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Asymptotic Time Behavior of Correlation Functions. I. Kinetic Terms

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The asymptotic time behavior ($\sim ct^{-d/2}$, where d is the dimensionality of the system) of the velocity autocorrelation function and of the kinetic parts of the correlation functions for the shear viscosity and the heat conductivity is derived on the basis of a local equilibrium assumption and the linearized Navier-Stokes equations. The coefficients c are expressed in terms of the transport coefficients and thermodynamic quantities. The physical mechanism responsible for the long-time tail is indicated, and the connections between the present work and investigations based on molecular dynamics and on kinetic theory are discussed.

I. INTRODUCTION

Until recently the velocity autocorrelation function and other time correlation functions relevant for the computation of transport coefficients were believed to decay exponentially for long times. The evidence supporting this belief was partly furnished by semiphenomenological theories such as the Langevin equation, and for dilute gases the Boltzmann equation strengthened the case for an exponential decay. However, Alder and Wainwright,[1] in their molecular-dynamics study of systems of hard disks and hard spheres, discovered that the velocity autocorrelation function does *not* decay exponentially for long times. On the contrary, they observed a long-lived tail of the form $t^{-d/2}$, where d is the dimensionality of the system. Alder and Wainwright furthermore proposed a hydrodynamical explanation of their observations in terms of a numerical solution of the Navier-Stokes equations. Zwanzig and Bixon[2] also based their work on a hydrodynamical model and reached a similar conclusion for the asymptotic decay.

Dorfman and Cohen,[3] on the other hand, studied the the correlation functions from the point of view of kinetic theory. Taking into account more elaborate collision sequences than the uncorrelated binary collisions contained in the Boltzmann equation, they were able to show that not only the velocity autocorrelation function, but also the correlation functions associated with the shear viscosity η and the heat conductivity λ, decay as $t^{-d/2}$. In addition they calculated the coefficients of the $t^{-d/2}$ tails.

The purpose of this and a subsequent paper, brief accounts of which have been published previously,[4] is to show that, on the basis of a local equilibrium assumption, the asymptotic behavior of these correlation functions can be obtained precisely in terms of transport coefficients and thermodynamic quantities. If one restricts oneself to the kinetic parts of the correlation functions, i.e., if one neglects terms explicitly containing the intermolecular potential, the anlaysis is considerably simplified.

We shall therefore only calculate the kinetic parts of the correlation functions in this paper. This is not as severe a restriction as it may seem, for the following reasons: (i) The velocity autocorrelation function does not contain potential terms. (ii) The potential terms in the shear viscosity correlation function can be shown not to contribute to the asymptotic tail. (iii) The contributions from the potential terms are of higher order in the density, and in the low-density limit the tail of the kinetic parts can therefore be directly compared with the results obtained by Dorfman and Cohen. (iv) The kinetic parts of the correlation functions are in themselves well-defined objects for any density, and can be studied by computer experiments.[1]

In a subsequent paper the full correlation functions, including that pertaining to the bulk viscosity, will be considered. The basic ideas will be essentially the same as those presented here, but a more elaborate formalism is called for. Within that formalism one can also study the connection between our method and the mode-mode coupling theories[5] used to discuss transport coefficients close to critical points. In the present paper, however, we shall take advantage of the simplifications that arise from restricting one's attention to the kinetic parts of the correlation functions, and try to bring out the physical content of the theory as clearly as possible.

In Sec. II the relevant Green-Kubo formulas for the transport coefficients are presented and transformed to expressions suitable for our purpose. The basic assumptions on which the present work rests will be presented in Sec. III. The general solution of the initial-value problem of linearized hydrodynamics, which is needed in the calculation, is summarized in Sec. IV. In Sec. V the appropriate choice of initial values for the hydrodynamic fields is considered, and the final results are derived in Sec. VI. In the closing section, Sec. VII, we discuss the assumptions and the results of the present work, and its connections with related investigations.

II. BASIC FORMULAS

The Green-Kubo formulas[6] express the transport coefficients as integrals over corresponding time correlation functions $C(t)$. We shall use normalizations[7] such that

$$\begin{aligned} D &= n^{-1}\int_0^\infty dt\, C_D(t), \quad \eta = \beta\int_0^\infty dt\, C_\eta(t), \\ \lambda &= \beta T^{-1}\int_0^\infty dt\, C_\lambda(t), \end{aligned} \tag{2.1}$$

where D is the self-diffusion coefficient, η the shear viscosity, λ the heat conductivity, n the equilibrium number density, and $T=(k_B\beta)^{-1}$ the temperature.

The simplest case, contained already in Einstein's work on Brownian motion, is that of the self-diffusion coefficient for which $C_D(t)$ is the velocity autocorrelation function

$$C_D(t) = \lim_{V\to\infty} V^{-1}\langle \textstyle\sum_i v_{ix}(0)v_{ix}(t)\rangle, \tag{2.2}$$

where $v_{ix}(t)$ is the x component of the velocity of particle i in a fluid of N similar particles, $\langle\cdots\rangle$ denotes an average over a grand canonical ensemble, V is the volume of the system, and the thermodynamic limit $V\to\infty$ is taken as the final step.

With the convention (2.1) the remaining correlation functions can be written

$$C(t) = \lim_{V\to\infty} V^{-1}\langle J(0)J(t)\rangle, \tag{2.3}$$

where the currents J are given by

$$J_\eta = \sum_i \left(m v_{ix}v_{iy} - \tfrac{1}{2}\sum_j{}' r_{ij,x}\frac{\partial\,\Phi(r_{ij})}{r_{ij,y}}\right), \tag{2.4}$$

$$J_\lambda = \sum_i \left[(\tfrac{1}{2}m\, v_i^2 - h)v_{ix} + \tfrac{1}{2}\sum_j{}' \left(\Phi(r_{ij})v_{ix} - r_{ij,x}\frac{\partial\,\Phi(r_{ij})}{\partial\vec{r}_{ij}}\cdot\vec{v}_i\right)\right]. \tag{2.5}$$

Here m is the mass of the particles, $r_{ij,x}$ is the x component of the vector measuring the relative positions of particles i and j, $\Phi(r)$ is the intermolecular pair potential, and $\sum_j{}'$ sums over all $j\neq i$. The equilibrium enthalpy per particle is denoted by h. The kinetic part of h, $h^K=\frac{1}{2}(d+2)\beta^{-1}$, will be used below.

From now on we consider only the kinetic parts J^K of J and the corresponding correlation functions. Since the averages are symmetric sums over N particles one can rewrite all correlation functions as

$$C_\alpha^K(t) = \lim_{V\to\infty} V^{-1}\langle N j_\alpha(\vec{v}_1(0))J_\alpha^K(t)\rangle, \tag{2.6}$$

where the currents referring to the self-diffusion $(\alpha=D)$, the shear viscosity $(\alpha=\eta)$, and heat conductivity $(\alpha=\lambda)$ are defined as

$$\begin{aligned} &j_D(\vec{v}_1) = v_{1x}, \quad J_D^K = j_D(\vec{v}_1), \\ &j_\eta(\vec{v}_1) = m\, v_{1x}v_{1y}, \quad J_\eta^K = \textstyle\sum_i j_\eta(\vec{v}_i), \\ &j_\lambda(\vec{v}_1) = [\tfrac{1}{2}m\, v_1^2 - \tfrac{1}{2}(d+2)\beta^{-1}]v_{1x}, \quad J_\lambda^K = \textstyle\sum_i j_\lambda(\vec{v}_i). \end{aligned} \tag{2.7}$$

In the following we shall compute averages such as (2.6) in two steps. First, the average (2.6) over a spatially uniform system is decomposed into partial averages over spatially nonuniform systems in which, initially, particle 1 has a given velocity $\vec{v}_1(0)=\vec{v}_0$ and its position is constrained to the neighborhood of $\vec{r}_0$ by the smeared out probability density $W(\vec{r}_1(0)-\vec{r}_0)$. The long-time behavior of these partial averages is then calculated. Second, the results are averaged over all $\vec{v}_0$ and $\vec{r}_0$ in the equilibrium ensemble.

