a temperature $T = (k\beta)^{-1}$, relative to this particle. The distribution function of this particular labeled particle at a later time t is designated $f_s(\vec{x}; t)$. Letting particle number one be the labeled particle, we have

$$f_s(\vec{x}_1; t) = \int d\vec{x}_2 \cdots \int d\vec{x}_N \, \mu_1(\vec{x}_1, \ldots, \vec{x}_N; t) . \quad (1.1)$$

Here $\mu_1(\vec{x}_1, \ldots, \vec{x}_N; t)$ is the ensemble density at time t obtained from the solution of the Liouville equation, with the initial condition

$$\mu_1(\vec{x}_1, \ldots, \vec{x}_N; 0) = N\mu_0(\vec{x}_1, \ldots, \vec{x}_N) \, W(\vec{x}_1)/f_1^{\,0}(\vec{x}_1) , \quad (1.2)$$

where μ_0 is the canonical distribution and $f_1^{\,0}(\vec{x}_1) = \rho h_0(\vec{v}_1)$ is the one-particle equilibrium distribution function in a uniform equilibrium system, $h_0(\vec{v})$ being the Maxwellian velocity distribution function. At $t = 0$, $f_s(\vec{x}; 0) = W(\vec{x})$ and we usually have $\int d\vec{x} \, W(\vec{x}) = 1$. The one-particle density of the other particles in the system is given by

$$f_d(\vec{x}_2; t) = (N - 1) \int d\vec{x}_1$$

$$\times \int d\vec{x}_3 \cdots \int d\vec{x}_N \, \mu_1(\vec{x}_1, \ldots, \vec{x}_N; t) . \quad (1.3)$$

We have in mind here a situation in which the labeled particle (particle 1) is of the same kind as the other particles of the system. This is not necessary, however, and in the usual kinetic theory of tracer diffusion, electrical conductivity, Brownian motion, etc., the labeled particle is really different from the other fluid particles. Many of our later manipulations in dealing with f_s can be readily modified to this more general case, and this is useful in gaining insight into some approximations we shall use.

The total one-particle distribution function is

$$f(\vec{x}; t) = f_s(\vec{x}; t) + f_d(\vec{x}; t) . \quad (1.4)$$

It can also be defined[2] as the one-particle distribution function in a symmetrized ensemble:

$$\mu(\vec{x}_1, \ldots, \vec{x}_N; t) = N^{-1} \sum_{i=1}^{N} \mu_i(\vec{x}_1, \ldots, \vec{x}_N; t), \quad (1.5)$$

$$f(\vec{x}_1; t) = N \int d\vec{x}_2 \cdots \int d\vec{x}_N \, \mu(\vec{x}_1, \ldots, \vec{x}_N; t) , \quad (1.6)$$

where μ_i is obtained from μ_1 by interchanging 1 and i, and

$$\mu(\vec{x}_1, \ldots, \vec{x}_N; 0) = \mu_0(\vec{x}_1, \ldots, \vec{x}_N) \sum_{i=1}^{N} \frac{W(\vec{x}_i)}{f_1^{\,0}(\vec{x}_i)} . \quad (1.7)$$

At $t = 0$, $\quad f(\vec{r}, \vec{v}, 0) = W(\vec{r}, \vec{v}) + \rho^{-1} h_0(\vec{v})$

$$\times \int d\vec{r}' \int d\vec{v}' \rho_2^{\,0}(\vec{r}, \vec{r}') W(\vec{r}', \vec{v}') , \quad (1.8)$$

where $\rho_2^{\,0}(\vec{r}, \vec{r}')$ is the configurational two-particle equilibrium distribution function.

We shall also be interested later in the higher-order self- and total distribution functions,

$$f_{s,m}(\vec{x}_1, \ldots, \vec{x}_m; t)$$

$$= \frac{(N-1)!}{(N-m)!} \int d\vec{x}_{m+1} \cdots \int d\vec{x}_N \mu_1(\vec{x}_1, \ldots, \vec{x}_N; t), \quad (1.9)$$

$$f_m(\vec{x}_1, \ldots, \vec{x}_m; t)$$

$$= \frac{N!}{(N-m)!} \int d\vec{x}_{m+1} \cdots \int d\vec{x}_N \mu(\vec{x}_1, \ldots, \vec{x}_N; t) \quad (1.10)$$

so that $f_{s,1} = f_s$, $f_1 = f$. The deviations of the f_m from their equilibrium values $f_m^{\,0}$ will be denoted by η_m:

$$\eta_m(\vec{x}_1, \ldots, \vec{x}_m; t) = f_m(\vec{x}_1, \ldots, \vec{x}_m; t)$$

$$- f_m^{\,0}(\vec{x}_1, \ldots, \vec{x}_m) \int d\vec{x} W(\vec{x}) \quad (1.11)$$

with $f_m^{\,0}(\vec{x}_1, \ldots, \vec{x}_m)$

$$= \prod_{i=1}^{m} h_0(\vec{v}_i) \rho_m^{\,0}(\vec{x}_1, \ldots, \vec{x}_m) . \quad (1.12)$$

Integrating over velocities, we obtain the coordinate distributions

$$n_{s,m}(\vec{r}_1, \ldots, \vec{r}_m; t)$$

$$= \int d\vec{v}_1 \cdots \int d\vec{v}_m f_{s,m}(\vec{x}_1, \ldots, \vec{x}_m; t) , \quad (1.13)$$

$$n_m(\vec{r}_1, \ldots, \vec{r}_m; t)$$

$$= \int d\vec{v}_1 \cdots \int d\vec{v}_m \eta_m(\vec{x}_1, \ldots, \vec{x}_m; t) . \quad (1.14)$$

The Van Hove self- and total correlation functions,[6] $G_s(\vec{r}, t)$ and $G(\vec{r}, t)$, correspond to

$$n_s(\vec{r}, t) = n_{s,1}(\vec{r}, t) \quad \text{and} \quad n(\vec{r}, t) = n_1(\vec{r}, t) ,$$

with the particular choice

$$W(\vec{r}, \vec{v}) = \delta(\vec{r}) h_0(\vec{v}) . \quad (1.15)$$

We shall also be interested in the current-current correlation tensors $\vec{U}_s(\vec{r}, t)$ and $\vec{U}(\vec{r}, t)$. These correspond formally to

$$\vec{U}_s(\vec{r}, t) = \int d\vec{v} \, \vec{v} f_s(\vec{r}, \vec{v}, t) , \quad (1.16)$$

$$\vec{U}(\vec{r}, t) = \int d\vec{v} \, \vec{v} \eta(\vec{r}, \vec{v}, t) , \quad (1.17)$$

with $\quad W(\vec{r}, \vec{v}) = \vec{v} h_0(\vec{v}) \delta(\vec{r}) . \quad (1.18)$

Since we are dealing with macroscopic systems, we have to consider, as in equilibrium, the thermodynamic limit of the distribution functions, i.e., $N \to \infty$, ρ and β fixed. While there is no general proof at present for the existence of this limit for time-dependent distributions, we shall assume that such a limit exists for the correlation functions at fixed values of their arguments.

II. TIME EVOLUTION OF DISTRIBUTION FUNCTIONS

Since our initial ensembles are linear in W, the distribution functions will also be linear in W, i.e.,

$$f_{s,m}(\vec{x}_1, \ldots, \vec{x}_m; t)$$

$$= \int d\vec{x}' f_{s,m}(\vec{x}_1, \ldots, \vec{x}_m; t/\vec{x}') W(\vec{x}') , \quad (2.1)$$

$$\eta_m(\vec{x}_1, \cdots, \vec{x}_m; t)$$

$$= \int d\vec{x}' \eta_m(\vec{x}_1, \cdots, \vec{x}_m; t/\vec{x}') W(\vec{x}'), \quad (2.2)$$

where the conditional distributions appearing in the integrands are the values of $f_{s,m}$ and η_m at

time t for $W(\vec{x}) = \delta(\vec{x} - \vec{x}')$. They depend only on $\vec{r}_i - \vec{r}'$, $i = 1, \ldots, m$ and also implicitly on the Hamiltonian of the system, i.e., the mass of the particles and the interaction potential $\phi(\vec{r})$, and on ρ and β. At $t = 0$,

$$f_{s,m}(\vec{x}_1, \ldots, \vec{x}_m; 0/\vec{x}')$$

$$= \delta(\vec{x}_1 - \vec{x}') \prod_{i=2}^{m} h_0(\vec{v}_i) \rho^{m-1} g_m(\vec{r}_1, \ldots, \vec{r}_m) , \quad (2.3)$$

where $g_m = \rho_m{}^0/\rho^m$ depends only on $\vec{r}_i - \vec{r}_1$, and, in particular, $g_1 = 1$ and $g_2(\vec{r}) = g(\vec{r})$ is the radial distribution function of the fluid. The conditional η_m's are symmetric in their arguments and consist of two types of terms: those in which one of the particles is the labeled one and those in which none is:

$$\eta_m(\vec{x}_1, \ldots, \vec{x}_m; 0/\vec{x}') = \rho^{m-1} g_m(\vec{r}_1, \cdots, \vec{r}_m)$$

$$\times \sum_{j=1}^{m} \left[\delta(\vec{x}_j - \vec{x}') \prod_{i \neq j}^{m} h_0(\vec{v}_i) \right] + \prod_{i=1}^{m} h_0(\vec{v}_i)$$

$$\times \rho^m \left[g_{m+1}(\vec{r}_1, \cdots, \vec{r}_m, \vec{r}') - g_m(\vec{r}_1, \cdots, \vec{r}_m) \right] . \quad (2.4)$$

In particular, for $m = 1, 2$

$$\eta_1(\vec{r}, \vec{v}, 0/\vec{r}', \vec{v}')$$

$$= \delta(\vec{r} - \vec{r}') \delta(\vec{v} - \vec{v}') + h_0(\vec{v}) G(\vec{r} - \vec{r}') , \quad (2.5)$$

$$\eta_2(\vec{x}_1, \vec{x}_2, 0/\vec{x}') = \rho g(\vec{r}_1 - \vec{r}_2) [\delta(\vec{r}_1 - \vec{r}')$$

$$\times \delta(\vec{v}_1 - \vec{v}') h_0(\vec{v}_2) + \delta(\vec{r}_2 - \vec{r}') \delta(\vec{v}_2 - \vec{v}') h_0(\vec{v}_1)]$$

$$+ h_0(\vec{v}_1) h_0(\vec{v}_2) \rho^2 [g_3(\vec{r}_1, \vec{r}_2, \vec{r}') - g_2(\vec{r}_1, \vec{r}_2)], \quad (2.6)$$

where $\quad G(\vec{r}) = \rho[g(\vec{r}) - 1] = G(\vec{r}, 0) - \delta(\vec{r}) . \quad (2.7)$

The right-hand side of (2.5) is a generalization of the modified equilibrium configurational two-particle Ursell function to include velocities[3] and has as its inverse the correspondingly generalized modified direct correlation function

$$\hat{I}(\vec{r}, \vec{v} : \vec{r}', \vec{v}') = \delta(\vec{r} - \vec{r}') \delta(\vec{v} - \vec{v}') - \rho h_0(\vec{v}) C(\vec{r} - \vec{r}') , \quad (2.8)$$

i.e., $\quad W(\vec{x}) = \int d\vec{x}' \hat{I}(\vec{x} : \vec{x}') \eta(\vec{x}', 0) , \quad (2.9)$

with $C(\vec{r})$ being the usual equilibrium direct correlation function. By combining Eqs. (2.2), (2.4), and (2.9), we can express the higher order η_m as

linear functionals of $\eta = \eta_1$ at $t = 0$.

The change with time of the $f_{s,m}$ and η_m is given by the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) infinite hierarchy of equations

$$
\frac{\partial f_{s,m}(t)}{\partial t} + \sum_{i=1}^{m} \left(\vec{v}_i \cdot \frac{\partial f_{s,m}(t)}{\partial \vec{r}_i} \right.
$$

$$
\left. - \frac{1}{M} \sum_{j=1}^{m} {}' \frac{\partial \phi(\vec{r}_i - \vec{r}_j)}{\partial \vec{r}_i} \cdot \frac{\partial f_{s,m}(t)}{\partial \vec{v}_i} \right)
$$

$$
= \frac{1}{M} \sum_{j=1}^{m} \int d\vec{r}_{m+1} \int d\vec{v}_{m+1}
$$

$$
\times \frac{\partial \phi(\vec{r}_j - \vec{r}_{m+1})}{\partial \vec{r}_j} \cdot \frac{\partial f_{s,m+1}(t)}{\partial \vec{v}_j}
$$

$$
= \Gamma_m f_{s,m+1}(t) , \tag{2.10}
$$

where M is the mass of a particle. The η_m satisfy the same equations, only the initial conditions are different. Equation (2.10) has to be modified, in obvious ways, when $\phi(r)$ has discontinuities, e.g., the particles have hard cores. We shall now assume that there exists, formally at least, an inverse matrix to $f_s(\vec{x}, t/\vec{x}')$, i.e.,

$$
W(\vec{x}) = \int d\vec{x}' \, T^{-1}(\vec{x}, t : \vec{x}') f_s(\vec{x}', t) . \tag{2.11}
$$

This permits us to express the $f_{s,m}(t)$ and $\eta_m(t)$ as linear time-dependent functionals of $f_s(t)$ and $\eta(t)$ at any time t. More specifically, we shall formally write

$$
f_{s,m}(\vec{x}_1, \ldots, \vec{x}_m; t) = \int d\vec{x}'
$$

$$
\times f_{s,m}(\vec{x}_1, \ldots, \vec{x}_m, 0/\vec{x}') f_s(\vec{x}', t) + \int d\vec{x}' \int_0^t dt'
$$

$$
\times K_{s,m}(\vec{x}_1, \ldots, \vec{x}_m, t - t' : \vec{x}') f_s(\vec{x}', t') \tag{2.12}
$$

and

$$
\eta_m(\vec{x}_1, \ldots, \vec{x}_m; t) = \int d\vec{x}' \int d\vec{x}''
$$

$$
\times \eta_m(\vec{x}_1, \ldots, \vec{x}_m; 0/\vec{x}'') \tilde{l}(\vec{x}'' : \vec{x}') \eta(\vec{x}', t)
$$

$$
+ \int d\vec{x}' \int_0^t dt' K_m(\vec{x}_1, \ldots, \vec{x}_m, t - t' : \vec{x}') \eta(\vec{x}', t') . \tag{2.13}
$$

Substituting Eqs. (2.12) and (2.13) into (2.10), we obtain for $m = 1$

$$
\frac{\partial f_s(t)}{\partial t} + \vec{v} \cdot \frac{\partial f_s(t)}{\partial \vec{r}} = \underline{B}_s f_s(t)
$$

$$
+ \int_0^t dt' \underline{M}_s (t - t') f_s(t') \tag{2.14}
$$

and

$$
\frac{\partial \eta(t)}{\partial t} + \vec{v} \cdot \frac{\partial \eta(t)}{\partial \vec{r}} = \underline{B} \eta(t)
$$

$$
+ \int_0^t dt' \underline{M}(t - t') \eta(t') , \tag{2.15}
$$

where the <u>B</u>'s are time-independent operators obtained by operating with Γ_1 on the first term of the right-hand side of (2.12) or (2.13) with $m = 2$.

Equations (2.14) and (2.15) are exact but useless as they stand since the non-Markovian memory terms $\underline{M}_s(t)$ and $\underline{M}(t)$ cannot be found explicitly for a three-dimensional system. These equations are, however, in a form suitable for deriving approximate kinetic equations for f_s and η. Such equations, of which the Boltzmann equation for gases and the Fokker-Planck equation for a Brownian particle in a fluid are prototypes, are characterized by the breaking of the BBGKY hierarchy, Eq. (2.10), at $m = 1$ (or in the Kirkwood theory of transport in liquids[7] at $m = 2$). The breaking of the hierarchy is accomplished by what amounts to making some ansatz which gives the two- (more generally $m + 1$) particle distribution at time t in terms of the one- (or m) particle distribution at that time. This leads then to a Markovian equation for the one-particle distribution. The physical idea underlying this derivation of kinetic equations is that the higher-order distributions accommodate themselves to the one-particle distribution, approaching a state of conditional equilibrium relative to the one-particle distribution, in a time which is short on the time scale in which the latter varies. In effect the rest of the system follows adiabatically or with only a slight time lag the variations of $f_1(t)$. The actual forms which one assumes for the two-particle distribution vary with the problem. For the test particle problem corresponding to f_s one assumes generally that the particles of the rest of the system are in equilibrium prior to a collision with the test particle. More recent derivations of transport equations involve expansions in some small parameter such as the density, the interaction potential, or the mass ratio in Brownian motion.[8] These expansions generally agree with the older, intuitively derived, kinetic equations to lowest order only. Higher-order terms give rise to non-Markovian equations which may be interpreted to reflect the noninstantaneous readjustment of the system to the time varying one-particle distribution.

Since there is no suitable small parameter in

fluids, we are by necessity forced to rely on some sort of *ad hoc* approximations. Therefore, we have carried the formal analysis as far as we could to obtain Eqs. (2.14) and (2.15). To proceed requires making some good approximations for $\underline{M}_S(t)$ and $\underline{M}(t)$.

Our lowest-order kinetic equations for f_S and η are obtained by setting the integrals on the right-hand side of (2.14) and (2.15) equal to zero. This results in a Markovian equation for f_S and η. The equation for η was found to be exact for a one-dimensional system of hard rods.[3] The equation for f_S is never exact, even in one dimension. It does, however, yield the correct $G_S(\vec{r}, t)$ for some special equilibrium velocity distributions in that system.

To obtain the form of $\underline{B}_S$ and $\underline{B}$, we let $t \to 0^+$ in Eqs. (2.14) and (2.15). In this limit, the integral on the right-hand side of (2.14) or (2.15) vanishes and our approximate kinetic equation thus becomes exact at $t = 0^+$ for all $W(\vec{x})$. Hence, since $\underline{B}$ is a time-independent operator, it may be obtained by considering $\partial \eta / \partial t$ at $t = 0^+$. We find now a marked difference between continuous (piecewise differentiable) pair potentials and discontinuous ones, e.g., containing hard-core interactions. In the first case, the velocities of all the particles are continuous functions of the time, while in the latter case, there can be discontinuous changes in the velocities. This leads to an effective field type of equation in the continuous case and to an irreversible linearized Boltzmann-Enskog type of equation in the hard-core case.

The reason for this qualitative difference lies, of course, in the fact that we are looking at the system at $t = 0^+$ when the continuous potential has not yet had a chance to assert itself. If we were to look at the system on a time scale which is large compared to a collision time, the gross difference between these potentials would disappear and we would obtain some kind of Enskog equation also for the continuous potentials.[9] The mathematical simplicity of our present approach would, however, disappear then and we shall not pursue that approach here.

The outline of the remainder of this paper is as follows. In Sec. III, we derive the first-order kinetic equations for the continuous and hard-core potentials. In Sec. IV, we discuss the short-time behavior of these equations. Then, in Sec. V, we obtain the full solution of the equation for the continuous case and show that it does not have a proper hydrodynamical limit. The solution of the kinetic equations when the potential has a hard-core part is discussed in Secs. VI and VII. Finally, in Sec. VIII, we derive and solve a higher-order kinetic equation for continuous potentials. This equation contains both Vlasov- and Fokker-Planck-type terms and, therefore, does not suffer from the defects of the first-order

equation.

III. FIRST-ORDER KINETIC EQUATIONS

A. Continuous Potentials

It is seen from Eq. (1.2) that at $t = 0$ the non-labeled particles are in equilibrium relative to the labeled particle. Hence, if the labeled particle could be held fixed in its position for $t > 0$, there would be no change in the distribution of the other particles. The only reason for distributions changing with time is the motion of the labeled particle. For continuous potentials, however, this motion of the labeled particle only produces a finite rate of change in its own position, not in its own or other particles' velocities at $t = 0^+$. Therefore, we have at $t = 0^+$

$$\frac{\partial f_S(\vec{r}, \vec{v}, 0^+)}{\partial t} + \vec{v} \cdot \frac{\partial W(\vec{r}, \vec{v})}{\partial \vec{r}} = 0 , \qquad (3.1)$$

$$\frac{\partial f_d(\vec{r}, \vec{v}, 0^+)}{\partial t} = 0 , \qquad (3.2)$$

and

$$\frac{\partial \eta(\vec{r}, \vec{v}, 0^+)}{\partial t} + \vec{v} \cdot \frac{\partial W(\vec{r}, \vec{v})}{\partial \vec{r}} = 0 . \qquad (3.3)$$

Hence, since

$$W(\vec{x}) = f_S(\vec{x}, 0) = \int d\vec{x}' \, \hat{l}(\vec{x} : \vec{x}') \eta(\vec{x}', 0) , \qquad (3.4)$$

we obtain immediately as our lowest-order kinetic equations for continuous potentials

$$\frac{\partial f_S(\vec{r}, \vec{v}, t)}{\partial t} + \vec{v} \cdot \frac{\partial f_S(\vec{r}, \vec{v}, t)}{\partial \vec{r}} = 0 , \qquad (3.5)$$

$$\frac{\partial \eta(\vec{r}, \vec{v}, t)}{\partial t} + \vec{v} \cdot \frac{\partial \eta(\vec{r}, \vec{v}, t)}{\partial \vec{r}}$$

$$= \rho h_0(\vec{v}) \vec{v} \cdot \frac{\partial}{\partial \vec{r}} \int d\vec{r}' \, C(\vec{r} - \vec{r}')$$

$$\times n(\vec{r}', t) = \frac{\rho}{M} \frac{\partial h_0(\vec{v})}{\partial \vec{v}} \cdot \frac{\partial}{\partial \vec{r}}$$

$$\times \int d\vec{r}' \, [-\beta^{-1} C(\vec{r} - \vec{r}')] n(\vec{r}', t) . \qquad (3.6)$$

In other words, $\underline{B}_S = 0$ and $\underline{B}\eta(t)$ is given by the right-hand side of (3.6). The second equality on the right-hand side of (3.6) shows clearly that this approximate kinetic equation for η has the form of a linearized Vlasov (i.e., time-dependent self-consistent field) equation with $-\beta^{-1} C(\vec{r})$ playing the part of an effective potential $V(\vec{r})$. Equation (3.6) has also been derived by Nelkin and

Ranganathan[10] (and other authors[11]) from a different starting point. Equation (3.5) for f_S is that appropriate for an ideal gas and is, therefore, of no practical interest. This ideal-gas equation for f_S results clearly from the fact that at $t = 0$, when the equation is exact, the distribution of the other fluid particles is spherically symmetric about the position of the labeled particle and hence produces no force on it.

B. Systems with Hard Cores

We shall consider now the case where the interparticle potential is infinite for $|\vec{r}| < a$, a being the diameter of the hard cores:

$$\phi(\vec{r}) = \phi^0(\vec{r}) + \phi^1(\vec{r}) \ , \qquad (3.7)$$

where $\phi^0(r) = \infty$,   for $r < a$

$$= 0, \quad \text{for} \quad r > a$$

and $\phi^1(r)$ is continuous. For this potential the velocities of the particles can change discontinuously due to collisions. Collisions take place between particles whose centers were separated by the distance a^+ at $t = 0$. The density of particles at this distance from the test particle is equal to $\rho g(a)$ at $t = 0$. Hence the kinetic equation obtained from (2.14), by neglecting the M_S term there, is

$$\frac{\partial f_S(\vec{r},\vec{v},t)}{\partial t} + \vec{v} \cdot \frac{\partial f_S(\vec{r},\vec{v},t)}{\partial \vec{r}} = B_s f_S(\vec{r},\vec{v},t)$$

$$\equiv \rho g(a) a^2 \int d\hat{\kappa} \int d\vec{v}_1 (\vec{v}_1 - \vec{v}) \cdot \hat{\kappa} \ \epsilon [(\vec{v}_1 - \vec{v}) \cdot \hat{\kappa}]$$

$$\times [h_0(\vec{v}_1') f_S(\vec{r},\vec{v}',t) - h_0(\vec{v}_1) f_S(\vec{r},\vec{v},t)] \ , \quad (3.8)$$

where $\vec{v}' = \vec{v} + \hat{\kappa}[(\vec{v}_1 - \vec{v}) \cdot \hat{\kappa}]$,

$$\vec{v}_1' = \vec{v}_1 - \hat{\kappa}[(\vec{v}_1 - \vec{v}) \cdot \hat{\kappa}],$$

and ϵ is the step function

$$\epsilon(y) = 0, \quad \text{for} \quad y < 0$$

$$= 1, \quad \text{for} \quad y > 0 \ .$$

The right-hand side of (3.8) is the usual linear Boltzmann operator with the Enskog factor $g(a)$.

When the $\hat{\kappa}$ integration is done, the equation reduces to

$$\frac{\partial}{\partial t} f_S(\vec{r},\vec{v},t) + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} f_S(\vec{r},\vec{v},t) = \int d\vec{v}' L_S(\vec{v},\vec{v}')$$

$$\times [f_S(\vec{r},\vec{v}',t) h_0(\vec{v}) - f_S(\vec{r},\vec{v},t) h_0(\vec{v}')], \quad (3.9a)$$

where $L_s(\vec{v},\vec{v}') = \rho a^2 g(a)(2\pi/\beta m | \vec{v} - \vec{v}' |)$

$$\times \exp\{\beta m [v^2 v'^2 - (\vec{v} \cdot \vec{v}')^2]/2 | \vec{v} - \vec{v}' |^2\}$$

$$= L_s(\vec{v}',\vec{v}) \ . \qquad (3.9b)$$

This equation has been investigated in detail by Desai and Nelkin.[12]