A decomposition into partial averages is obtained by the insertion of a factor $\delta(\vec{v}_1(0)-\vec{v}_0)W(\vec{r}_1(0)-\vec{r}_0)$ into the equilibrium average, and the correlation functions are accordingly rewritten as

$$\begin{aligned} C_\alpha^K(t) = \lim_{V\to\infty} V^{-1}&\int_V d\vec{r}_0 \int d\vec{v}_0 j_\alpha(\vec{v}_0) \int_V d\vec{r} \\ &\times\langle j_\alpha(\vec{r},t\,|\,\Gamma)\delta(\vec{v}_1(0)-\vec{v}_0)W(\vec{r}_1(0)-\vec{r}_0)N\rangle. \end{aligned} \tag{2.8}$$

We have here introduced the microscopic current densities

$$\begin{aligned} &j_D(\vec{r},t\,|\,\Gamma) = v_{1x}\delta(\vec{r}_1(t)-\vec{r}), \\ &j_\eta(\vec{r},t\,|\,\Gamma) = \textstyle\sum_i m\, v_{ix}(t)v_{iy}(t)\delta(\vec{r}_i(t)-\vec{r}), \\ &j_\lambda(\vec{r},t\,|\,\Gamma) = \textstyle\sum_i [\tfrac{1}{2}m\, v_i^2(t) - \tfrac{1}{2}(d+2)\beta^{-1}] \\ &\qquad\times v_{ix}(t)\delta(\vec{r}_i(t)-\vec{r}), \end{aligned} \tag{2.9}$$

where Γ indicates that j is a function of the initial phases. By direct integration, one verifies that (2.8) reduces to (2.6) if the otherwise arbitrary function $W(\vec r)$ is normalized to unity:

$$\int d\vec r\, W(\vec r) = 1. \tag{2.10}$$

This arbitrariness will later prove useful. We shall choose $W(\vec r)$ to be slowly varying.

Finally, the partial averages are written as averages over a normalized nonequilibrium ensemble $\langle \cdots \rangle_n$, defined for an arbitrary F by

$$\begin{aligned}\langle F(\vec r, t\,|\,\Gamma)\,\delta(\vec v_1(0)-\vec v_0)\,W(\vec r_1(0)-\vec r_0)N\rangle &\equiv \langle \delta(\vec v_1(0)-\vec v_0)W(\vec r_1(0)-\vec r_0)N\rangle \\ &\qquad \times\langle F(\vec r, t\,|\,\Gamma)\rangle_n \\ &= f_0(v_0)\langle F(\vec r, t\,|\,\Gamma)\rangle_n\,,\end{aligned} \tag{2.11}$$

where $f_0(v_0) = n(\beta m/2\pi)^{d/2}\exp(-\frac{1}{2}\beta m v_0^2)$ is the equilibrium one-particle distribution function. The correlation function (2.8) can now be expressed as

$$\begin{aligned}C_\alpha^K(t) &= \lim_{V\to\infty} V^{-1}\int_V d\vec r_0 \int d\vec v_0\, f_0(v_0)\, j_\alpha(\vec v_0) \\ &\qquad \times \int_V d\vec r\,\langle j_\alpha(\vec r, t\,|\,\Gamma)\rangle_n\,.\end{aligned} \tag{2.12}$$

III. ASSUMPTIONS

The manipulations of Sec. II were purely formal and no simplifying assumptions have thus far been introduced. In particular, the time evolution of the constrained averages in (2.12) involves the full N-body Liouville equation.

In order to proceed we now formulate two simplifying assumptions that will enable us to introduce hydrodynamic concepts and on which the subsequent development is based. The first assumption concerns the rate at which the initial nonequilibrium distribution approaches a local equilibrium distribution, and the second one concerns the equations governing the time evolution from local to total equilibrium.

For the purpose of giving these assumptions a precise form, we associate the hydrodynamic fields $n(\vec r, t)$ (number density), $\vec u(\vec r, t)$ (velocity), $e(\vec r, t)$ (energy density), and $P(\vec r, t)$ (probability density of particle 1), to the nonequilibrium ensemble in the following way:

$$\begin{aligned} n(\vec r, t) &= \langle \textstyle\sum_i \delta(\vec r_i(t)-\vec r)\rangle_n\,, \\ n(\vec r, t)\vec u(\vec r, t) &= \langle \textstyle\sum_i \vec v_i(t)\,\delta(\vec r_i(t)-\vec r)\rangle_n\,, \\ e(\vec r, t) &= \langle \textstyle\sum_i e_i(t)\,\delta(\vec r_i(t)-\vec r)\rangle_n\,, \\ P(\vec r, t) &= \langle \delta(\vec r_1(t)-\vec r)\rangle_n\,, \end{aligned} \tag{3.1}$$

where e_i is the energy of particle i,

$$e_i = \tfrac{1}{2} m v_i^2 + \tfrac{1}{2}\textstyle\sum_j{}'\,\Phi(r_{ij})\,. \tag{3.2}$$

Our first assumption then reads as follows.

Assumption I

The approach of the nonequilibrium distribution to a local equilibrium distribution is faster than the asymptotic decay of the correlation functions.

As we are only concerned in this paper with the decay of the kinetic parts of the correlation functions, we will use I only as a statement about the approach of the one-particle distribution function $f(\vec r, \vec v, t)$, defined by

$$f(\vec r, \vec v, t) = \langle \textstyle\sum_i \delta(\vec r_i(t)-\vec r)\,\delta(\vec v_i(t)-\vec v)\rangle_n\,, \tag{3.3}$$

to the local equilibrium distribution function, defined by

$$\begin{aligned} f_l(\vec r, \vec v, t) &= n(\vec r, t)\,[m/2\pi k_B T(\vec r, t)]^{d/2} \\ &\qquad \times \exp[-\tfrac{1}{2} m(\vec v - \vec u(\vec r, t))^2/k_B T(\vec r, t)]. \end{aligned} \tag{3.4}$$

The temperature field $T(\vec r, t)$ in (3.4) is constructed through the relation

$$\delta T(\vec r, t) = \left(\frac{\partial T}{\partial n}\right)_e \delta n(\vec r, t) + \left(\frac{\partial T}{\partial e}\right)_n \delta e(\vec r, t)\,, \tag{3.5}$$

where $\delta T(\vec r, t) = T(\vec r, t) - T$, $\delta n(\vec r, t) = n(\vec r, t) - n$, and $\delta e(\vec r, t) = e(\vec r, t) - e$ are the deviations of the hydrodynamic fields from their equilibrium values. The derivatives of the temperature are taken at equilibrium.

Using I in the sense that for the calculation of the asymptotics, (3.4) can be substituted for (3.3), one can write for the currents ($\alpha = \eta, \lambda$) in the nonequilibrium ensemble after a sufficiently long time

$$\langle j_\alpha(\vec r, t\,|\,\Gamma)\rangle_n \simeq \int d\vec v\, j_\alpha(\vec v) f_l(\vec r, \vec v, t)\,, \tag{3.6}$$

which gives for the shear- and heat-current densities

$$\begin{aligned} \langle j_\eta(\vec r, t\,|\,\Gamma)\rangle_n &\simeq m\,n(\vec r, t)\,u_x(\vec r, t)\,u_y(\vec r, t), \\ \langle j_\lambda(\vec r, t\,|\,\Gamma)\rangle_n &\simeq \tfrac{1}{2}(d+2)k_B n(\vec r, t)\,\delta T(\vec r, t)\,u_x(\vec r, t) \\ &\qquad + \tfrac{1}{2} m\,n(\vec r, t)\,u^2(\vec r, t)\,u_x(\vec r, t). \end{aligned} \tag{3.7}$$

For the velocity autocorrelation function we need assumption I for the probability density $f^s(\vec r, \vec v, t)$ of finding the tagged particle 1 at position $\vec r$ with velocity $\vec v$. The local equilibrium form for $f^s(\vec r, \vec v, t)$ is the same as (3.4) with $n(\vec r, t)$ replaced by the probability density $P(\vec r, t)$. The current density associated with the tagged particle is thus for sufficiently long times

$$\langle j_D(\vec r, t\,|\,\Gamma)\rangle_n \simeq u_x(\vec r, t)\,P(\vec r, t). \tag{3.8}$$

The results of the present section can be summarized as follows. It is a consequence of assumption I that for the determination of the asymptotic time behavior of the correlation functions one can replace the constrained averages in (2.12) by products of hydrodynamic fields as given by (3.7) and (3.8).