To obtain $\underline{B} \eta$, we note, using (1.4), that the change in η at $t = 0^+$ due to collisions will involve, in addition to $\underline{B} f_S$ as given in (3.8), also changes in f_d due to collisions at $t = 0^+$ of a fluid particle, say particle j ($j \neq 1$), with the labeled particle, (particle 1). In addition, particle j will suffer collisions with the other particles of the fluid, say a particle i ($j \neq i$), whose spatial distribution at $t = 0^+$ is influenced by the presence of particle 1 at a given position (but is independent of the velocity of the labeled particle). Now if the labeled particle were fixed in position – "nailed down" – then the effect of these collisions would be to maintain f_d in its conditional equilibrium value. The net change in f_d at $t = 0^+$ will therefore be given by the difference between collisions with a labeled particle which can move and a labeled particle which is fixed in position, i.e., the rate of change of η at $t = 0^+$ is given by

$$\frac{\partial \eta}{\partial t} + \vec{v} \cdot \frac{\partial f_S}{\partial \vec{r}} = \underline{B} \eta = \underline{B}_s f_s + \frac{\delta_1 f_d}{\delta t} - \frac{\delta_0 f_d}{\delta t} \ , \quad (3.10)$$

with $\dfrac{\delta_1 f_d}{\delta t} = \rho g(a) a^2 \int d\hat{\kappa} \int d\vec{v}_1 (\vec{v}_1 - \vec{v}) \cdot \hat{\kappa}$

$$\times \epsilon [(\vec{v}_1 - \vec{v}) \cdot \hat{\kappa}][h_0(\vec{v}') f_S(\vec{r} + a\hat{\kappa}, \vec{v}_1', 0)$$

$$- h_0(\vec{v}) f_S(\vec{r} - a\hat{\kappa}, \vec{v}_1, 0)] \qquad (3.11a)$$

and $\dfrac{\delta_0 f_d}{\delta t} = \rho g(a) a^2 \int d\hat{\kappa} (- \vec{v} \cdot \hat{\kappa}) \epsilon(- \vec{v} \cdot \hat{\kappa})$

$$\times [h_0(\vec{v} - 2\hat{\kappa} \vec{v} \cdot \hat{\kappa}) n_s(\vec{r} + a\hat{\kappa}, 0)$$

$$- h_0(\vec{v}) n_s(\vec{r} - a\hat{\kappa}, 0)] \ . \qquad (3.11b)$$

Equation (3.11) represents scattering of particles with velocity distribution $h_0(\vec{v})$ and density (at contact) $\rho g(a)$ from a moving and nailed-down hard sphere, respectively. Using now (2.9) we find after some manipulations (a derivation using the BBGKY equations is given in Appendix A)

$$\frac{\partial \eta(\vec{r},\vec{v},t)}{\partial t} + \vec{v} \cdot \frac{\partial \eta(\vec{r},\vec{v},t)}{\partial \vec{r}} = \underline{B} \eta(\vec{r},\vec{v},t)$$

$$= - \beta \rho h_0(\vec{v}) \vec{v} \cdot \frac{\partial}{\partial \vec{r}} \int d\vec{r}' V(\vec{r} - \vec{r}') n(\vec{r}', t) + \rho g(a) a^2$$

$$\times \int d\hat{\kappa} \int d\vec{v}_1 (\vec{v}_1 - \vec{v}) \cdot \hat{\kappa} \, \epsilon [(\vec{v}_1 - \vec{v}) \cdot \hat{\kappa}] [\, h_0(\vec{v}_1') \eta(\vec{r}, \vec{v}', t)$$

$$- h_0(\vec{v}_1) \eta(\vec{r}, \vec{v}, t) + h_0(\vec{v}') \eta(\vec{r} + a\hat{\kappa}, \vec{v}_1', t)$$

$$- h_0(\vec{v}) \eta(\vec{r} - a\hat{\kappa}, \vec{v}_1, t)] \; , \qquad (3.12)$$

where the effective potential $V(\vec{r})$ is given by

$$- \beta V(\vec{r}) = C(\vec{r}) + g(a) \epsilon(a - |\vec{r}|) \; . \qquad (3.13)$$

Equation (3.12) or what corresponds to it for a one-dimensional system of hard rods was found to be exact in Ref. 3.

When $a = 0$, Eq. (3.12) reduces to Eq. (3.6) with $C(\vec{r})$ the direct correlation function of particles interacting with a smooth potential only. Note, however, that when the particles have hard cores the effective potential is still continuous, even at $r = a$, since $C(\vec{r}) - g(\vec{r})$ is continuous everywhere. Note also that even in the absence of a soft potential $\phi^1(r)$, the hard core produces an effective field or Vlasov term in addition to the collision term. Since to lowest order in ρ (with a fixed) we generally have $g(a) = \exp[-\beta\phi^1(a)]$

$$- \beta V(r) = \exp[-\beta\phi^1(a)] - 1, \quad \text{for} \quad r < a$$

$$= \exp[-\beta\phi^1(r)] - 1, \quad \text{for} \quad r > a. \quad (3.14)$$

The effective potential thus has the form of a square well for $r < a$ when the density is small.

There is also another limit which one can take of Eq. (3.12). This is the Boltzmann limit of Grad,

$$\rho \to \infty, \quad a \to 0 \quad \text{with } \rho a^2 \text{ fixed}, \qquad (3.15)$$

when, according to Grad,[13] the Boltzmann equation for gases is exact. In this limit, the right-hand side of (3.12) becomes identical with the linearized Boltzmann equation, i.e., the one-particle distribution function, $f(\vec{r}, \vec{v}, t)$, appearing in the standard Boltzmann equation is set equal to $\rho h_0(\vec{v}) + \eta(\vec{r}, \vec{v}, t)$ and linear terms in η are kept. [Recent work of Gallavotti[14] would seem to indicate that in this limit (3.9) and (3.12) would be exact when $\phi^1(\vec{r}) = 0$]. Quite generally, (3.12) can be written in the form

$$\frac{\partial}{\partial t} \eta(\vec{r}, \vec{v}, t) + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} \eta(\vec{r}, \vec{v}, t) = \rho h_0(\vec{v}) \vec{v} \cdot \frac{\partial}{\partial \vec{r}}$$

$$\times \int d\vec{r}' \, C(\vec{r} - \vec{r}') \int d\vec{v}' \eta(\vec{r}', \vec{v}', t)$$

$$+ \int d\vec{r}' \int d\vec{v}' \, L(\vec{r} - \vec{r}', \vec{v}, \vec{v}')$$

$$\times [\eta(\vec{r}', \vec{v}', t) h_0(\vec{v}) - \eta(\vec{r}', \vec{v}, t) h_0(\vec{v}')] \; , \quad (3.16)$$

with $\quad L(\vec{r}, \vec{v}, \vec{v}') = L(\vec{r}, \vec{v}', \vec{v}) \; .$

IV. SHORT-TIME BEHAVIOR OF FIRST-ORDER KINETIC EQUATIONS

The kinetic equations derived in Sec. III are characterized completely by their being (i) Markovian and (ii) exact at $t = 0^+$. Considering now the positional distributions, we have generally the continuity equation

$$\frac{\partial}{\partial t} n(\vec{r}, t) + \frac{\partial}{\partial \vec{r}} \cdot \vec{J}(\vec{r}, t) = 0 \; , \qquad (4.1)$$

where $\quad n(\vec{r}, t) = \int d\vec{v} \, \eta(\vec{r}, \vec{v}, t) \; , \qquad (4.2)$

and $\quad \vec{J}(\vec{r}, t) = \int d\vec{v} \, \vec{v} \eta(\vec{r}, \vec{v}, t) \; ,$

with similar equations for n_S and $\vec{J}_S$. Taking the time derivative of (4.1) gives

$$\frac{\partial^2}{\partial t^2} n(\vec{r}, t) + \frac{\partial}{\partial \vec{r}} \cdot \int d\vec{v} \, \vec{v} \frac{\partial}{\partial t} \eta(\vec{r}, \vec{v}, t) = 0 \; . \qquad (4.3)$$

Our first-order kinetic equations will thus give exactly the first and second derivatives of $n(\vec{r}, t)$ with respect to t at $t = 0^+$.

Considering now, in particular, the initial distribution of (1.15), $W(\vec{r}, \vec{v}) = \delta(\vec{r}) h_0(\vec{v})$, we find, as expected, the well-known exact sum rule:

$$\frac{\partial^2}{\partial t^2} \chi(\vec{k}, t) \Big|_{0^+} = \frac{\partial^2}{\partial t^2} \chi_S(\vec{k}, t) \Big|_{0^+} = -k^2 (\beta m)^{-1} \; , \qquad (4.4)$$

while $\quad \frac{\partial}{\partial t} \chi(\vec{k}, t) \Big|_{0^+} = \frac{\partial}{\partial t} \chi_S(\vec{k}, t) \Big|_{0^+} = 0 \; , \qquad (4.5)$

where $\chi(\vec{k}, t)$ and $\chi_S(\vec{k}, t)$ are the spatial Fourier transforms of $G(\vec{r}, t)$ and $G_S(\vec{r}, t)$. For continuous potentials all the odd derivatives of $\chi(\vec{k}, t)$ and $\chi_S(\vec{k}, t)$ vanish at $t = 0^+$ exactly and also in our kinetic model. For potentials with hard cores, on the other hand, the third and higher odd derivatives do not vanish at $t = 0^+$. In particular, we find from Eqs. (3.8) and (3.12)

$$\frac{\partial^3}{\partial t^3} \chi_S(\vec{k}, t) \Big|_{0^+} = \rho g_2(a) k^2 a^2 \left(\frac{(4)^3 \pi}{9(\beta m)^3} \right)^{1/2} \qquad (4.6)$$

and $\quad \frac{\partial^3}{\partial t^3} \chi(\vec{k}, t) \Big|_{0^+} = \rho g_2(a) k^2 a^2 \left(\frac{(4)^3 \pi}{9(\beta m)^3} \right)^{1/2}$

$$\times \left[1 - 6 \frac{\cos ka}{(ka)^2} - 3 \frac{\sin ka}{ka} \left(1 - \frac{2}{(ka)^2} \right) \right] \; , \qquad (4.7)$$

which agree with the exact results.

To see that our kinetic equations give the exact third derivative of χ_S and χ at $t = 0^+$, we make use

of their definitions as time-dependent correlations in an equilibrium ensemble μ_0:

$$\chi_s(\vec{k}, t - t') = \left\langle e^{i\vec{k}\cdot[\vec{r}_1(t) - \vec{r}_1(t')]} \right\rangle \tag{4.8}$$

and

$$\chi(\vec{k}, t - t') = \sum_j \left\langle e^{i\vec{k}\cdot[\vec{r}_j(t) - \vec{r}_1(t')]} \right\rangle, \qquad k \neq 0. \tag{4.9}$$

It follows directly from these definitions that

$$\frac{\partial^2}{\partial t^2} \chi_s(\vec{k}, t) = -\vec{k}\,\vec{k} : \vec{U}_s(\vec{k}, t) = -\langle \vec{k}\cdot\vec{v}_1(t)$$

$$\times e^{i\vec{k}\cdot[\vec{r}_1(t) - \vec{r}_1(0)]}\vec{k}\cdot\vec{v}_1(0)\rangle, \tag{4.10}$$

and

$$\frac{\partial^2}{\partial t^2}\chi(\vec{k}t) = -\vec{k}\vec{k} : \vec{U}(\vec{k}, t) = -\sum_j \langle \vec{k}\cdot\vec{v}_j(t)$$

$$\times e^{i\vec{k}\cdot[\vec{r}_j(t) - \vec{r}_1(0)]}\vec{k}\cdot\vec{v}_1(0)\rangle, \tag{4.11}$$

where $\vec{U}_s(\vec{k}, t)$ and $\vec{U}(\vec{k}, t)$ are the Fourier transforms of the self- and total current-current correlations. As mentioned in the Introduction, the exact $\vec{U}_s$, $\vec{U}$ may be obtained via Eqs. (1.16) and (1.17) from the exact f_s, η with the initial $W(\vec{r}, \vec{v})$, given in (1.18). The exact third time derivative of χ_s and χ may therefore be obtained from the first time derivative of f_s and η. Now, since our kinetic equations give the first time derivative of f_s and η exactly at $t = 0^+$ for an arbitrary $W(\vec{r}, \vec{v})$, we will obtain the exact $\chi_s'''(\vec{k}, 0^+)$ and $\chi'''(\vec{k}, 0^+)$ whenever (4.10) and (4.11) are satisfied by our approximate kinetic equations. There is, however, no a priori guarantee that (4.10) and (4.11) will be satisfied by the approximate χ_s, χ and $\vec{U}_s$, $\vec{U}$ for $t > 0$.

To see what is involved, we derive (4.10) and (4.11) for the exact Van Hove correlation functions in an alternative way which is more readily applicable also to approximate correlation functions. From (4.1)

$$\frac{\partial^2}{\partial t^2}\chi(\vec{k}, t) = \frac{\partial}{\partial t}\int d\vec{v}\int d\vec{v}' i\vec{k}\cdot\vec{v}\,\eta(\vec{k}, \vec{v}, t/\vec{v}')h_0(\vec{v}'),$$
$$\tag{4.12}$$

where $\eta(\vec{k}, \vec{v}, t/\vec{v}') = \int d\vec{r}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}\eta(\vec{r}, \vec{v}, t/\vec{r}', \vec{v}')$.

It follows from the time reversibility of the Hamiltonian and translational invariance (and may be verified explicitly for the exact solution of the one-dimensional hard-rod system) that the exact solution has the property

$$\eta(\vec{k}, \vec{v}, t/\vec{v}')h_0(\vec{v}') = \eta(-\vec{k}, -\vec{v}', t/-\vec{v})h_0(\vec{v}),$$

$$= \eta(\vec{k}, \vec{v}', t/\vec{v})h_0(\vec{v}), \tag{4.13}$$

and $f_s(\vec{k}, \vec{v}, t/\vec{v}')h_0(\vec{v}') = f_s(\vec{k}, \vec{v}', t/\vec{v})h_0(\vec{v})$. (4.14)

Substituting (4.13) into (4.12) yields

$$\frac{\partial^2}{\partial t^2}\chi(\vec{k}, t) = \frac{\partial}{\partial t}\int d\vec{v}'\int d\vec{v}\,\eta(\vec{k}, \vec{v}', t/\vec{v})\,i\vec{k}\cdot\vec{v}h_0(\vec{v}).$$

$$\tag{4.15}$$

Using now the identity (4.1) again for $\eta(\vec{k}, \vec{v}', t)$ obtained from an initial $W(\vec{k}, \vec{v}) = i\vec{k}\cdot\vec{v}h_0(\vec{v})$, we obtain

$$\frac{\partial^2}{\partial t^2}\chi(\vec{k}, t) = -\int d\vec{v}'\int d\vec{v}\,\vec{k}\cdot\vec{v}'$$

$$\times \eta(\vec{k}, \vec{v}', t/\vec{v})\vec{k}\cdot\vec{v}h_0(\vec{v}), \tag{4.16}$$

which is identical to (4.11). A similar analysis holds for (4.10).