To carry out actual computations, one needs the precise form of the equations governing the asymptotic decay of the hydrodynamic fields. Consequently a second assumption is called for.

Assumption II

The long-wavelength components of $n(\vec{r}, t)$, $\vec{u}(\vec{r}, t)$, and $T(\vec{r}, t)$ obey the linearized Navier-Stokes equations for sufficiently long times. In the same sense, $P(\vec{r}, t)$ is governed by the diffusion equation.

In Sec. V it will be shown that both the use of linearized equations and the restriction to the long-wavelength regime can be formally justified by an appropriate choice of the function $W(\vec{r}-\vec{r}_0)$.

When the linearized rather than the full Navier-Stokes equations are used,[8] consistency requires that only the leading terms (which are of second order) in the deviations from over-all equilibrium be kept in (3.7). The resulting expressions are

$$\begin{aligned} \langle j_\eta(\vec{r}, t \,|\, \Gamma)\rangle_n &\simeq m\,n\,u_x(\vec{r}, t)u_y(\vec{r}, t), \\ \langle j_\lambda(\vec{r}, t \,|\, \Gamma)\rangle_n &\simeq \tfrac{1}{2}(d+2)k_B n\,\delta T(\vec{r}, t)u_x(\vec{r}, t)\,. \end{aligned} \tag{3.9}$$

We make the following comments.

(i) That the third order products neglected in (3.9) do not contribute to the long time tails is shown explicitly in Appendix A.

(ii) It is well known from transport theory based on the Boltzmann equation that the deviations from the local equilibrium distribution $f_l(\vec{r}, \vec{v}, t)$ can never be completely neglected, since they represent the forces driving the hydrodynamic development towards over-all equilibrium. These corrections to $f_l(\vec{r}, \vec{v}, t)$ do not influence the asymptotic behavior of the correlation functions, however, as will be shown at the end of Sec. IV.

(iii) The standard form of the hydrodynamic equations is valid only when the system is close to local equilibrium. In particular, the existence of a single temperature field implies local equilibrium between the kinetic and the potential energy densities. As a consequence, assumptions I and II contain the assumption that part of the initial excess of kinetic energy $\frac{1}{2}(mv_0^2 - d k_B T)$ (see Sec. V) is rapidly transformed into potential energy. Only after this transformation has taken place is the kinetic energy density related to the temperature in the usual manner.

(iv) The preceding remarks serve to emphasize the point that (3.5) has thermodynamic significance only after local equilibrium has been established. For shorter times it should be viewed as nothing more than a convenient construction, motivated by the fact that in the standard formulation of hydrodynamics, the field $T(\vec{r}, t)$ is used rather than $e(\vec{r}, t)$.

(v) It is interesting to consider an example for which assumption I is *not* valid. In the Lorentz model,[9] local equilibrium means that the velocity of the moving particles has a uniform angular distribution. Consequently, approach to local equilibrium and decay of $\langle v_{1x}(0)v_{1x}(t)\rangle$ are inseparable in this model. It is therefore reassuring that if one nevertheless makes assumption I and calculates the asymptotic decay of the velocity autocorrelation function according to the method of the present paper, one finds that the hydrodynamic tail is identically zero.

IV. LINEARIZED HYDRODYNAMICS

The linearized hydrodynamic equations[10] on the Navier-Stokes level can be written in the form

$$\begin{aligned} \frac{\partial n(\vec{r}, t)}{\partial t} &= -n\,\nabla\cdot\vec{u}(\vec{r}, t)\,, \\ \frac{\partial \vec{u}(\vec{r}, t)}{\partial t} &= -(c_0^2/\gamma n)\,\nabla n(\vec{r}, t) + \nu\,\nabla^2\vec{u}(\vec{r}, t) \\ &\quad + (D_l - \nu)\,\nabla(\nabla\cdot\vec{u}(\vec{r}, t)) - (c_0^2\alpha/\gamma)\,\nabla T(\vec{r}, t), \\ \frac{\partial T(\vec{r}, t)}{\partial t} &= -[(\gamma-1)/\alpha]\,\nabla\cdot\vec{u}(\vec{r}, t) + \gamma D_T\nabla^2 T(\vec{r}, t), \end{aligned} \tag{4.1}$$

where $\gamma = C_p/C_v$ is the ratio of the specific heats per particle at constant pressure and density respectively, $p = p(n, T)$ is the equilibrium pressure, $\alpha = -n^{-1}(\partial n/\partial T)_p$ is the thermal expansion coefficient, $c_0 = [m^{-1}\gamma(\partial p/\partial n)_T]^{1/2}$ is the long-wavelength sound velocity, $\nu = \eta/nm$ is the kinematic viscosity, ζ is the bulk viscosity, $D_T = \lambda/nC_p$ is the thermal diffusivity, and $D_l = n^{-1}m^{-1}[2d^{-1}(d-1)\eta + \zeta]$.

In addition, the diffusion equation governing the probability density of particle 1 reads

$$\frac{\partial P(\vec{r}, t)}{\partial t} = D\,\nabla^2 P(\vec{r}, t). \tag{4.2}$$

We shall need the general solutions of (4.1) and (4.2) in terms of the initial distributions of $n(\vec{r}, 0)$, $\vec{u}(\vec{r}, 0)$, $T(\vec{r}, 0)$, and $P(r, 0)$. After the introduction of the hydrodynamic fields in (2.12) by means of (3.8) and (3.9), the passage to the thermodynamic limit $V \to \infty$ has become a mere formality, and thus the only boundary conditions which the hydrodynamic fields must obey are the trivial ones at infinity $n(\vec{r} \to \infty, t) = n$, $\vec{u}(\vec{r} \to \infty, t) = 0$, $T(\vec{r} \to \infty, t) = T$, $P(\vec{r} \to \infty, t) = 0$. In order to solve the initial-value problem of (4.1) and (4.2), it is convenient to introduce Fourier transforms

$$n_k(t) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, \delta n(\vec{r}, t) \tag{4.3}$$

and similarly for $\vec{u}(\vec{r}, t)$, $\delta T(\vec{r}, t)$ and $P(\vec{r}, t)$. Equation (4.1) and (4.2) transform to

$$\begin{aligned}
\frac{\partial n_k}{\partial t} &= -n\, i\vec{k}\cdot\vec{u}_k\, ,\\
\frac{\partial \vec{u}_k}{\partial t} &= \frac{c_0^2}{\gamma n} i\, \vec{k} n_k - \nu k^2 \vec{u}_k - (D_l - \nu)\vec{k}\,(\vec{k}\cdot\vec{u}_k) - \frac{c_0^2\alpha}{\gamma}\, i\vec{k}\, T_k\, ,\\
\frac{\partial T_k}{\partial t} &= -\frac{\gamma-1}{\alpha}\, i\,\vec{k}\cdot\vec{u}_k - \gamma D_T k^2 T_k\, ,\\
\frac{\partial P_k}{\partial t} &= -D k^2 P_k\, .
\end{aligned} \tag{4.4}$$

The diffusion equation is immediately integrated to give

$$P_k(t) = P_k(0) e^{-Dk^2 t}. \tag{4.5}$$

Similarly, by separating the longitudinal and transverse parts of $\vec{u}_k$ (with respect to $\vec{k}$)

$$\vec{u}_k = \hat{k}(\hat{k}\cdot\vec{u}_k) + [\vec{u}_k - \hat{k}(\hat{k}\cdot\vec{u}_k)], \tag{4.6}$$

where $\hat{k} = \{\hat{k}_x, \hat{k}_y, \ldots\} = \vec{k}/|\vec{k}|$, one sees from (4.4) that the transverse part does not couple to n_k and T_k and one has[11]

$$\vec{u}_k(t) - \hat{k}(\hat{k}\cdot\vec{u}_k(t)) = [\vec{u}_k(0) - \hat{k}(\hat{k}\cdot\vec{u}_k(0))] e^{-\nu k^2 t}. \tag{4.7}$$

The three coupled equations for n_k, $\hat{k}\cdot\vec{u}_k$, and T_k can subsequently be solved to give

$$\begin{aligned}
n_k(t) &= n c_0^{-1}\{A_k^+(0)\exp(-\omega_k^+ t) + A_k^-(0)\exp(-\omega_k^- t)\}\\
&\qquad + A^H(0)\exp(-\omega_k^H t)\, ,\\
\hat{k}\cdot\vec{u}_k(t) &= A_k^+(0)\exp(-\omega_k^+ t) - A_k^-(0)\exp(-\omega_k^- t)\, , \qquad (4.8)\\
T_k(t) &= (\gamma-1)c_0^{-1}\alpha^{-1}\{A_k^+(0)\exp(-\omega_k^+ t) + A_k^-(0)\\
&\qquad \times\exp(-\omega_k^- t)\} - n^{-1}\alpha^{-1}A^H(0)\exp(-\omega_k^H t)\, ,
\end{aligned}$$

where

$$\begin{aligned}
\omega_k^{\pm} &= \pm i c_0 k + \tfrac{1}{2}\Gamma_s k^2\, , \quad \omega_k^H = D_T k^2\, ,\\
A_k^{\pm}(0) &= \tfrac{1}{2}\{c_0 n^{-1}\gamma^{-1}[n_k(0) + n\alpha T_k(0)] \pm \hat{k}\cdot\vec{u}_k(0)\}\, , \qquad (4.9)\\
A^H(0) &= \gamma^{-1}\{(\gamma-1)n_k(0) - n\alpha T_k(0)\}\, ,
\end{aligned}$$

and the sound-wave damping constant is given by

$$\Gamma_s = D_l + (\gamma-1)D_T\, . \tag{4.10}$$

Since these are the quantities occurring directly in (3.8) and (3.9), we have chosen to give the general solution in terms of the fields P_k, n_k, $\vec{u}_k$, and T_k. One could, however, regard (4.4) as a matrix equation and proceed to diagonalize it. In this way one would be led to the "hydrodynamic modes," defined as the eigenfunction, decaying like $\exp(-w_k^i t)$, produced by the diagonalization. The self-diffusion mode ($\omega_k^i = \omega_k^D = Dk^2$) and the $d-1$ viscous modes ($i = \epsilon = 1, \ldots, d-1$; $\omega_k^\epsilon = \nu k^2$) are already given explicitly by (4.5) and (4.7), while the two sound modes ($i = \pm$) and the heat mode ($i = H$) are linear combinations of n_k, $\hat{k}\cdot\vec{u}_k$ and T_k as seen from (4.8) and (4.9). Combination of (2.12) with (3.8) and (3.9) yields, after introduction of Fourier transforms,

$$C_D(t) \simeq \int d\vec{v}_0 f_0(v_0) v_{0x} (2\pi)^{-d} \int d\vec{k}\, u_{kx}(t) P_{-k}(t)\, , \tag{4.11}$$

$$C_\eta^K(t) \simeq m^2 n \int d\vec{v}_0 f_0(v_0) v_{0x} v_{0y} (2\pi)^{-d} \int d\vec{k}\, u_{kx}(t) u_{-ky}(t)\, , \tag{4.12}$$

$$\begin{aligned}
C_\lambda^K(t) &\simeq \tfrac{1}{2}(d+2)k_B n \int d\vec{v}_0 f_0(v_0) v_{0x}[\tfrac{1}{2} m v_0^2 - (d+2)/2\beta]\\
&\qquad \times (2\pi)^{-d}\int d\vec{k}\, u_{kx}(t) T_{-k}(t)\, .
\end{aligned} \tag{4.13}$$

The long-time decay of the correlation functions (4.11)–(4.13) is determined by the behavior of the integrands for small k. The leading terms are those for which $(\omega_k^i + \omega_k^j) \simeq \mathrm{const}\times k^2$ for small k, and asymptotically one has

$$\int d\vec{k}\, F_k(t=0)\exp(-\mathrm{const}\times k^2 t) \simeq \mathrm{const}'\times F_0(t=0) t^{-d/2}\, . \tag{4.14}$$

As already mentioned at the end of Sec. III, the corrections to the local equilibrium distribution function do not influence the dominant asymptotic behavior. Such corrections, if taken into account, give rise to contributions proportional to the gradients of the hydrodynamic fields. In addition, these contributions may or may not contain hydrodynamic fields as factors. In either case, the gradient introduces an extra factor of k in the Fourier transform, and one easily sees that such terms, if they do not vanish, decay faster than $t^{-d/2}$.

From (4.14) it is clear that to complete the calculation one needs the properly chosen initial values of the hydrodynamic fields in the $k \to 0$ limit. These initial values will be the subject of Sec. V.

V. INITIAL VALUES

The question concerning the appropriate initial values for the hydrodynamic fields in a system fundamentally governed by the Liouville equation is in general a nontrivial one.[12] The point can be understood by considering the decay of a Fourier component $n_k(t)$ of the constrained average of the density deviation $\langle \sum_i \delta(\vec{r}_i(t) - \vec{r}) - n\rangle_n$. A typical case is sketched in Fig. 1.

The fully drawn curve shows the exact development of $n_k(t)$ according to the Liouville equation. The initial value A_k is simply the value of $n_k(0)$ as calculated in the constrained ensemble. For short times, $n_k(t)$ evolves in a complicated fashion, but

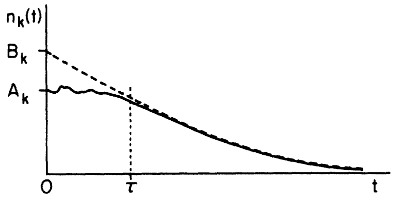

FIG. 1. Decay of $n_k(t)$.

for t larger than some characteristic time τ, it approaches the dashed curve which depicts the decay as given by hydrodynamics. In order to select that hydrodynamic curve with which the exact one asymptotically coincides, one should *not* use A_k as the initial value, however, but B_k, obtained by backward extrapolation of the dashed curve. It is evident that the precise relation between B_k and A_k is in general very complicated and involves in principle the full solution of the Liouville equation.

However, since the total number of particles is a constant of the motion for every member of the ensemble, it must also be conserved for the constrained average (2.11), i.e.,

$$\int d\vec{r}\,\langle\textstyle\sum_i\delta(\vec{r}_i(t)-\vec{r})-n\rangle_n=\lim_{k\to 0} n_k(t)=\text{const.} \qquad (5.1)$$

The validity of (5.1) for all times implies, in particular, for $t=0$, that

$$\lim_{k\to 0} B_k=\lim_{k\to 0} A_k\ , \qquad (5.2)$$

and it follows from (4.14) that for a calculation of the asymptotic tails of (4.11)–(4.13) one is justified in using the initial value $n_k(0)$ as calculated in the constrained ensemble (2.11).

The same argument holds for the remaining conserved quantities and as a result the initial values of the velocity field $\vec{u}_k$, the energy density field e_k, and the tagged particle field P_k are, in the $k\to 0$ limit, those calculated in the constrained ensemble. From the initial values of n_k and e_k, the initial value of the temperature field T_k is found (again in the $k\to 0$ limit) by use of relation (3.5).

We now proceed to calculate $\delta n(\vec{r},0)$, $\vec{u}(\vec{r},0)$, $\delta e(\vec{r},0)$, $\delta T(\vec{r},0)$, and $P(\vec{r},0)$ in the constrained ensemble (2.11). First $\delta n(\vec{r},0)$:

$$\begin{aligned} n(\vec{r},0)&=\langle\textstyle\sum_i\delta(\vec{r}_i(0)-\vec{r})\rangle_n\\ &=n^{-1}\langle\textstyle\sum_i\delta(\vec{r}_i-\vec{r})NW(\vec{r}_1-\vec{r}_0)\rangle\ , \end{aligned} \qquad (5.3)$$

where (2.11) has been used and one writes $\vec{r}_i(0)=\vec{r}_i$ for simplicity. Rewriting (5.3), using the symmetry in the particle label, one finds

$$n(\vec{r},0)=n^{-1}\int d\vec{r}\,W(\vec{r}\,'-\vec{r}_0)\langle\textstyle\sum_i\delta(\vec{r}_i-\vec{r})\sum_j\delta(\vec{r}_j-\vec{r}\,')\rangle\ ,$$

$$\delta n(\vec{r},0)=n^{-1}\int d\vec{r}\,'\,W(\vec{r}\,'-\vec{r}_0)\langle\delta n(\vec{r}\,|\,\Gamma)\delta n(\vec{r}\,'\,|\,\Gamma)\rangle\ , \qquad (5.4)$$

In the last step the product of the average $\langle n(\vec{r}\,|\,\Gamma)\rangle\times\langle n(\vec{r}\,'\,|\,\Gamma)\rangle=n^2$ was subtracted and the normalization (2.10) used.