The approximate kinetic equations (3.5) and (3.8) for f_s clearly have the symmetry of (4.14) and (4.10) therefore holds. It will also be shown in Secs. V and VII that the solutions of (3.6) and (3.12) satisfy (4.13), and (4.7) is exact.

The higher-order time derivatives of χ_s and χ obtained from our first-order kinetic equations will coincide with the exact ones only for weak potentials, i.e., to terms linear in ϕ

V. SOLUTIONS OF FIRST-ORDER KINETIC EQUATIONS FOR CONTINUOUS POTENTIALS

Taking the Fourier-Laplace transform of (3.6), we find

$$(s - i\vec{k}\cdot\vec{v})\tilde{\eta}(\vec{k}, \vec{v}, s)$$

$$= \eta(\vec{k}, \vec{v}, 0) - i\vec{k}\cdot\vec{v}h_0(\vec{v})\rho\,C(k)\tilde{n}(\vec{k}, s), \tag{5.1}$$

where $\tilde{n}(\vec{k}, s) = \int d\vec{v}\,\tilde{\eta}(\vec{k}, \vec{v}, s)$. (5.2)

We then have, using (2.5),

$$\tilde{\eta}(\vec{k}, \vec{v}, s/\vec{v}') = \{\delta(\vec{v} - \vec{v}') + h_0(\vec{v})[S(k) - 1]$$

$$- i\vec{k}\cdot\vec{v}h_0(\vec{v})\rho C(k)\tilde{\eta}(\vec{k}, s/\vec{v}')\}/(s - i\vec{k}\cdot\vec{v}), \tag{5.3}$$

where $\tilde{\eta}(\vec{k}, s/\vec{v}')$ is the Fourier-Laplace transform of the density when the test particle is at the origin with velocity $\vec{v}'$ at $t = 0$. Integrating over $\vec{v}$, we find

$$\tilde{\eta}(\vec{k}, s/\vec{v}') = \frac{S(k)}{s - i\vec{k}\cdot\vec{v}'}\left(1 - \frac{i\vec{k}\cdot\vec{v}'[S(k) - 1]\,\tilde{Y}(s)}{\{1 + [S(k) - 1]s\tilde{Y}(s)\}}\right),$$

$$\tag{5.4}$$

so that

$$\bar{\eta}(\vec{k}, \vec{v}, s/\vec{v}') = \frac{\delta(\vec{v} - \vec{v}')}{s - i\vec{k}\cdot\vec{v}} + \frac{h_0(\vec{v})[S(k) - 1]^2 \bar{Y}(s)}{\{1 + [S(k) - 1]s\bar{Y}(s)\}}$$

$$+ \frac{h_0(\vec{v})[S(k) - 1][s - i\vec{k}\cdot(\vec{v} + \vec{v}')]}{(s - i\vec{k}\cdot\vec{v})(s - i\vec{k}\cdot\vec{v}')\{1 + [S(k) - 1]s\bar{Y}(s)\}} , \quad (5.5)$$

where $\quad S(k) = \chi(k, 0) = [1 - \rho C(k)]^{-1} , \quad (5.6)$

and $\quad \bar{Y}(s) = \displaystyle\int d\vec{v} \frac{h_0(\vec{v})}{s - i\vec{k}\cdot\vec{v}} . \quad (5.7)$

Equation (4.13) is thus satisfied at all times.

In order to investigate the properties of the above equations in the complex s plane, it is convenient to define the entire function

$$D(z) = \int_0^\infty du\, e^{-uz} e^{-u^2/2}$$

$$= (\tfrac{1}{2}\pi)^{1/2} e^{z^2/2} [1 - (2\pi^{-1})^{1/2} \int_0^z du\, e^{-u^2/2}] \quad (5.8)$$

Then, for a Maxwellian velocity distribution, we may write

$$\bar{Y}(s) = [(\beta m)^{1/2}/k] D(z) , \quad (5.9)$$

with $z = s(\beta m)^{1/2}/k$, which extends $\bar{Y}(s)$ into the left-hand side of the complex plane.

The initial $W(\vec{r}, \vec{v})$ of Eq. (1.15) then yields for the Laplace transform of $\chi(\vec{k}, t)$

$$\chi(\vec{k}, s) = \int d\vec{v} \int d\vec{v}'\, \bar{\eta}(\vec{k}, \vec{v}, s/\vec{v}') h_0(\vec{v}')$$

$$= (\beta m)^{1/2}/k \frac{S^2(k)D(z)}{1 + [S(k) - 1]zD(z)} , \quad (5.10)$$

so that for an ideal gas where $C(k) = 0$ and $S(k) = 1$

$$\bar{\chi}^0(\vec{k}, s) = [(\beta m)^{1/2}/k] D(z) .$$

The relation (5.10) between $\bar{\chi}(\vec{k}, s)$ and $\bar{\chi}^0(\vec{k}, s)$ is a special case of a general relationship between $\bar{\chi}$'s with different values of $C(\vec{r})$ derived in Sec. VII. Using the initial $W(\vec{r}, \vec{v})$ of Eq. (1.18) we find explicitly that

$$\vec{U}(\vec{k}, t) = \left(\vec{1} - \frac{\vec{k}\vec{k}}{k^2}\right)(\beta m)^{-1} e^{-k^2 t^2/2\beta m}$$

$$- \frac{\vec{k}\vec{k}}{k^4} \frac{\partial^2}{\partial t^2} \chi(\vec{k}, t) , \quad (5.11)$$

with $\chi(\vec{k}, t)$ obtained from (5.10). Equation (4.11) follows from this at once. Equation (5.11) also shows that the transverse current correlations are those of an ideal gas. For the self-function we,

of course, always have in this approximation just the ideal-gas result.

The coherent scattering function, $S(\vec{k}, \omega) = \pi^{-1} \times \mathrm{Re}\bar{\chi}(\vec{k}, i\omega)$, may be readily obtained from (5.10) and has been investigated extensively by Nelkin and Ranganathan[10] in that form. For the equilibrium $S(k)$ they used the Wertheim-Thiele solution of the Percus-Yevick equation for a system of hard spheres with the parameters $a = 3.0$ Å; $\tfrac{1}{6}\pi\rho a^3 = 0.45$. Their results were generally of the form expected for $S(\vec{k}, \omega)$ except near $\omega = 0$ where one expects a Rayleigh peak for small k. Comparing their results with Rahman's machine computations on Lennard-Jones particles they also found large disagreements.

Looking directly at (5.10), we see first that $\chi(\vec{k}, t)$ will have its ideal-gas form for any value of k for which $S(k) = 1$, i.e., $C(k) = 0$, [which also follows from (3.6)]. For such values of k,

$$S(\vec{k}, \omega) = (\beta m/2\pi k^2)^{1/2} e^{-\beta m\omega^2/2k^2} \quad (5.12)$$

When $S(k) \neq 1$, one may use contour integration to obtain

$$\chi(k, t) = \sum_n A_n \exp[ktz_n/(\beta m)^{1/2}] ,$$

where the z_n are the zeros of the denominator on the right-hand side of (5.10) and the A_n are residues. Note that both A_n and z_n depend only on $S(k)$ and hence are even functions of k. For real values of z, $zD(z) < 1$, hence since $S(k) \geq 0$ none of the z_n will be real positive or indeed have a positive real part. Furthermore, if $S(k) < 1$, none of the z_n will be real. If, however, $S(k) > 1$ there will always be one real negative z_n which corresponds to a pure dissipative mode albeit with a damping coefficient which is linear in k for small k. When $S(k) \gg 1$, the damping becomes small so that for long times

$$\chi(\vec{k}, t) \sim S(k) \exp[- (2/\pi\beta m)^{1/2} kt/S(k)]. \quad (5.13)$$

Now since

$$S(0) = \left(\frac{\partial}{\partial\rho}(\beta p)\right)^{-1} = \rho k T \kappa_T,$$

where κ_T is the isothermal compressibility, the above behavior will occur near the critical point. In any case, the behavior of $\chi(\vec{k}, t)$ will never be hydrodynamic where the damping goes as k^2 for small k. This shows that the various approximate theories do not have a realistic dissipative mechanism in them. This is remedied when there is in addition to the Vlasov term which gives a Landau damping a real irreversible term in the kinetic equation coming from hard-core collisions (cf Sec. VII and Appendix B) or from a Fokker-Planck-type term (Sec. VIII). [It is interesting to note here that if one uses an approximate equilibrium

$S(k)$, such as that obtained from mean-field theory, then the unstable uniform fluid is characterized by a negative compressibility which would give rise to an unbounded $\chi(\vec{k}, t)$ in our kinetic equation.][15]

VI. FORM OF f_s FOR SYSTEMS WITH HARD CORES

The solutions of Eqs. (3.8) and (3.12) are considerably more complicated than the corresponding equations for continuous potentials considered before. Since these equations are, however, in essence just linear or linearized Boltzmann equations there is much relevant information in the literature of the kinetic theory of gases about them. In particular, the asymptotic form of their solutions has been investigated extensively. Also many approximate methods of solution and alternate simpler kinetic equations which are approximations to, or related to, the Boltzmann equation have been considered. Many of these equations have already been used to investigate the Van Hove functions. In particular, Desai and Nelkin[12] have studied in detail the solutions of Eq. (3.8) for the moments of $G_s(\vec{r}, t)$. In their calculation $\rho g(a) \to \rho$, the actual density, as is proper for a dilute gas of hard spheres, $\phi^1(r) = 0$, when $g(a) = 1$. This has no effect on the solutions of (3.8) where $\rho g(a)$ is just a parameter. The inclusion of the Enskog $g(a)$ term, which depends also on the temperature when $\phi^1(r) \neq 0$, is necessary for obtaining the exact third time derivative at $t = 0^+$ and is known to yield good agreement with experiment for the diffusion coefficient of dense fluids[16] when the actual interparticle potential is represented by a hard core plus soft potential with parameters chosen to fit the equilibrium properties of the fluid. The self-diffusion coefficient is given generally as

$$D = \tfrac{1}{3} \int_0^\infty dt \, \langle \vec{v}(t) \cdot \vec{v}(0) \rangle$$

$$= \tfrac{1}{3} \int_0^\infty dt \int d\vec{v} \int d\vec{v}' \, \vec{v} \cdot f_s(\vec{k} = 0, \vec{v}, t/\vec{v}') \vec{v}' h_0(\vec{v}')$$

$$= \tfrac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \int d\vec{r} \, r^2 G_s(\vec{r}, t)$$

$$= -\tfrac{1}{6} \lim_{t \to \infty} \frac{d}{dt} [\nabla_k^2 \chi_s(\vec{k}, t)]_{k=0}$$

$$= 1.02 \, \tfrac{3}{8} \, (\beta m \pi)^{-1/2} / \rho g(a) a^2 . \qquad (6.1)$$

The last equality is that computed from (3.8).[12] The relationship between the mean-square displacement and the velocity autocorrelation function is a special case of Eq. (4.10).

The relationship between the self-function obtained from (3.8) and Rahman's molecular dynamic computation of $G_s(\vec{r}, t)$ for a system of par-

ticles interacting with a Lennard-Jones potential at a temperature and density corresponding to liquid argon is discussed by Desai.[17] Desai also makes comparison of Rahman's data with computations based on a Boltzmann equation like (3.8) but with a scattering kernel $W(\vec{v}, \vec{v}')$ appropriate for Lennard-Jones or for an exp–6 potential. The results are similar for these various potentials and in qualitative agreement with Rahman's data for the deviation of $G_s(\vec{r}, t)$ from a Gaussian form.

As pointed out by Desai,[17] however, equations like (3.8) do not yield a striking feature of molecular dynamic computations, namely, the velocity autocorrelation function becoming negative at large times. This is similar to what we found in the one-dimensional hard-rod system where the exact velocity autocorrelation function for a Maxwellian velocity distribution $h_0(v)$ (in a one-dimensional system of hard rods there are also non-Maxwellian equilibrium velocity distributions) was negative for large times but not the one obtained from the approximate kinetic equation.[2]

It is interesting to note that had we approximated $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle$ by $\langle v^2 \rangle \, e^{-\gamma t}$ with γ chosen so as to make the time derivative of $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle$ exact at $t = 0^+$ as given by (4.6) we would have obtained the same answer for D as in (6.1) with 1.02 replaced by 1. A similar situation occurs in the one-dimensional hard-rod case where the exponential approximation gives a result for D which is very close to the exact one despite the fact that $\langle \vec{v}(t) \cdot \vec{v}(0) \rangle$ is negative for large t.

VII. GENERAL SOLUTION OF FIRST-ORDER KINETIC EQUATIONS

Turning our attention now to Eq. (3.12) we see that it is more complex than (3.8). In addition to having a Vlasov term, the collision term now involves the instantaneous transfer of momentum between colliding particles. Before attempting to solve (3.12) in some approximate analytical way (cf Appendix B) or numerically (now being carried out) we shall derive here some general results about the solutions of kinetic equations of the kind discussed above.

Denoting the Fourier-Laplace transform of a one-particle distribution function $f(\vec{r}, \vec{v}, t)$ by $\bar{f}(\vec{k}, \vec{v}, s)$ we consider the case where $\bar{f}$ satisfies the equation

$$(s - i\vec{k} \cdot \vec{v}) \bar{f}(\vec{k}, \vec{v}, s) = f(\vec{k}, \vec{v}, 0) + i h_0(\vec{v}) \vec{k} \cdot \vec{v} Q(\vec{k}, s)$$

$$+ \xi(\vec{k}, s) \int d\vec{v}' B_0(\vec{k}, s; \vec{v}, \vec{v}') \bar{f}(\vec{k}, \vec{v}', s), \qquad (7.1)$$

where Q and ξ are for the present arbitrary functions of $\vec{k}$ and s. We assume now that the collision operator B_0 conserves particle number and satisfies detailed balancing, i.e.,

$$\int d\vec{v}\, B_0(\vec{v},\vec{v}') = 0 \qquad (7.2)$$

and $B_0(\vec{v},\vec{v}')h_0(\vec{v}') = B_0(\vec{v}',\vec{v})h_0(\vec{v}),$ (7.3)

where we have not written explicitly the dependence of B_0 on $\vec{k}$ and s, which are just parameters. Let $G_0(\vec{k},s,\vec{v}|\vec{v}':\xi)$ be the Green's function of Eq. (7.1) when $Q=0$, i.e., G_0 satisfies the equation

$$(s - i\vec{k}\cdot\vec{v})G_0(\vec{v}|\vec{v}')$$

$$= \delta(\vec{v}-\vec{v}') + \xi\int d\vec{w}\,B_0(\vec{v}|\vec{w})G_0(\vec{w}|\vec{v}'). \qquad (7.4)$$

It follows from (7.3) that

$$G_0(\vec{v}|\vec{v}')h_0(\vec{v}') = G_0(\vec{v}'|\vec{v})h_0(\vec{v}) . \qquad (7.5)$$

Integrating (7.4) over the velocity $\vec{v}$ and using (7.2) yields

$$i\vec{k}\cdot\int d\vec{v}\,\vec{v}\,G_0(\vec{v}|\vec{v}') = s\int d\vec{v}\,G_0(\vec{v}|\vec{v}') - 1. \qquad (7.6)$$

The solution of (7.1) with the initial condition

$$f(\vec{k},\vec{v},0) = N(k)h_0(\vec{v}) \qquad (7.7)$$

is given by

$$\vec{f}(\vec{k},\vec{v},s) = \int d\vec{v}'\,G_0(\vec{v}|\vec{v}')[N(\vec{k}) + i\vec{k}\cdot\vec{v}Q]h_0(\vec{v}')$$

$$= h_0(\vec{v})[(N+sQ)\int d\vec{v}'\,G_0(\vec{v}'|\vec{v}) - Q] , \quad (7.8)$$

where use has been made of (7.5) and (7.6). Rearranging terms in (7.8) gives

$$\frac{\vec{f}(\vec{k},\vec{v},s) + Qh_0(\vec{v})}{(N+sQ)} = \int d\vec{v}'\,G_0(\vec{v}|\vec{v}')h_0(\vec{v}'). \qquad (7.9)$$

The right-hand side of (7.9) is independent of Q and of the initial conditions, i.e., $N(k)$. This implies in particular that

$$\frac{\vec{f}_2(\vec{k},\vec{v},s) + Q_2 h_0(\vec{v})}{(N_2 + sQ_2)} = \frac{\vec{f}_1(\vec{k},\vec{v},s) + Q_1 h_0(\vec{v})}{(N_1 + sQ_1)}, \qquad (7.10)$$

where $\vec{f}_2$ and $\vec{f}_1$ are solutions of (7.1) with different values of Q and initial conditions (7.7).

The Fourier-Laplace transforms of (3.16) and (5.1), which is a special case of (3.16) when the hard-core diameter $a=0$, are of the form (7.1) with

$$Q(\vec{k},s) = -\rho C(k)\int d\vec{v}\,\vec{f}(\vec{k},\vec{v},s)$$

$$= -\rho C(k)\vec{n}(\vec{k},s), \qquad (7.11)$$

and $\xi = \rho g(a).$

Hence, integrating (7.9) over the velocity gives

$$\frac{[1-\rho C(k)]\vec{n}(\vec{k},s)}{N(k) - s\rho C(k)\vec{n}(\vec{k},s)} = \int d\vec{v}\int d\vec{v}'\,G_0(\vec{v}|\vec{v}')h_0(\vec{v}')$$

$$\equiv \Phi(\vec{k},s:\xi). \qquad (7.12)$$

Choosing $N(\vec{k}) = S(\vec{k})$ makes $\vec{n}(\vec{k},s) = \vec{\chi}(\vec{k},s)$ and we obtain then in analogy with (7.10)

$$s\vec{\chi}(\vec{k},s) - S(\vec{k}) = \frac{s\,\Phi(\vec{k},s:\xi) - 1}{1 + \rho C(k)[s\Phi(\vec{k},s:\xi) - 1]} . \qquad (7.13)$$

This leads to the following general relation between the intermediate scattering functions for different values of the continuous interparticle potential $\phi^1(\vec{r})$ or for the same potential at different temperatures:

$$\vec{\chi}(\vec{k},s:\xi)/S(k) = \{[1 - \rho_0 C_0(k)]\vec{\chi}_0(\vec{k},s:\xi)/S_0(k)\}$$

$$\times\{1 - \rho C(k) + [\rho C(k) - \rho_0 C_0(k)]$$

$$\times s\vec{\chi}_0(\vec{k},s:\xi)/S_0(k)\}^{-1} = [S(k)\vec{\chi}_0(\vec{k},s:\xi)/S_0^2(k)]$$

$$\times\{1 + [S(k) - S_0(k)]s\,\vec{\chi}_0(\vec{k},s:\xi)/S_0^2(k)\}^{-1}, \qquad (7.14)$$

where the subscript zero refers to some specified reference system with the same value of ξ as the actual system. It is readily checked that $\vec{\chi}(\vec{k},s)$ in (5.10) for a system with continuous potentials is of this form with the subscript zero referring to the noninteracting system so that $C_0(k) = 0$ and $S_0(k) = 1$. In the more general case, we can take the subscript zero to refer to a system in which there are only hard-core interactions. Equation (7.14) then tells us how $\vec{\chi}(\vec{k},s)$ is modified by the attractive interactions. It is important to note, however, that in this case the value of $\xi = \rho g(a)$ in the reference system has to be adjusted to coincide with that in the system under consideration. This corresponds to considering the hard-core system at a density ρ' such that

$$\rho' g_0(\rho'a^3) = \rho g(a,\rho,\beta),$$

since the contact value of the radial distribution function for hard cores is only a function of ρa^3. [In Appendix C, Eq. (7.14) is used to give an explicit expression for $\vec{\chi}(k,s)$ of a one-dimensional system of hard rods with an additional continuous interaction. In this case, the correct $\vec{\chi}_0(\vec{k},s)$ is known and is given exactly by the first-order kinetic equation, (3.12).]

Equation (7.13) is of the same form as that found by Nelkin[18] to be given by several different effective-field approximations. Some of these theories use a $\Phi(\vec{k},s)$ appropriate for a noninteracting gas and hence our analysis in Sec. V shows that they fail to give the correct damping in the hydrodynamical region. It is only by introducing a dissipative collision term, which in our for-

malism comes in the lowest-order kinetic equation from hard-core collisions, that one obtains a correct hydrodynamics. To see this clearly we give in Appendix B an explicit form of $\bar{\chi}(\vec{k}, s)$ when the hard-sphere collision operator, B_0 in Eq. (7.1), is approximated by a Bhatnagar, Gross, and Krook[19] (BGK) single relaxation-time collision integral. This equation was also considered and formally solved by Nelkin and Ranganathan. These authors did not, however, obtain an explicit expression for $\bar{\chi}(\vec{k}, s)$. We find that the hydrodynamical limit of $\bar{\chi}(\vec{k}, s)$ has diffusive and sound modes and is precisely of the form calculated by Kadanoff and Martin[20] and by Mountain[21] with approximate expressions for the transport coefficients, which depend on the relaxation time introduced in the BGK collision integral. We expect that the solution of the full kinetic equation (3.12) will yield a similar $\bar{\chi}(\vec{k}, s)$ in the hydrodynamical limit with different transport coefficients.

We note here that $\bar{\eta}(\vec{k}, \vec{v}, s/\vec{v}')$ corresponds according to (2.5) to the solution of (7.1) with

$$f(\vec{k}, \vec{v}, 0) = \delta(\vec{v} - \vec{v}') + [S(k) - 1] h_0(\vec{v}).$$

It may now be readily verified, using (7.6) and (7.13), that (4.15) is satisfied.

The current-current correlation function $\vec{U}(\vec{k}, s)$ may be analyzed in a manner similar to that used for obtaining (7.13). In this case,

$$f(\vec{k}, \vec{v}, 0) = \vec{v} h_0(\vec{v})$$

is a vector and so is $\vec{Q}(\vec{k}, s)$. We find

$$\vec{U}(\vec{k}, s) = \vec{U}_0(\vec{k}, s) - \frac{s\rho C(k)}{1 - \rho C(k) + s\rho C(k)\Phi(\vec{k}, s:\xi)}$$

$$\times \vec{J}_0(\vec{k}, s)\vec{J}_0(\vec{k}, s), \qquad (7.15)$$

where Φ is defined in (7.12) and

$$\vec{U}_0(\vec{k}, s) = \int d\vec{v} \int d\vec{v}' \vec{v} G_0(\vec{v}|\vec{v}')v' h_0(\vec{v}'), \qquad (7.16)$$

with $\vec{J}_0(\vec{k}, s) = \int d\vec{v} \int d\vec{v}' \vec{v} G_0(\vec{v}|\vec{v}') h_0(\vec{v}')$

$$= j_0(\vec{k}, s)\vec{k}. \qquad (7.17)$$

The second equality in (7.17) follows from the fact that $\vec{k}$ is the only vector in the problem.

VIII. SECOND-ORDER KINETIC EQUATION

Our first-order kinetic equations were based on neglecting entirely the memory terms in (2.14) and (2.15). In the language of the BBGKY hierarchy this corresponds to assuming that the two-particle correlation at any time t is related to the one-particle distribution at the same t in

the same fashion as at $t = 0$. This assumption can be weakened in various ways leading hopefully to better kinetic equations. One criterion that can be used for a systematic improvement is requiring successively higher time derivatives of f_S and η to be given exactly at $t = 0^+$. This is not unique but can be achieved to order j, for example, by taking j time derivatives of Eq. (2.10) for $m = 1$ and assuming that the jth time derivatives of $f_{S, 2}(t)$ [or $\eta_2(t)$] appearing on the right side of (2.10) depend on $f_S(t)$ [or $\eta(t)$] in the same way as they do at $t = 0^+$. This procedure leads, however, to the appearance of secular terms for long times. An alternative is to expand $\underline{M}(t)$ in (2.14) and (2.15) in a Taylor series in t and keep only a certain number of terms. This is similar to the suggestion of Ortoleva and Nelkin.[22] This procedure, however, lacks an aesthetic appeal and probably also leads to the appearance of secular terms. Therefore, we have decided to make the following ansatz:

$$\underline{M}_S(t) = W_S(t)\underline{M}_S ; \qquad \underline{M}_S = \underline{M}_S(0) \qquad (8.1)$$

$$\underline{M}(t) = W(t)\underline{M} ; \qquad \underline{M} = \underline{M}(0) , \qquad (8.2)$$

where the functions (not operators) $W_S(t)$ and $W(t)$ are yet to be specified. Substituting (8.1) and (8.2) into (2.14) and (2.15) then gives our second-order kinetic equations:

$$\frac{\partial}{\partial t} f_S(t) + \vec{v} \cdot \frac{\partial f_S(t)}{\partial \vec{r}}$$

$$= \underline{B}_S f_S(t) + \int_0^t dt' W_S(t - t')\underline{M}_S f_S(t') , \qquad (8.3)$$

$$\frac{\partial}{\partial t} \eta(t) + \vec{v} \cdot \frac{\partial \eta(t)}{\partial \vec{r}}$$

$$= \underline{B}\eta(t) + \int_0^t dt' W(t - t')\underline{M}\eta(t') . \qquad (8.4)$$

The condition $\quad W_S(0) = W(0) = 1 \qquad (8.5)$

ensures that both the first and second time derivatives of f_S and η will be given exactly at $t = 0^+$ for an arbitrary initial $W(\vec{r}, \vec{v})$. Similar arguments to those used in Sec. IV show that this also makes the first four time derivatives of χ_S and χ exact at $t = 0^+$.