At this point our freedom in the choice of $W(\vec{r})$ mentioned in Sec. II, proves useful. The equilibrium correlation function $\langle\delta n(\vec{r}\,|\,\Gamma)\delta n(\vec{r}\,'\,|\,\Gamma)\rangle$ is practically zero for $|\vec{r}-\vec{r}\,'|\gg\Lambda_c$, where Λ_c is an equilibrium correlation length. If one is not too close to the critical point, Λ_c will be of the order of the range of the interparticle forces. Choosing $W(\vec{r}\,'-\vec{r}_0)$ to be slowly varying over distances of the order Λ_c, one is entitled to pull $W(\vec{r}-\vec{r}_0)$ outside the integral, and use of the density-density fluctuation theorem of equilibrium statistical mechanics then yields

$$\delta n(\vec{r},0)=\beta^{-1}\left(\frac{\partial n}{\partial p}\right)_T W(\vec{r}-\vec{r}_0)\ . \qquad (5.5)$$

For the initial velocity field (2.11) and (3.1) give

$$\begin{aligned} n(\vec{r},0)\vec{u}(\vec{r},0)&=f_0^{-1}(v_0)\langle\textstyle\sum_i\vec{v}_i\delta(\vec{r}_i-\vec{r})\\ &\qquad\times N\delta(\vec{v}_1-\vec{v}_0)W(\vec{r}_1-\vec{r}_0)\rangle\\ &=n^{-1}\vec{v}_0\langle N\delta(\vec{r}_1-\vec{r})W(\vec{r}_1-\vec{r}_0)\rangle\ . \end{aligned} \qquad (5.6)$$

To lowest order in deviations from over-all equilibrium one can neglect δn as compared to n, and (5.6) thereby simplified to

$$\vec{u}(\vec{r},0)=n^{-1}\vec{v}_0W(\vec{r}-\vec{r}_0)\ . \qquad (5.7)$$

Furthermore we need the initial energy density

$$\begin{aligned} e(\vec{r},0)&=f_0^{-1}(v_0)\langle\textstyle\sum_i e_i\delta(\vec{r}_i-\vec{r})\\ &\qquad\times N\delta(\vec{v}_1-\vec{v}_0)W(\vec{r}_1-\vec{r}_0)\rangle\ , \end{aligned} \qquad (5.8)$$

where e_i is given by (3.2). The factor $\delta(\vec{v}_1-\vec{v}_0)$ only affects the kinetic part of e_1, and (5.8) can thus be written

$$\begin{aligned} e(\vec{r},0)&=(\tfrac{1}{2}mv_0^2-\tfrac{1}{2}d\beta^{-1})W(\vec{r}-\vec{r}_0)\\ &\quad+n^{-1}\langle\textstyle\sum_i e_i\delta(\vec{r}_i-\vec{r})NW(\vec{r}_1-\vec{r}_0)\rangle\ . \end{aligned} \qquad (5.9)$$

The subtraction of $\frac{1}{2}d\beta^{-1}$ in (5.9) compensates for the fact that the kinetic part of e_1 has again been included in the $\sum_i$. By steps corresponding to those that led from (5.3) through (5.4) to (5.5), one arrives at

$$\begin{aligned} \delta e(\vec{r},0)&=[\tfrac{1}{2}mv_0^2-\tfrac{1}{2}d\beta^{-1}+n^{-1}\textstyle\int d\vec{r}\,'\\ &\qquad\times\langle\delta e(\vec{r}\,|\,\Gamma)\delta n(\vec{r}\,'\,|\,\Gamma)\rangle]W(\vec{r}-\vec{r}_0)\\ &=\left[\tfrac{1}{2}mv_0^2-\tfrac{1}{2}d\beta^{-1}+n^{-1}\beta^{-1}\left(\frac{\partial e}{\partial\mu}\right)_T\right]W(\vec{r}-\vec{r}_0)\ , \end{aligned} \qquad (5.10)$$

where μ is the chemical potential and the mixed density-energy fluctuation theorem was used in the final step.

From the results (5.5) and (5.10) and the relations (3.5) and $(\partial p/\partial\mu)_T = n$, one obtains the proper initial data for the temperature field:

$$\delta T(\vec{r}, 0) = (nC_v)^{-1}[\tfrac{1}{2}mv_0^2 - \tfrac{1}{2}d\beta^{-1}]W(\vec{r}-\vec{r}_0) \ . \qquad (5.11)$$

Finally the one-particle field $P(\vec{r}, 0)$ at $t=0$ is needed. From the definition (3.1) one finds immediately

$$\begin{aligned} P(\vec{r}, 0) &= f_0^{-1}(v_0)\langle\delta(\vec{r}_1-\vec{r})N\delta(\vec{v}_1-\vec{v}_0)W(\vec{r}_1-\vec{r}_0)\rangle \\ &= W(\vec{r}-\vec{r}_0) \ . \end{aligned} \qquad (5.12)$$

We make the following comments.

(i) The most important property of the calculated initial data (5.6), (5.8), (5.12), and (5.13) is that they are all controlled by the form of $W(\vec{r}-\vec{r}_0)$. In the passing from (5.4) to (5.5) we already capitalized on our freedom with regard to W by choosing it to be slowly varying on the scale of an equilibrium correlation length Λ_c. One can go a step further, however, and choose W to be sufficiently slowly varying that only Fourier components with small k are present from the beginning. This amounts to the requirement that $\Lambda/l \ll 1$, where Λ is the mean free path, and l is the linear dimension of the region covered by $W(\vec{r}-\vec{r}_0)$. In a liquid $\Lambda \sim \Lambda_c$, but in a gas $\Lambda \gg \Lambda_c$. One can easily show that the stronger requirement $\Lambda/l \ll 1$ not only implies $\Lambda_c/l \ll 1$, but also, because of the normalization (2.10), $\delta n/n \ll 1$, $u(\beta m)^{1/2} \ll 1$, and $\delta T/T \ll 1$ for v_0 within the thermal range. The above reasoning provides a formal justification for (a) restricting one's consideration to small values of k, and (b) describing the decay by linearized hydrodynamics and for consistently retaining only the lowest-order terms in the deviations from complete equilibrium. For the argument to be valid, however, one should find *a posteriori* that the final results are independent of the shape of $W(\vec{r}-\vec{r}_0)$.

(ii) The linear dimensions l of the region covered by $W(\vec{r}-\vec{r}_0)$ are, however, intimately connected with the time scale on which our asymptotic results become relevant. On the basis of (4.8) and (4.11)–(4.13) one finds that (4.14) can be used only after a time of the order l^2/Δ, where Δ is the appropriate combination of damping constants (ν, D, D_T, Γ_s, see Sec. VI). For this reason the spatial extent of $W(\vec{r}-\vec{r}_0)$ cannot be increased indefinitely.

(iii) Finally we give a word of caution on the calculation of the initial temperature field. *After* local equilibrium has been established the temperature is related to the kinetic energy density in the usual manner:

$$\langle\textstyle\sum_i m[\vec{v}_i(t)-\vec{u}(\vec{r}, t)]^2\delta(\vec{r}_i(t)-\vec{r})\rangle_n = dk_B\, n(\vec{r}, t)T(\vec{r}, t) \ . \qquad (5.13)$$

If one erroneously had based the calculation of $\delta T(\vec{r}, 0)$ on (5.13) rather than proceeding via (3.5) and the densities $\delta n(\vec{r}, 0)$, and $\delta e(\vec{r}, 0)$ of the conserved quantities, one would have obtained the same result (5.11), except that $\tfrac{1}{2}dk_B$ would have replaced C_v. For an ideal gas (of molecules without internal degrees of freedom) or a hard sphere gas, this result would remain valid, but for any other system it would be incorrect since part of the initial excess of kinetic energy is transformed into potential energy when local equilibrium is established [see comment (iii), at the end of Sec. III]. Equivalently one might say that (5.13) fails to give the correct initial data for the temperature field because (5.2) does not hold for the density of the (nonconserved) kinetic energy.