The form of $\underline{M}_S$ and $\underline{M}$ can be obtained in a manner similar to that used in Sec. III for obtaining $\underline{B}_S$ and $\underline{B}$. For continuous potentials this yields, after taking the Fourier-Laplace transform of (8.3) and (8.4), the following second-order kinetic equations:

$$(s - i\vec{k} \cdot \vec{v}) f_S(\vec{k}, \vec{v}, s) = f_S(\vec{k}, \vec{v}, 0) + \bar{W}_S(s)\tfrac{1}{3}\lambda$$

$$\times \frac{\partial}{\partial \vec{v}} \cdot \left(\vec{v} f_S(\vec{k}, \vec{v}, s) + (\beta m)^{-1} \frac{\partial}{\partial \vec{v}} f_S(\vec{k}, \vec{v}, s) \right) \qquad (8.6)$$

and

$$(s - i\vec{k}\cdot\vec{v})\eta(\vec{k},\vec{v},s) = \eta(\vec{k},\vec{v},0) - i\vec{k}\cdot\vec{v}h_0(\vec{v})\rho C(k)\bar{n}(\vec{k},s)$$

$$+ \bar{W}(s)[\tfrac{1}{3}\lambda\frac{\partial}{\partial\vec{v}}\cdot\left(\vec{v}\,\bar{\eta}(\vec{k},\vec{v},s) + (\beta m)^{-1}\frac{\partial}{\partial\vec{v}}\bar{\eta}(\vec{k},\vec{v},s)\right)$$

$$- h_0(\vec{v})\vec{v}\cdot\overset{\leftrightarrow}{\Lambda}(k)\cdot\vec{J}(\vec{k},s)] \quad , \qquad (8.7)$$

where $\tilde{W}_S(s)$ and $\tilde{W}(s)$ are the Laplace transforms of $W_S(t)$ and $W(t)$ and

$$\overset{\leftrightarrow}{\Lambda}(k) = A(k)\vec{k}\vec{k}/k^2 + B(k)(\overset{\leftrightarrow}{1} - \vec{k}\vec{k}/k^2) \quad , \qquad (8.8)$$

with[23] $A(k) = k^2\rho C(k) - \rho\beta\int d\vec{r}\cos\vec{k}\cdot\vec{r}g(r)$

$$\times(\hat{k}\cdot\nabla)^2\phi(r) \quad , \qquad (8.9)$$

$$B(k) = -\tfrac{1}{2}\rho\beta\int d\vec{r}\cos\vec{k}\cdot\vec{r}g(r)[\nabla^2$$

$$- (\hat{k}\cdot\nabla)^2]\phi(r) \quad , \qquad (8.10)$$

and $\lambda = -4\pi\dfrac{\rho}{m}\displaystyle\int_0^\infty dr\,r^2\dfrac{dg(r)}{dr}\dfrac{d}{dr}\phi(r) \quad .$ (8.11)

$\vec{J}(\vec{k},s)$ is the Fourier-Laplace transform of the current density $\vec{J}(\vec{r},t)$ given in (4.2):

$$\vec{J}(\vec{k},s) = \int d\vec{v}\,\vec{v}\bar{\eta}(\vec{k},\vec{v},s) \quad . \qquad (8.12)$$

The right-hand side of (8.6) will be recognized as the Fokker-Planck operator of the theory of Brownian motion with a frequency-dependent friction coefficient

$$\zeta(s) = \tfrac{1}{3}\lambda\tilde{W}_S(s) \quad .$$

This friction coefficient $\zeta(s)$ is directly related to the Laplace transform of the velocity autocorrelation function

$$\tilde{\psi}(s) = \int d\vec{v}\int d\vec{v}'\vec{v}\cdot\vec{v}'\tilde{f}_S(\vec{k}=0,\vec{v},s/\vec{v}')h_0(\vec{v}')$$

$$= \frac{3}{\beta m}[s + \zeta(s)]^{-1} \quad , \qquad (8.13)$$

the last equality coming from the solution of (8.6). When $\zeta(s)$ (sometimes called the memory function[24]) is independent of s, (8.13) yields the well-known exponential decay of the velocity autocorrelation of Brownian motion theory. This corresponds to

$$W_S(t) \sim \delta(t) \quad ,$$

which violates (8.5), i.e., inconsistent with the correct short-time behavior of a system with continuous interparticle potentials. On the other hand, if we assume $\tilde{\psi}(s)$ known (e.g., from molecular dynamic computations), we may use (8.13) to determine $\zeta(s)$ and hence $W_S(t)$. We can then check the goodness of Eq. (8.6) by comparing the $\chi_S(\vec{k},t)$ obtained from the solution of that equation with that obtained from machine computations or experiment for the same $\tilde{\psi}(s)$.

The solution of (8.6) corresponding to the initial condition (1.15) may be written after some manipulation in the form (see Appendix D)

$$\tilde{f}_S(\vec{k},\vec{\mu},s) = \int d\vec{v}\,e^{i\vec{\mu}\cdot\vec{v}}\tilde{f}_S(\vec{k},\vec{v},s)$$

$$= [\zeta(s)]^{-1}e^{-\mu^2/2\beta m}e^\lambda|\lambda|^{-(z+\kappa^2)}$$

$$\times \text{sgn}\lambda\int_0^\lambda dx\,e^{-x}|x|^{(z+\kappa^2-1)} \qquad (8.14)$$

where $\vec{\kappa} = \vec{k}/[\zeta(s)(\beta m)^{1/2}] \quad , \quad z = s/\zeta(s) \quad ,$ (8.15)

and $\lambda = \kappa^2 - \vec{\kappa}\cdot\vec{\mu}/(\beta m)^{1/2} \quad .$

Setting $\vec{\mu} = 0$ in (8.14) we obtain

$$\tilde{\chi}_S(\vec{k},s) = [\zeta(s)]^{-1}e^{\kappa^2}\kappa^{-2(z+\kappa^2)}\int_0^{\kappa^2}dx\,e^{-x}x^{(z+\kappa^2-1)}$$

$$= \frac{\zeta(s)\beta m}{k^2 + s\zeta(s)\beta m}[1 + e^{\kappa^2}\kappa^{-2(z+\kappa^2)}$$

$$\times\int_0^{\kappa^2}dx\,e^{-x}x^{(z+\kappa^2)}] \quad . \qquad (8.16)$$

It is readily seen that for $\kappa \ll 1$, $z \ll 1$, $\tilde{\chi}_S(\vec{k},s)$ has a diffusion type of behavior with a diffusion constant

$$D = \tfrac{1}{3}\tilde{\psi}(0)$$

in accordance with (8.13). [This may also be verified directly from (8.16) using (6.1).] $\tilde{f}_S$ and $\tilde{\chi}_S$ may be expressed in terms of incomplete γ functions or confluent hypergeometric functions and are thus available for numerical computations.

The solution of Eq. (8.7) for the total distribution function may be obtained in terms of the self-distribution by methods similar to those developed in Sec. VII. As in Sec. VII we need the self-distribution with the parameter $\tilde{W}_S(s)$ replaced by $\tilde{W}(s)$. Denoting $\tilde{\chi}_S(\vec{k},s;\tilde{W}(s))$ by $\tilde{\chi}_S'(\vec{k},s)$ we find

$$\tilde{\chi}(\vec{k},s) = S(k)a(\vec{k},s)/\{(1 - \rho C(k))b(\vec{k},s) + sa(\vec{k},s)\} \quad , \qquad (8.17)$$

where $a(\vec{k},s) = s^{-1}\{1 - [1 - s\tilde{W}(s)k^{-2}A(k)]$

$$\times[1 - s\tilde{\chi}_S'(\vec{k},s)]\} \qquad (8.18)$$

and $b(\vec{k},s) = 1 - s\tilde{\chi}_S'(\vec{k},s) \quad .$

Likewise, the whole analysis can be repeated with the initial condition (1.18) to obtain the current-current correlation functions. For the self-function we find

$$\tilde{U}_S(\vec{k},s) = (s/k^2)[1 - s\tilde{\chi}_S(\vec{k},s)]\vec{k}\vec{k}/k^2$$

$$+\frac{\zeta(s)}{k^2}\left[\left(\frac{k^2}{\beta m\zeta(s)}+s\right)\tilde{\chi}_S(\vec{k},s)-1\right]\left[\vec{1}-\frac{\vec{k}\,\vec{k}}{k^2}\right].\quad(8.19)$$

The inverse Laplace transform can easily be taken to obtain

$$\vec{U}_S(\vec{k},t)=-\frac{1}{k^2}\frac{\partial^2}{\partial t^2}\chi_S(\vec{k},t)\frac{\vec{k}\,\vec{k}}{k^2}+\left(\frac{1}{\beta m}\chi_S(\vec{k},t)+\frac{1}{k^2}\right.$$

$$\left.\times\int_0^t dt'\zeta(t-t')\frac{\partial}{\partial t'}\chi_S(\vec{k},t')\right)\left(\vec{1}-\frac{\vec{k}\,\vec{k}}{k^2}\right).\quad(8.20)$$

The longitudinal part of these expressions follows directly from the symmetry properties of f_S. For the total function

$$\vec{U}(\vec{k},s)=\vec{U}^L(\vec{k},s)\frac{\vec{k}\,\vec{k}}{k^2}+\vec{U}^T(\vec{k},s)\left(\vec{1}-\frac{\vec{k}\,\vec{k}}{k^2}\right),$$

$$(8.21)$$

where, as expected, the longitudinal part is given by

$$\tilde{U}^L(\vec{k},s)=(s/k)^2[1-s\tilde{\chi}(\vec{k},s)],\quad(8.22)$$

while for the transverse component

$$\tilde{U}^T(\vec{k},s)=\tilde{U}_S^{T'}(\vec{k},s)/[1+\tilde{W}(s)B(k)\tilde{U}_S^{T'}(\vec{k},s)].$$

$$(8.23)$$

In Eq. (8.23) we have written the transverse component of the self-current-current correlation function $\tilde{U}_S^T[\vec{k},s;\tilde{W}(s)]$ as $\tilde{U}_S^{T'}(\vec{k},s)$.

The memory function $W(t)$ is completely unde-termined so far. If, for lack of any better idea, we set

$$W(t)=W_S(t),$$

which as we have already mentioned can be determined from the velocity autocorrelation function, then

$$\tilde{\chi}_S'(\vec{k},s)=\tilde{\chi}_S(\vec{k},s),$$

and $\quad\tilde{U}_S^{T'}(\vec{k},s)=\tilde{U}_S^T(\vec{k},s).$

Equations (8.17) and (8.21) then give expressions for $\tilde{\chi}(\vec{k},s)$ and $\tilde{U}(\vec{k},s)$ in terms of $\psi(s)$ and equilibrium properties of the fluid. We plan to compare the results thus obtained with molecular dynamic computations.

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APPENDIX A

We illustrate the mathematical method of deriving the first-order short-time kinetic equation by considering the case of the total function for a pure hard-core potential.

The change with time of the distribution function f_m, defined in Eq. (1.10), is given by the BBGKY infinite hierarchy of equations. For a pure hard-core potential, the first equation in this hierarchy is

$$\frac{\partial}{\partial t}f_1(\vec{q}_1,\vec{v}_1,t)+\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1}f_1(\vec{q}_1,\vec{v}_1,t)$$

$$=a^2\int d\vec{\kappa}\int d\vec{v}_2(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}\epsilon[(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}]$$

$$\times[f_2(\vec{q}_1,\vec{v}_1';\vec{q}_1+a\hat{\kappa},\vec{v}_2':t)-f_2(\vec{q}_1,\vec{v}_1;\vec{q}_1-a\hat{\kappa};\vec{v}_2:t)],$$

$$(A1)$$

where $\quad\vec{v}_1'=\vec{v}_1+\hat{\kappa}[(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}]$

and $\quad\vec{v}_2'=\vec{v}_2-\hat{\kappa}[(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}].\quad(A2)$

We now put $\quad f_1(\vec{q}_1,\vec{v}_1,t)=\rho h_0(\vec{v}_1)+\eta(\vec{q}_1,\vec{v}_1,t),\quad(A3)$

and assume that the displacement η satisfies the kinetic equation

$$\frac{\partial}{\partial t}\eta(\vec{q}_1,\vec{v}_1,t)+\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1}\eta(\vec{q}_1,\vec{v}_1,t)=\underline{B}\eta(\vec{q}_1,\vec{v}_1,t).$$

$$(A4)$$

The time-independent operator $\underline{B}$ is chosen to make (A3) exact at $t=0$. Whence,

$$\underline{B}\eta(\vec{q}_1,\vec{v}_1,0)=a^2\int d\hat{\kappa}\int d\vec{v}_2(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}\epsilon[(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}]$$

$$\times[f_2(\vec{q}_1,\vec{v}_1';\vec{q}_1+a\hat{\kappa},\vec{v}_2';0)-f_2(\vec{q}_1,\vec{v}_1;\vec{q}_1-a\hat{\kappa},\vec{v}_2;0)].$$

$$(A5)$$

From (1.10) and (1.7), we see that

$$f_2(\vec{q}_1,\vec{v}_1;\vec{q}_2,\vec{v}_2:0)=\rho g_2(\vec{q}_1,\vec{q}_2)h_0(\vec{v}_2)W(\vec{q}_1,\vec{v}_1)$$

$$+\rho g_2(\vec{q}_1,\vec{q}_2)h_0(\vec{v}_1)W(\vec{q}_2,\vec{v}_2)+\rho h_0(\vec{v}_1)h_0(\vec{v}_2)$$

$$\times\int d\vec{q}_0 g_3(\vec{q}_0,\vec{q}_1,\vec{q}_2)\int d\vec{v}_0 W(\vec{q}_0,\vec{v}_0),\quad(A6)$$

where W is related to $\eta(0)$ by Eq. (2.9). [We have taken $\int d\vec{x}\,W(x)=1$, although this condition is not necessary.] Thus the operator $\underline{B}$ can be determined explicitly.