VI. RESULTS

We are now in a position to calculate the asymptotic tails of the correlation functions (4.11)–(4.13). Consider first the simplest one, $C_D(t)$. According to the discussion at the end of Sec. IV, the combinations for which $\omega_k^i + \omega_k^j = O(k^2)$ will be the dominant ones asymptotically. Inspection of (4.6)–(4.8) then shows that only the transverse part (4.7) of $\vec{u}_k$ is relevant when combined with P_{-k} of (4.5). Insertion of (4.7) and (4.5) into (4.11) with initial values (5.7) and (5.12) yields

$$\begin{aligned} C_D(t) &\simeq \int d\vec{v}_0 v_{0x} f_0(v_0) \int \frac{d\vec{k}}{(2\pi)^d} n^{-1}[v_{0x} - \hat{k}_x(\hat{k}\cdot\vec{v}_0)]\ W_k|^2 \\ &\qquad \times \exp[-(\nu + D)k^2 t] \\ &= \beta^{-1}m^{-1}(2\pi)^{-d}\int d\vec{k}(1-\hat{k}_x^2)|W_k|^2\exp[-\nu + D)k^2 t] \ . \end{aligned} \qquad (6.1)$$

Angular integrations in d-dimensional space are readily performed on the basis of the results of Appendix B. The normalization (2.10) of W implies that $\lim_{k\to 0} W_k = 1$, so that finally

$$C_D(t) \simeq (d-1)(d\beta m)^{-1}[4\pi(\nu + D)t]^{-d/2} \ . \qquad (6.2)$$

Turning next to the shear viscosity correlation function $C_\eta^K(t)$ in (4.12), one notes that there are now *two* distinct combinations of modes for which $\omega_k^i + \omega_k^j = O(k^2)$. The transverse (shear) part of u_{kx} combined with the transverse part of u_{-ky} is clearly one. But also the combinations of sound modes, appearing in the longitudinal part of $\vec{u}_k$, in which ω_k^+ is combined with ω_k^-, satisfy the above requirement. Calculating the shear-shear part first, one inserts (4.7) and (5.7) into (4.12) to find

$$\begin{aligned} [C_\eta^K(t)]^{\epsilon\epsilon} &\simeq m^2 n^{-1}\int d\vec{v}_0 f_0(v_0)v_{0x}v_{0y} \\ &\qquad \times (2\pi)^{-d}\int d\vec{k}[v_{0x} - \hat{k}_x(\hat{k}\cdot\vec{v}_0)] \\ &\qquad \times [v_{0y} - \hat{k}_y(\hat{k}\cdot\vec{v}_0)]|W_k|^2\exp(-2\nu k^2 t) \end{aligned}$$

$$\simeq m^2 n^{-1}\int d\vec{v}_0 f_0(v_0) v_{0x}^2 v_{0y}^2 (2\pi)^{-d}$$

$$\times \int d\vec{k}\,[1-\hat{k}_x^2-\hat{k}_y^2+2\hat{k}_x^2\hat{k}_y^2]$$

$$\times \exp(-2\nu k^2 t)$$

$$= [(d^2-2)/d(d+2)\beta^2][8\pi\nu t]^{-d/2}\,. \qquad (6.3)$$

For the angular integrations we again refer to Appendix B. The sound-sound contribution follows from (4.6), (4.8), and (4.9):

$$[C_\eta^K(t)]^{+-} \simeq m^2 n \int d\vec{v}_0 f_0(v_0) v_{0x} v_{0y} (2\pi)^{-d}\int d\vec{k}\,\hat{k}_x \hat{k}_y$$

$$\times [A_{\hat{k}}^{+} A_{-\hat{k}}^{-} + A_{\hat{k}}^{-} A_{-\hat{k}}^{+}] \exp[-(\omega_k^{+}+\omega_k^{-})t]$$

$$\simeq m^2 n^{-1}\int d\vec{v}_0 f_0(v_0) v_{0x}^2 v_{0y}^2 (2\pi)^{-d}$$

$$\times \int d\vec{k}\,\hat{k}_x^2 \hat{k}_y^2 \exp(-\Gamma_s k^2 t)$$

$$= [1/d(d+2)\beta^2]\,[4\pi\Gamma_s t]^{-d/2}. \qquad (6.4)$$

Summation of (6.3) and (6.4) gives the complete asymptotic tail of $C_\eta^K(t)$

$$C_\eta^K(t) \simeq \frac{1}{d(d+2)\beta^2}\left(\frac{d^2-2}{(8\pi\nu t)^{d/2}}+\frac{1}{(4\pi\Gamma_s t)^{d/2}}\right). \qquad (6.5)$$

The heat conductivity correlation function $C_\lambda^K(t)$ of (4.13) remains to be considered. Inspection of (4.8) and (4.9) shows that again two distinct mode-mode combinations dominate asymptotically. Since both u_{kx} and T_{-k} contain sound terms, there is a sound-sound contribution. In addition, the transverse part of u_{kx} combines with the heat mode in T_{-k} to a shear-heat term. Consider the latter contribution first. On symmetry grounds, only the part of u_{kx} proportional to v_{0x} contributes, and because of the factor $v_{0x}^2[\frac{1}{2}mv_0^2-\frac{1}{2}(d+2)\beta^{-1}]$ in the integrand of (4.13), only the part of A^H proportional to v_0^2 survives the final integration over $\vec{v}_0$. Thus one finds from (4.7)–(4.9), (5.7) and (5.11):

$$[C_\lambda^K(t)]^{\epsilon H} \simeq \tfrac{1}{2}(d+2)k_B\, n^{-1}\int d\vec{v}_0 f_0(v_0) v_{0x}^2$$

$$\times [\tfrac{1}{2}mv_0^2-\tfrac{1}{2}(d+2)\beta^{-1}]$$

$$\times \tfrac{1}{2}mv_0^2\gamma^{-1}C_v^{-1}(2\pi)^{-d}$$

$$\times \int d\vec{k}\,(1-\hat{k}_x^2)\,|W_k|^2 \exp[-(\nu+D_T)k^2 t]$$

$$\simeq \frac{(d+2)^2(d-1)k_B}{4dC_p m\beta^3}\,[4\pi(\nu+D_T)t]^{-d/2}\,. \qquad (6.6)$$

The arguments used to simplify the calculation of the shear-heat term (6.6) also apply to the sound-sound term:

$$[C_\lambda^K(t)]^{+-} \simeq \tfrac{1}{2}(d+2)k_B\, n\int d\vec{v}_0 f_0(v_0) v_{0x}$$

$$\times [\tfrac{1}{2}mv_0^2-\tfrac{1}{2}(d+2)\beta^{-1}]$$

$$\times (\gamma-1)c_0^{-1}\alpha^{-1}(2\pi)^{-d}$$

$$\times \int d\vec{k}\,\hat{k}_x [A_{\hat{k}}^{+} A_{-\hat{k}}^{-} - A_{\hat{k}}^{-} A_{-\hat{k}}^{+}] \exp(-\Gamma_s k^2 t)$$

$$\simeq \frac{(d+2)^2(\gamma-1)k_B}{4dC_p m\beta^3}\,[4\pi\Gamma_s t]^{-d/2}\,. \qquad (6.7)$$

The complete asymptotic tail of $C_\lambda^K(t)$ follows by summation of (6.6) and (6.7):

$$C_\lambda^K(t) \simeq \frac{(d+2)^2 k_B}{4dC_p m\beta^3}\left(\frac{d-1}{[4\pi(\nu+D_T)t]^{d/2}}+\frac{\gamma-1}{[4\pi\Gamma_s t]^{d/2}}\right). \qquad (6.8)$$

Note that since only the limit $k\rightarrow 0$ of W_k was needed in the above calculation, all our results are independent of the shape of $W(\vec{r}-\vec{r}_0)$, as was required.