In the calculation, it is convenient to divide $\underline{B}$ into three parts which correspond to the contributions from the three terms in (A6):

$$\underline{B}\eta(\vec{q}_1,\vec{v}_1,0)=\frac{\delta f_s}{\delta t}+\frac{\delta_1 f_d}{\delta t}-\frac{\delta_0 f_d}{\delta t}.\quad(A7)$$

First,

$$\frac{\delta f_s}{\delta t}=\rho a^2 g_2(a)\int d\hat{\kappa}\int d\vec{v}_2(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}\epsilon[(\vec{v}_2-\vec{v}_1)\cdot\hat{\kappa}]$$

$$\times[h_0(\vec{v}_2')W(\vec{q}_1,\vec{v}_1')-h_0(\vec{v}_2)W(\vec{q}_1,\vec{v}_1)]$$

$$= \rho a^2 g_2(a) \int d\hat{\kappa} \int d\vec{v}_2 (\vec{v}_2 - \vec{v}_1)\cdot\hat{\kappa}\epsilon[(\vec{v}_2 - \vec{v}_1)\cdot\hat{\kappa}]$$

$$\times [h_0(\vec{v}_2')\eta(\vec{q}_1, \vec{v}_1', 0) - h_0(\vec{v}_2)\eta(\vec{q}_1, \vec{v}_1, 0)] \ , \tag{A8}$$

so that $\quad \delta f_s/\delta t = \underline{B}_s\,\eta(\vec{q}_1, \vec{v}_1, 0) \ . \tag{A9}$

Second,

$$\delta_1 f_d/\delta t = \rho a^2 g_2(a) \int d\hat{\kappa} \int d\vec{v}_2 (\vec{v}_2 - \vec{v}_1)\cdot\hat{\kappa}$$

$$\times \epsilon[(\vec{v}_2 - \vec{v}_1)\cdot\hat{\kappa}][h_0(\vec{v}_1')W(\vec{q}_1+a\hat{\kappa}, \vec{v}_2')$$

$$- h_0(\vec{v}_1)W(\vec{q}_1 - a\hat{\kappa}, \vec{v}_2)] = \rho a^2 g_2(a) \int d\hat{\kappa} \int d\vec{v}_2$$

$$\times (\vec{v}_2 - \vec{v}_1)\cdot\hat{\kappa}\epsilon[(\vec{v}_2 - \vec{v}_1)\cdot\hat{\kappa}][h_0(\vec{v}_1')\eta(\vec{q}_1$$

$$+ a\hat{\kappa}, \vec{v}_2', 0) - h_0(\vec{v}_1)\eta(\vec{q}_1 - a\hat{\kappa}, \vec{v}_2, 0)]$$

$$- \rho^2 a^2 g_2(a)h_0(\vec{v}_1) \int d\hat{\kappa}\, \vec{v}_1\cdot\hat{\kappa}$$

$$\times \int d\vec{r}C(\vec{q}_1 - a\hat{\kappa}, \vec{r}) \int d\vec{w}\,\eta(\vec{r}, \vec{w}, 0) \ . \tag{A10}$$

Finally, $\quad \dfrac{\delta_0 f_d}{\delta t} = - \rho^2 a^2 h_0(\vec{v}_1) \int d\hat{\kappa}\, \vec{v}_1\cdot\hat{\kappa}$

$$\times \int d\vec{r}g_3 (\vec{r}, \vec{q}_1, \vec{q}_1 - a\hat{\kappa}) \int d\vec{w}\, W(\vec{r}, \vec{w}) \ . \tag{A11}$$

In order to proceed further, we must express g_3 in terms of lower-order distribution functions. From either the next higher order, equilibrium BBGKY equation, or the definitions, we find

$$\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_2}g_2(\vec{q}_1, \vec{q}_2)+g_2(a^+)\delta(|\vec{q}_1 - \vec{q}_2| - a^+)$$

$$\times \vec{v}_1\cdot(\vec{q}_1 - \vec{q}_2)/|\vec{q}_1 - \vec{q}_2| + \rho \int d\vec{q}_3\delta(|\vec{q}_1 - \vec{q}_3|- a^+)$$

$$\times g_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)\vec{v}_1\cdot(\vec{q}_1 - \vec{q}_3)/|\vec{q}_1 - \vec{q}_3| = 0 \ , \tag{A12}$$

so that

$$\rho a^2 \int d\hat{\kappa}\, \vec{v}_1\cdot\hat{\kappa} g_3(\vec{q}_1, \vec{q}_2, \vec{q}_1 - a\hat{\kappa}) = -\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_2} g_2(\vec{q}_1, \vec{q}_2)$$

$$- g_2(a^+)\delta(|\vec{q}_1 - \vec{q}_2| - a^+)\vec{v}_1\cdot(\vec{q}_1 - \vec{q}_2)/|\vec{q}_1 - \vec{q}_2| \ . \tag{A13}$$

But this is precisely the integral over g_3 appearing in the right-hand side of (A11). Thus

$$\frac{\delta_0 f_d}{\delta t} = - \rho h_0(\vec{v}_1) \int d\vec{r}\, \vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1} g_2(\vec{q}_1, \vec{r}) \int d\vec{w}\, W(\vec{r}, \vec{w})$$

$$+ \rho a^2 g_2(a)h_0(\vec{v}_1) \int d\hat{\kappa}\, \vec{v}_1\cdot\hat{\kappa} \int d\vec{w}\, W(\vec{q}_1 - a\hat{\kappa}, \vec{w}). \tag{A14}$$

From Eq. (2.9) and the Ornstein Zernnike equation,

$$g_2(\vec{r}_1, \vec{r}_2) - 1 = C(\vec{r}_1, \vec{r}_2) + \rho \int d\vec{r}'C(\vec{r}_1, \vec{r}')[g_2(r', \vec{r}_2) - 1], \tag{A15}$$

Eq. (A.14) becomes

$$\frac{\delta_0 f_d}{\delta t} = - \rho h_0(\vec{v}_1)\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1} \int d\vec{r}\, C(\vec{q}_1, \vec{r}) \int d\vec{w}\,\eta(\vec{r}, \vec{w}, 0)$$

$$+ \rho a^2 g_2(a)h_0(\vec{v}_1) \int d\hat{\kappa}\, \vec{v}_1\cdot\hat{\kappa}[\int d\vec{w}\eta(\vec{q}_1 - a\hat{\kappa}, \vec{w}, 0)$$

$$- \rho \int d\vec{r}\, C(\vec{q}_1 - a\hat{\kappa}, \vec{r}) \int d\vec{w}\,\eta(\vec{r}, \vec{w}, 0)] \ . \tag{A16}$$

When all the terms are added together, we see that the last part of (A16) is cancelled by the last term in (A16). Since

$$a^2 \int d\hat{\kappa}\, \vec{v}_1\cdot\hat{\kappa}\,\eta(\vec{q}_1 - a\hat{\kappa}, \vec{w}, 0)$$

$$= - \vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1} \int d\vec{r}\, \epsilon(a - |\vec{q}_1 - \vec{r}|)\eta(\vec{r}_1\vec{w}, 0), \tag{A17}$$

we finally obtain from (A8), (A10), and (A16)

$$\underline{B}\eta(\vec{q}_1, \vec{v}_1, 0) = - \beta\rho h_0(\vec{v}_1)\vec{v}_1\cdot\frac{\partial}{\partial\vec{q}_1} \int d\vec{r}\, V(\vec{q}_1 - \vec{r}) \int d\vec{w}$$

$$\times \eta(\vec{r}, \vec{w}, 0) + \rho a^2 g_2(a) \int d\hat{\kappa} \int d\vec{v}_2[(\vec{v}_2 - \vec{v}_1)\cdot\hat{\kappa}]\,\epsilon[(\vec{v}_2$$

$$- \vec{v}_1)\cdot\hat{\kappa}][h_0(\vec{v}_2')\eta(\vec{q}_1, \vec{v}_1', 0) - h_0(\vec{v}_2)\eta(\vec{q}_1, \vec{v}_1, 0)$$

$$+ h_0(\vec{v}_1')\eta(\vec{q}_1 + a\hat{\kappa}, \vec{v}_2', 0) - h_0(\vec{v}_1)\eta(\vec{q}_1 - a\hat{\kappa}, \vec{v}_2, 0) \ , \tag{A18}$$

where $\quad - \beta V(\vec{r}) = C(\vec{r}) + g_2(a)\epsilon(a - |\vec{r}|) \ . \tag{A19}$

Equation (A18) is the desired explicit expression for $\underline{B}$ so that the short-time kinetic equation (A4) is completely determined.

APPENDIX B

In this Appendix, we consider the kinetic equation

$$\frac{\partial}{\partial t}\eta(\vec{k}, \vec{v}, t) - i\vec{k}\cdot\vec{v}\,\eta(\vec{k}, \vec{v}, t) - \frac{C(k)}{\beta m}\int d\vec{w}\,\eta(\vec{k}, \vec{w}, t)$$

$$\times i\vec{k}\cdot\nabla_{\vec{v}}\rho h_0(\vec{v}) = - \lambda\,\eta(\vec{k}, \vec{v}, t) + \lambda h_0(\vec{v}) \int d\vec{w}\,\eta(\vec{k}, \vec{w}, t)$$

$$+ \lambda h_0(\vec{v})[\tfrac{3}{2}\int d\vec{w}\eta(\vec{k}, \vec{w}, t) - \tfrac{1}{2}\beta m\int d\vec{w}\, w^2\,\eta(\vec{k}, \vec{w}, t)]$$

$$+ \lambda h_0(\vec{v})\beta m\vec{v}\cdot \int d\vec{w}\,\vec{w}\,\eta(\vec{k}, \vec{w}, t) - \tfrac{1}{3}\lambda\beta mv^2 h_0(\vec{v})$$

$$\times [\tfrac{3}{2}\int d\vec{w}\,\eta(\vec{k}, \vec{w}, t) - \tfrac{1}{2}\beta m \int d\vec{w}\, w^2\,\eta(\vec{k}, \vec{w}, t)] \ , \tag{B1}$$

where $\quad \lambda = \rho/\tau \tag{B2}$

and τ is the relaxation time. The left-hand side of (B1) is the linearized Vlasov equation (3.6) and the right-hand side is the BGK linearized collision integral.[19] This collision integral has a simple first term proportional to $\eta(\vec{k}, \vec{v}, t)$ plus additional

terms which are included to ensure the conversation of particle number, momentum, and energy. The Laplace transform of (B1) can be written

$$[s - i\vec{k}\cdot\vec{v} + \lambda]\,\eta(\vec{k}, \vec{v}, s) + \rho C(k)i\,\vec{k}\cdot\vec{v}h_0(\vec{v})\tilde{\chi}(k, s)$$

$$= \eta(\vec{k}, \vec{v}, 0) + \lambda h_0(\vec{v})\tilde{\chi}(k, s) + \tfrac{1}{2}\lambda h_0(\vec{v})$$

$$\times [3\tilde{\chi}(k, s) - \beta m\tilde{Z}(k, s)] + \lambda\beta m h_0(\vec{v})\vec{v}\cdot\vec{\tilde{Y}}(k, s)$$

$$-\tfrac{1}{6}\lambda\beta m v^2 h_0(\vec{v})\,[3\tilde{\chi}(k, s) - \beta m\tilde{Z}(k, s)]\,, \qquad (B3)$$

where $\quad \tilde{\chi}(k, s) = \int d\vec{w}\,\tilde{\eta}(\vec{k}, \vec{w}, s)\,,$

$$\vec{\tilde{Y}}(k, s) = \int d\vec{w}\vec{w}\,\tilde{\eta}(\vec{k}, \vec{w}, s)\,, \qquad (B4)$$

and $\quad \tilde{Z}(k, s) = \int d\vec{w}\,w^2\tilde{\eta}(\vec{k}, \vec{w}, s)\,.$

The solution $\tilde{\eta}(\vec{k}, \vec{v}, s)$ is obtained simply by dividing (B3) by $[s - i\vec{k}\cdot\vec{v} + \lambda]$. When the solution is substituted into (B4), three simultaneous equations are obtained which determine the quantities $\tilde{\chi}, \vec{\tilde{Y}}$, and $\tilde{Z}$. As in Ref. 19, all the integrals can be expressed in terms of the single integral

$$\tilde{A}(k, s) = \int d\vec{v}\,\frac{h_0(\vec{v})}{[s - i\vec{k}\cdot\vec{v} + \lambda]}\,. \qquad (B5)$$

For the particular initial condition

$$\eta(\vec{k}, \vec{v}, 0) = \chi(k, 0)h_0(\vec{v})\,,$$

$\tilde{\chi}(k, s)$ is the coherent scattering function. A formal expression for this has already been given by Nelkin and Ranganathan[10] who solved the three simultaneous equations in matrix form. In a straightforward but tedious way, $\tilde{\chi}(k, s)$ can be calculated explicitly. The result is

$$\tilde{\chi}(k, s) = \chi(k, 0)\tilde{\alpha}(k, s)/\{[1 - \rho C(k)]\,\tilde{\beta}(k, s) + s\tilde{\alpha}(k, s)\}\,, \qquad (B6)$$

where $\quad \tilde{\alpha}(k, s) = 2k^2\tilde{A}(k, s)[3 - 2\lambda\tilde{A}(k, s)]$

$$- \lambda\beta m s\tilde{A}(k, s) - \lambda\beta m[6 - 4\lambda\tilde{A}(k, s)]$$

$$- \beta m s(s + \lambda)/k^2[1 - (s + \lambda)\tilde{A}(k, s)]\,, \qquad (B7)$$

and $\quad \tilde{\beta}(k, s) = -k^2\lambda\tilde{A}(k, s) + k^2[6 - 4\lambda\tilde{A}(k, s)]$

$$+ \lambda\beta m(s + \lambda)/k^2[1 - (s + \lambda)\tilde{A}(k, s)]\,. \qquad (B8)$$

For $\lambda = 0$, (B6) reduces to (5.10) as expected.

In the hydrodynamical limit, $k \to 0$ with s/k constant, $\tilde{\chi}(k, s)$ becomes identical to the Kadanoff and Martin[20] and Mountain[21] result. Define

$$P = [(s + \lambda)/k](\tfrac{1}{2}\beta m)^{1/2}, \qquad (B9)$$

then in the hydrodynamical limit, for fixed λ, $P \to \infty$ so that

$$(s + \lambda)\tilde{A}(k, s) \equiv (\pi)^{1/2}Pe^{P^2}\text{erfc}P$$

$$\to 1 + \sum_{m=1}^{\infty}(-1)^m 1\times 3\times\cdots\times(2m - 1)/(2P^2)^m. \qquad (B10)$$

When this expansion is used in (B7) and (B8) and the leading order terms collected together, $\tilde{\chi}(k, s)$ is given by

$$\tilde{\chi}(k, s) = \chi(k, 0)\tilde{\sigma}(k, s)\,, \qquad (B11)$$

where $\quad \tilde{\sigma}(k, s) = (1/\lambda\epsilon)$

$$\times\frac{6x^2 + 9\epsilon x + 2 + O(\epsilon^2)}{[6x^3 + 9\epsilon x^2 + \{5 - 3\rho C(0)\}x + \tfrac{5}{2}\epsilon\{1 - \rho C(0)\} + O(\epsilon^2)]}$$

$$(B12)$$

and $\quad x = (s/k)(\tfrac{1}{2}\beta m)^{1/2}; \ \epsilon = (k/\lambda)(2/\beta m)^{1/2}\,. \qquad (B13)$

We now factorize the cubic expression in the denominator and write $\tilde{\sigma}(k, s)$ as the sum of three partial fractions. Keeping only the leading order terms, we obtain in k, t space the familiar result

$$\sigma(k, t) = (1 - c_v/c_p)\exp[-(\kappa/\rho c_p)k^2 t$$

$$+ (c_v/c_p)\exp(-\Gamma k^2 t)\cos u kt\,, \qquad (B14)$$

with $\quad u^2 = (\beta m)^{-1}[\tfrac{5}{3} - \rho C(0)]\,,$

$$c_v/c_p = [1 - \rho C(0)]/[\tfrac{5}{3} - \rho C(0)]\,,$$

$$\kappa/\rho c_p = (\lambda\beta m)^{-1}\tfrac{2}{3}[1 - \rho C(0)]/[\tfrac{5}{3} - \rho C(0)]\,, \qquad (B15)$$

and $\quad 2\Gamma = \rho^{-1}(\tfrac{4}{3}\eta + \zeta) + (\kappa/\rho)[(c_v)^{-1} - (c_p)^{-1}]$

$$= (\lambda\beta m)^{-1}\tfrac{1}{3}[5 - 2\rho C(0)]/[\tfrac{5}{3} - \rho C(0)]\,,$$

or $\quad \rho^{-1}(\tfrac{4}{3}\eta + \zeta) = 2/\lambda\beta m\,.$

Finally, since

$$\tilde{\chi}(k, s) = \sum_{j=0}^{\infty}\frac{1}{s^{j+1}}\frac{\partial^j}{\partial t^j}\chi(k, t)\Big|_{t=0}\,, \qquad (B16)$$

we can calculate from the large s (i.e., large P) expansion the following sum rules:

$$\frac{\partial^2}{\partial t^2}\chi(k, t)\Big|_{t=0} = -\frac{k^2}{\beta m}\,,$$

$$\frac{\partial^4}{\partial t^4}\chi(k, t)\Big|_{t=0} = \frac{k^4}{(\beta m)^2}[3 - \rho C(k)]\,, \qquad (B17)$$

and $\quad \dfrac{\partial}{\partial t}\chi(k, t)\Big|_{t=0} = \dfrac{\partial^3}{\partial t^3}\chi(k, t)\Big|_{t=0} = 0\,,$

which are the same as those obtained from the collisionless equation.

APPENDIX C

In one dimension, the surface factor a^2 in Eq. (3.12) must be replaced by 1 and the $\hat{\kappa}$ integration by a summation over $\hat{\kappa} = \pm 1$. The Fourier-Laplace transform of (3.12) then becomes

$$[s - i\beta(k)v + \alpha(k)\mu(v)]\, \bar{\eta}(k,v,s) = \eta(k,v,0)$$

$$+ h_0(v)\int_{-\infty}^{\infty} dv'\bar{\eta}(k,v',s)\{\alpha(k)|v-v'|$$

$$+ i\lambda(k)v - i[\beta(k)-k]v'\} \quad , \tag{C1}$$

where $\alpha(k) = \rho g(a)(1 - \cos ka)$

$$\beta(k) = k + \rho g(a)\sin ka \quad , \tag{C2}$$

$$\mu(v) = \int_{-\infty}^{\infty} du\, h_0(u)|v-u| \quad , \tag{C3}$$

and $\quad \lambda(k) = k[1 - \rho C(k)] - \beta(k) \quad . \tag{C4}$

Equation (C1) has already been solved in Ref. 3, Sec. 5. For a pure hard-rod system (with quantities denoted by zero subscripts),

$$1 - \rho C_0(k) = (\alpha^2 + \beta^2)/k^2 = [S_0(k)]^{-1}, \tag{C5}$$

$$\tilde{\chi}_0(k,s) = \frac{k^2}{2\alpha}\int_{-\infty}^{\infty} dv[s - i\beta v + \alpha\mu(v)]^{-2} \quad , \tag{C6}$$

which is the exact result.

For a system of hard rods plus continuous potential, we can use (7.14) to express $\tilde{\chi}(k,s)$ at density ρ and reciprocal temperature β in terms of the pure hard-rod quantities with a density ρ' given by

$$\xi = \rho'g_0(a) = \rho'/(1 - \rho'a) = \rho g(a:\rho,\beta), \tag{C7}$$

or $\quad \rho' = \rho g(a:\rho,\beta)/[1 + \rho a g(a:\rho,\beta)], \tag{C8}$

where $g(a:\rho,\beta)$ is the contact value of the radial distribution function for the system of hard rods plus continuous potential.

APPENDIX D

In this Appendix, we solve in greater detail the second-order kinetic equations (8.6) and (8.7). The equation for the self-function (8.6) is

$$(s - i\vec{k}\cdot\vec{v})\bar{f}_s(\vec{k},\vec{v},s) = W(\vec{k},\vec{v})$$

$$+ \zeta(s)\frac{\partial}{\partial\vec{v}}\cdot\left(\vec{v}\bar{f}_s(\vec{k},\vec{v},s) + (\beta m)^{-1}\frac{\partial}{\partial\vec{v}}\bar{f}_s(\vec{k},\vec{v},s)\right),$$

$$\tag{D1}$$

where we have used

$$f_s(\vec{k},\vec{v},0) = W(\vec{k},\vec{v}) \quad \text{and} \quad \zeta(s) = \tfrac{1}{3}\lambda\tilde{W}_s(s) \quad .$$

We now take the velocity Fourier transform of this equation to obtain

$$[\vec{\mu} - (\beta m)^{1/2}\vec{\kappa}]\cdot\frac{\partial}{\partial\vec{\mu}}\bar{f}_s(\vec{k},\vec{\mu},s)$$

$$+ (z + \mu^2/\beta m)\bar{f}_s(\vec{k},\vec{\mu},s) = \zeta(s)^{-1}\overline{W}(\vec{k},\vec{\mu}), \tag{D2}$$

where $\quad \bar{f}_s(\vec{k},\vec{\mu},s) = \int d\vec{v}\, e^{i\vec{\mu}\cdot\vec{v}}\bar{f}_s(\vec{k},\vec{v},s) \quad ,$

$$\overline{W}(\vec{k},\vec{\mu}) = \int d\vec{v}\, e^{i\vec{\mu}\cdot\vec{v}}W(\vec{k},\vec{v}) \quad , \tag{D3}$$

and $\quad \vec{\kappa} = \vec{k}/\zeta(s)(\beta m)^{1/2}; \quad z = s/\zeta(s) \quad .$

$$\tag{D4}$$

The differential equation can be simplified by putting

$$\bar{f}_s(\vec{k},\vec{\mu},s) = y(\vec{\mu})\lambda^{-(\kappa^2+z)}e^{-\mu^2/2\beta m} \quad , \tag{D5}$$

where $\quad \lambda = \kappa^2 - \vec{\kappa}\cdot\vec{\mu}(\beta m)^{-1/2} \quad .$

Then the equation for $y(\vec{\mu})$ is

$$[\vec{\mu} - (\beta m)^{1/2}\vec{\kappa}]\cdot\left(\frac{dy(\vec{\mu})}{d\vec{\mu}} + \frac{\vec{\kappa}}{\beta m}y(\vec{\mu})\right)$$

$$= \zeta(s)^{-1}\overline{W}(\vec{k},\vec{\mu})\lambda^{(\kappa^2+z)}e^{\mu^2/2\beta m} \quad . \tag{D6}$$

The solution of the homogeneous equation is

$$y(\vec{\mu}) = A(\vec{k},s)e^{\lambda} \quad , \tag{D7}$$

where A is an integration constant and to this must be added any particular integral to obtain the general solution.

For the initial condition (1.15),

$$W(\vec{k},\vec{v}) = h_0(\vec{v}) \quad ,$$

so that if $h_0(v)$ is a Maxwellian velocity distribution then

$$\overline{W}(\vec{k},\vec{\mu}) = e^{-\mu^2/2\beta m} \quad . \tag{D8}$$

A particular integral of (D6) with (D8) is

$$y(\mu) = \zeta(s)^{-1}e^{\lambda}\int^{\lambda}dx\, e^{-x}x^{(\kappa^2+z-1)} \quad . \tag{D9}$$

Thus, from (D7), (D9), and (D5)

$$\bar{f}_s(\vec{k},\vec{\mu},s) = e^{-\mu^2/2\beta m}e^{\lambda}\lambda^{-(\kappa^2+z)}[A(\vec{k},s)$$

$$+ \zeta(s)^{-1}\int^{\lambda}dx\, e^{-x}x^{(\kappa^2+z-1)}] \quad . \tag{D10}$$

The integration constant $A(\vec{k},s)$ is determined by requiring that $\bar{f}_s(\vec{k},\vec{\mu},s)$ remains finite as $\lambda \to 0$. Whence

$$\bar{f}_s(\vec{k},\vec{\mu},s) = \zeta(s)^{-1}e^{-\mu^2/2\beta m}e^{\lambda}\lambda^{-(\kappa^2+z)}$$

$$\times \int_0^{\lambda}dx\, e^{-x}x^{(\kappa^2+z-1)} \quad , \tag{D11}$$

which is identical to (8.14) in the text.

For the initial condition (1.18)

$$W(\vec{k}, \vec{v}) = \vec{v} h_0(\vec{v}) \qquad (D12)$$

so that $\overline{W}(\vec{k}, \vec{\mu}) = (i/\beta m)\vec{\mu} \, e^{-\mu^2/2\beta m}$.   (D13)

The differential equation (D6) with (D13) can again be solved for $\vec{f}_s(\vec{k}, \vec{\mu}, s)$, which is now a vector:

$$\vec{f}_s(\vec{k}, \vec{\mu}, s) = \frac{i}{\beta m} \frac{1}{\zeta(s)} e^{-\mu^2/2\beta m}$$

$$\times \left[\frac{\vec{\kappa}(\beta m)^{1/2}}{\kappa^2 + z} + \left(\vec{\mu} - \frac{\vec{\kappa}}{\kappa^2 + z} \left[\vec{\mu} \cdot \vec{\kappa} + z(\beta m)^{1/2} \right] \right) \right.$$

$$\left. \times \lambda^{-(\kappa^2 + z + 1)} e^{\lambda} \int_0^\lambda dx \, e^{-x} x^{(\kappa^2 + z)} \right] . \qquad (D14)$$

In particular, the current-current correlation function is given by

$$\tilde{U}_s(\vec{k}, s) = i^{-1} \frac{d}{d\vec{\mu}} \vec{f}_s(\vec{k}, \vec{\mu}, s) \bigg|_{\mu = 0}$$

$$= \hat{\kappa}\hat{\kappa} \frac{z}{\beta m \zeta(s)\kappa^2} \left[1 - z\zeta(s)\tilde{\chi}_s(\vec{k}, s) \right]$$

$$+ (\vec{1} - \hat{\kappa}\hat{\kappa})[\beta m \zeta(s)\kappa^2]^{-1}[\zeta(s)(\kappa^2$$

$$+ z)\tilde{\chi}_s(\vec{k}, s) - 1] , \qquad (D15)$$

which is just (8.19).

The time correlations for the total equation (8.7) may be obtained by the method of Sec. VII from the solutions of the self-equation (8.6). If $\underline{B}_0(\vec{v})$ is the operator

$$\underline{B}_0(\vec{v}) = \zeta(s)\frac{\partial}{\partial \vec{v}} \cdot \left(\vec{v} + \frac{1}{\beta m} \frac{\partial}{\partial \vec{v}} \right) ,$$

then $\int d\vec{v} \, \underline{B}_0(\vec{v}) \equiv 0$,   (D16)

and again we can show from the structure of $\underline{B}_0(\vec{v})$ that

$$G_0(\vec{v} \mid \vec{v}') h_0(\vec{v}') = G_0(\vec{v}' \mid \vec{v}) h_0(\vec{v}) . \qquad (D17)$$

The analysis then proceeds as before and the results are given in the text.

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