VII. DISCUSSION

The crucial step in the present work is clearly represented by assumption I. The validity of this assumption must ultimately be decided on the basis of a more fundamental theory. In the absence of a proof from first principles, some support for our premise can be found in Refs. 1 and 3.

Alder and Wainwright[1] compared their molecular-dynamics calculation of the velocity autocorrelation function in two and three dimensions with the numerical solution of the Navier-Stokes equation and found that the hydrodynamical model could adequately reproduce the data after only 10–20 mean free times between collisions. In particular, the $t^{-d/2}$ decay seems well established on this time scale for $d=2$ and 3.

Dorfman and Cohen,[3] on the basis of kinetic theory, studied the asymptotic decay of $C_D(t)$, $C_\eta^K(t)$, and $C_\lambda^K(t)$. They also found a $t^{-d/2}$ decay and the coefficients (6.2), (6.5), and (6.8) check with their results in the low density regime. On the other hand, Dorfman and Cohen compared their results for the velocity autocorrelation function with those of Alder and Wainwright and found very good agreement.

The comparison of our results with the above-mentioned work is not so straightforward as it may seem, however. The case of two dimensions dramatically points to the difficulty. Since the integral over a long-time tail ~ t^{-1} does not exist, the integrated contributions to the transport coefficients from the tails of the correlation functions diverge for $d=2$. Our calculation of the tails themselves, however, was based on the premise that D, η, and λ are all finite. In two dimensions our results are thus self contradictory. The remarkable fact remains, however, that Alder and Wainwright seem to observe a t^{-1} decay of the velocity correlation function for $d=2$, and their data are beautifully fitted by the kinetic theory formula derived by Dorfman and Cohen. Also, if one simply ignores the inherent contradiction mentioned above and takes our result for $d=2$ at face value, it coincides with the kinetic theory formula in the low density limit!

A qualitative interpretation of these seemingly contradictory facts is suggested by considerations on the time scales involved. The molecular-dynamics experiments were restricted to times not exceeding 30 free mean times. For the interval 15–30 mean free times, Navier-Stokes hydrodynamics seems[1] to offer a reasonable description. With the existence of long-time tails in the correlation functions, however, one should not expect the transport coefficients to have attained their limiting values already on this time scale, since the slowly growing contributions from these tails have not yet had time to build up. (In this connection it is interesting to note that Alder and Wainwright at higher densities use the viscosity as determined by molecular dynamics and the diffusion coefficient given by the Enskog theory. Similarly, Dorfman and Cohen use the Enskog values for both D and η.) This distinction would only correspond to a minor quantitative correction in three dimensions, where the integrals over tails $\sim t^{-3/2}$ exist, whereas for $d=2$ it is of qualitative significance. Implicit in these remarks is the expectation that our basic assumption I remains valid in two dimensions, and that the difficulties should be attributed to the less fundamental assumption II. On the basis of this expectation one arrives at the conclusion that, although a consistent hydrodynamic theory is conceivable in two dimensions, it would not, even in the long-wavelength limit, be of the conventional Navier-Stokes form.[13]

Although the validity of the Navier-Stokes equations as a description of phenomena sufficiently slowly varying in space and time is not challenged for $d \geqslant 3$, an argument similar to the one above shows that the first correction to Navier-Stokes, as given by the Burnett equations, is meaningless[3,4] for $d=3$ and $d=4$. The precise region of validity of the Navier-Stokes description is therefore no longer entirely clear.

In contrast to work based on molecular dynamics and on kinetic theory which in principle can describe intermediate times as well as the true long-time behavior, our method yields asymptotic results only. An associated weakness of our theory is that it gives no prescription for the calculation of the first correction term, and as a result, the time scale on which the asymptotic form is actually approached cannot be determined in any but the loosest sense.

For small densities one can estimate the order of magnitude of the contributions from the integrated tails to the values of the transport coefficients. To this end, our asymptotic results (6.2), (6.5), and (6.8) should be integrated from some finite, characteristic time to infinity. As noted above, a precise value for this characteristic time cannot be determined by our method. It should, however, be proportional to the mean free time between collisions, i.e., for small densities of $O(n^{-1})$. Integrating the asymptotic results from $\tau = O(n^{-1})$ to ∞ one finds contributions to the order (Boltzmann value of the transport coefficient) $\times O(n^{d-1})$. This is precisely the order in which the well-known divergences in the density expansion of the transport coefficients manifest themselves.[14] That this fact is not an accidental one can be seen from the kinetic theory of Ref. 3.

On the basis of the present work it is natural to ask why the Boltzmann equation and theories of the Langevin type do not lead to the asymptotic decay found here. The point is that transport of a conserved quantity away from a local disturbance is, in a fluid, a slow process, eventually governed by the hydrodynamic modes. The effect of these slowly decaying modes back on the source of the disturbance can *not* be neglected in general. In the Boltzmann equation such a feedback is, however, automatically excluded by the "Stosszahlansatz." (A qualitative change in this respect is introduced by higher density corrections.[3]) It is also neglected in the classical Langevin equation which for this reason cannot be consistently applied to Brownian motion proper. (The latter fact was pointed out already by Lorentz,[15] but was subsequently overlooked and has only recently been rediscovered.[16])

Finally we make the following remarks.

(i) One can easily show that the potential terms do not contribute to the asymptotic tail of $C_\eta(t)$. The result (6.5) is therefore the long-time tail of the *complete* viscosity correlation function.

(ii) The contributions of the potential terms[4(b),17] to the asymptotic tails of the heat conductivity and bulk viscosity correlation functions will be discussed in a subsequent paper.

(iii) No reference to the detailed nature of the intermolecular forces, other than that implied by assumptions I and II, was made in the present work.

(iv) In particular, forces with a repulsive and an attractive part that produce phase transitions are not excluded. However, our assumptions must be modified close to critical points, and our analysis is thus not valid in the critical region.

(v) It is clearly of importance to investigate the consequence of the existence of the long-time tails discussed in this paper in the context of experimentally accessible phenomena. One of the candidates is the elastic incoherent neutron scattering by liquids. An attempt has been made to analyze the scattering data on liquid Ar in the light of the existence of a slowly decaying tail in the velocity autocorrelation function.[18]

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APPENDIX A: THREE-MODE TERMS

In this appendix we demonstrate that the three-mode terms decay faster than $t^{-d/2}$ and are thus irrelevant asymptotically. Take a typical example—the $\delta n(\vec{r},t)u_x(\vec{r},t)u_y(\vec{r},t)$ term neglected in the passing from (3.7) to (3.9). The problem at hand is to determine the asymptotic time dependence of the space integral of this term. In Fourier language one therefore considers

$$I(t)=v_{0x}v_{0y}\int d\vec{k}\,n_{-k}(t)\int d\vec{k}'\,u_{k',x}(t)\,u_{k-k',y}(t)\ . \qquad \text{(A1)}$$

From the discussion of the two-mode terms it follows that one of the leading contributions to $I(t)$ is the heat-shear-shear term. Using (4.7)-(4.8), and (5.8) one finds

$$\begin{aligned}I^{H\epsilon\epsilon}(t)=v_{0x}v_{0y}n^{-2}\int d\vec{k}\ d\vec{k}'A^H(0)W_{k'}W_{k-k'}\\ \times\{[v_{0x}-\hat{k}'_x(\hat{k}'\cdot\vec{v}_0)]\\ \times[v_{0y}-(k_y-k'_y)(\vec{k}-\vec{k}')\cdot\vec{v}_0|\vec{k}-\vec{k}'|^{-2}]\}\\ \times\exp[-D_Tk^2t-\nu k'^2t-\nu|\vec{k}-\vec{k}'|^2t]\ .\end{aligned} \qquad \text{(A2)}$$

The long-time decay is determined by the small $\vec{k}$, small $\vec{k}'$ behavior of the integral. One can therefore put $W_k=W_{k'}=W_{k-k'}=1$. The factor $\{\ \}$ depends on the directions of $\vec{k}$ and $\vec{k}'$, as well as on $\vec{v}_0$. Since it has a finite maximum proportional to $|\vec{v}_0|^2$, one can write

$$\begin{aligned}I^{H\epsilon\epsilon}(t)<Mv_0^4\int d\vec{k}\,d\vec{k}'\exp[-(a+c)k^2t\\ +2c\vec{k}\circ\vec{k}'t-(b+c)k'^2t],\end{aligned} \qquad \text{(A3)}$$

where M is independent of v_0 and t, and $a=D_T$, $b=c=\nu$. The $2d$-dimensional Gaussian integral can be readily performed to yield

$$I^{H\epsilon\epsilon}(t)<Mv_0^4(\pi^2/\Delta)^{d/2}t^{-d}\ , \qquad \text{(A4)}$$

where Δ^d is the determinant of the quadratic form in the exponential, i.e.,

$$\Delta=\begin{vmatrix}a+c & -c\\ -c & b+c\end{vmatrix}\ . \qquad \text{(A5)}$$

An upper bound of the form (A4) can be found for the other three-mode terms as well, and the asymptotic neglect of these terms is thereby justified. This conclusion is in conflict with the proposed explanation of the $t^{-d/2}$ tail given in Ref. 19.

APPENDIX B: ANGULAR INTEGRATIONS

In this appendix we give a simple method to carry out angular integrations in d dimensions. Consider an integral of the form $\int d\hat{k}\,\hat{k}_\alpha\hat{k}_\beta\hat{k}_\gamma\hat{k}_\delta\cdots$, where $\hat{k}_\alpha(\alpha=x,y,\ldots,\epsilon)$ are Cartesian components of d-dimensional unit vectors. The integration is to be carried out over a d-dimensional solid angle. Such integrals are only nonvanishing when the indices $(\alpha,\beta,\gamma,\delta,\ldots)$ are pairwise equal. Therefore, restricting our consideration to an integral with four indices we see that

$$\int d\hat{k}\,\hat{k}_\alpha\hat{k}_\beta\hat{k}_\gamma\hat{k}_\delta=C(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})\ , \qquad \text{(B1)}$$

where $\delta_{\alpha\beta}$ is a Kronecker δ. Owing to symmetry the three terms on the right-hand side of (B1) have the same coefficient, C, which can be determined by contractions. Take, e.g., $\alpha=\beta$ and $\gamma=\delta$, sum over all Cartesian components, and note that $\sum_\alpha\hat{k}_\alpha^2=1$. This yields

$$\sum_{\alpha,\gamma}\int d\hat{k}\,\hat{k}_\alpha^2\hat{k}_\gamma^2=\int d\hat{k}\equiv\Omega_d=Cd(d+2)\ , \qquad \text{(B2)}$$

where Ω_d is the surface of a d-dimensional sphere with radius equal to unity. Thus

$$\int d\hat{k}\,\hat{k}_\alpha\hat{k}_\beta\hat{k}_\gamma\hat{k}_\delta=\Omega_d[d(d+2)]^{-1}\{\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}\}\ . \qquad \text{(B3)}$$

By contraction this equation also yields

$$\int d\hat{k}\,\hat{k}_\alpha\hat{k}_\beta=\Omega_d d^{-1}\delta_{\alpha\beta}\ . \qquad \text{(B4)}$$

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[1] B. J. Alder and T. E. Wainwright, Phys. Rev. A 1, 18 (1970); see also B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970).

[2] R. Zwanzig and M. Bixon, Phys. Rev. A 2, 2005 (1970).

[3] J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Letters 25, 1257 (1970).

[4] (a) M. H. Ernst, E. H. Hauge, and J. M. J. van Leeu-

wen, Phys. Rev. Letters 25, 1254 (1970); (b) Phys. Letters 34A, 419 (1971).

[5] L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968).

[6] See, e.g., R. Zwanzig, Ann. Rev. Phys. Chem. 16, 67 (1965).

[7] The normalization chosen here coincides with that of Ref. 4(b). It differs, however, from that of Ref. 4(a).

[8] One obtains an *a posteriori* justification for using the linearized equation to compute the time dependence of the hydrodynamic fields in the entire spatial domain of importance to us, by inserting the *solution* of the linearized problem into the nonlinear *equation*. Comparison of orders of magnitude shows that the nonlinear term is indeed negligible for $|\vec{r}-\vec{r}_0|^2 \lesssim \nu t$.

[9] The asymptotic decay of the velocity correlation function for the Lorentz model is discussed on the basis of kinetic theory by M. H. Ernst and A. Weyland, Phys. Letters 34A, 39 (1971).

[10] See, e.g., L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959).

[11] By Fourier inversion one obtains from (4.7) essentially the double vortex flow pattern discussed in Ref. 1.

[12] The analogous point in connection with the contraction from the Boltzmann equation to hydrodynamics was considered in general by H. Grad, Phys. Fluids 6, 147 (1963). A specific example was discussed by E. H. Hauge, *ibid.* 13, 1201 (1970).

[13] This type of reasoning is implicit in a self-consistency argument, leading for $d=2$ to an asymptotic decay of the form $\sim (t\sqrt{\ln t})^{-1}$, as proposed by several authors: K. Kawasaki, Phys. Letters 34A, 12 (1971); T. E. Wainwright, B. J. Alder, and D. M. Gass, Phys. Rev. A 4, 233 (1971); J. R. Dorfman and E. G. D. Cohen (private communication); I. de Schepper and H. van Beijeren (private communication); R. Zwanzig, Proceedings of the International Union of Pure and Applied Physics Conference on Statistical Mechanics, 1971 (unpublished).

[14] J. R. Dorfman and E. G. D. Cohen, Phys. Letters 16, 124 (1965); J. Math. Phys. 8, 282 (1967); M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. 41, 292 (1969).

[15] H. A. Lorentz, *Lessen over Theoretische Natuurkunde. V. Kinetische Problemen* (1911-12) (E. J. Brill, Leiden, 1921). We are indebted to Professor M. S. Green for calling our attention to this work.

[16] A. Widom, Phys. Rev. A 3, 1394 (1971).

[17] K. Kawasaki, Progr. Theoret. Phys. (Kyoto) 45, 1691 (1971).

[18] C. D. Andriesse, Phys. Letters 33A, 419 (1970).

[19] K. Kawasaki, Phys. Letters 32A, 380 (1970).

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Self-Diffusion Model for Memory Functions in Classical Fluids*

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The Mori memory-function formalism is used to derive systematically a hierarchy of approximations relating the dynamic structure factor $S(k, \omega)$ of a dense classical fluid to its self-part $S_s(k, \omega)$. The formalism is applied to a column vector of dynamical variables whose components include the self and distinct parts, ρ_s and ρ_d, of the fluctuating density plus N time derivatives of these variables. Increasing N is analogous to a continued-fraction expansion of the memory functions, and builds in more short-time information about the correlation functions. In this manner approximations generated earlier by Vineyard, by Kerr, and by Ortoleva and Nelkin are concisely stated, and a new approximation which gives the first six frequency moments of $S(k, \omega)$ correctly is obtained. Since the sixth frequency moment of $S(k, \omega)$ is not known from molecular-dynamics calculations, it is used as a parameter to fit these calculations. Agreement for $S(k, \omega)$ to within a few percent is obtained for several k values and two thermodynamic states. The deduced value of the sixth frequency moment has a reasonable dependence on k, and may give useful information about the three-particle static correlation function.

I. INTRODUCTION

The dynamical structure factor $S(k, \omega)$ for a simple classical liquid is a convenient focal point for the study of collective motion in a strongly interacting disordered system. Its self-motion counterpart $S_s(k, \omega)$ gives similarly detailed information on the single-particle motion. The qualitative behavior of these functions is well understood, but there is considerable interest in a quantitatively accurate description of their behavior. For values of k greater than about 10^7 cm^{-1}, experimental information is available from neutron inelastic scattering, and accurate theoretical information comes from molecular-dynamics calculations of the classical motion of several hundred atoms interacting through a Lennard-Jones potential.[1-3] In particular the self-function $S_s(k, \omega)$ has been very accurately calculated for several thermodynamic states,[2] and this information has been analyzed in terms of a memory function with only a few parameters. A quantitative description of this function is thus now generally available, greatly facilitating further attempts at its theoretical understanding.

There have been several recent theoretical de-