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Fluctuations in a nonequilibrium steady state: Basic equations

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In this paper the correlation functions for fluctuations in a fluid kept in a nonequilibrium steady state are studied. Hydrodynamiclike equations for the unequal- and equal-time correlation functions of the microscopic densities of mass, momentum, and energy are derived both for a dilute gas on the basis of kinetic theory and for a fluid of arbitrary density from the Liouville equation. The connection of these equations with those of fluctuating hydrodynamics is discussed.

I. INTRODUCTION

In this and the two following papers we study the fluctuations in a fluid that is a nonequilibrium steady state, near or far from equilibrium. In particular, we will study the correlations in space and time of fluctuations in the microscopic densities of mass, momentum, and energy for a fluid subject to a temperature gradient. Because of the connection between the spectrum of the light scattered by such a fluid and the (mass) density fluctuations, information about the nature of these fluctuations and especially about the difference between them and those in a fluid in thermal equilibrium can be obtained. This will be discussed in the following two papers. In this paper the basic equations for the unequal- and equal-time correlation functions for the abovementioned densities in a fluid subject to a temperature and a velocity gradient will be derived.

Preliminary account of the work presented in these papers have appeared elsewhere,[1] and there is now a substantial literature of related work by several authors.[2-6] The particular interest in these nonequilibrium correlation functions has been stimulated by the fact that because of the gradients in the system, such correlation functions have a much longer range in space than their equilibrium counterparts, and that the existence of these long-range correlations can be detected by means of light-scattering techniques. The long-range correlations in a nonequilibrium fluid are due to the same mode-coupling effects that are the origin of the long-time tail contributions to the transport coefficients,[7] which, in turn, are related to the nonexistence of virial expansions of the transport coefficients.[8] Thus, the experimental detection of long-range correlations in nonequilibrium fluids by light scattering would provide support for the reality of the long-time tails and the nonanalytic terms in the density expansion of the transport coefficients, which have not been convincingly verified in real fluids so far.

In a typical light-scattering experiment one measures the dynamical structure factor $S(\vec{k},\omega)$, that is, the intensity of light scattered by the fluid where an amount of momentum $\hbar\vec{k}$, and energy $\hbar\omega$ has been transferred by the fluid to the light. In general, $S(\vec{k},\omega)$ can be related to the Fourier transform of the correlation function of the density fluctuations in the fluid.

The theory for the scattering of light by fluids not in thermal equilibrium was originated simultaneously and independently by Procaccia *et al.*[2] and by Kirkpatrick *et al.*[1] and subsequently pursued by many authors, in particular, by Tremblay *et al.*[3] Ronis and Putterman,[4] Dufty,[6] and Van der Zwan *et al.*[5] All these investigators found that correlation functions which are either zero or short ranged in equilibrium become long ranged in nonequilibrium. They calculated the effect of the presence of the gradients on $S(\vec{k},\omega)$ for the case where these gradients were sufficiently small that first-order perturbation theory around the equilibrium state could be applied. Later, Kirkpatrick and Cohen[1] were able to show how the case of a large temperature gradient could be treated. It should also be mentioned that the existence of long-range correlations in a nonequilibrium fluid was first noted by Ludwig.[9] Kawasaki was the first to apply mode-coupling theory to derive formal equations for the correlation functions in nonequilibrium steady states, and Onuki[11] computed the long-range part of the nonequilibrium pair-correlation function for a dilute gas to first order in the gradients, using the kinetic theory of gases.

We will be concerned here with deriving hydrodynamiclike equations of motion for correlation functions of the general form

$$M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)\equiv\langle\delta a_\alpha(\vec{R}_1,t_1)\delta a_\beta(\vec{R}_2,t_2)\rangle$$

where δa_α and δa_β are fluctuations in the microscopic mass, momentum, or energy densities of the fluid. In particular, the density-density correlation function $M_{\rho\rho}$ where $\delta a_\alpha=\delta a_\beta=\delta\rho$ determines directly $S(\vec{k},\omega)$. We will have to consider the full set of correlation functions $M_{\alpha\beta}$ rather than just the density-density correlation function, since the equations for this set of correlation functions are coupled to one another. We will use two distinct methods for deriving equations for $M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)$. One method, valid for gases at low densities is based on the kinetic theory of gases, the other method, valid for arbitrary fluid densities, is based on Liouville's equation and the construction of a solution of this equation that describes the nonequilibrium steady state. The kinetic-theory method has the disadvantage that it is only applicable to dilute or at best moderately dense gases. However, it has the advantage that the structure of the theory is simpler and more transparent and that the approximations made can be more easily discussed. Although a complete kinetic discussion of the light scattering by fluids in a nonequilibrium steady state has been presented elsewhere,[12] we will not give such a treatment here. Instead we will use kinetic theory in these papers only to derive a set of hydrodynamiclike equations for the $M_{\alpha\beta}$ and related quantities valid for low densities. Since the equations for the $M_{\alpha\beta}$ for a general fluid derived from the Liouville equation reduce for low densities to the equations based on kinetic theory, the latter can be used as a partial justification of the former. We remark in general that many details of the calculations sketched in this and two following papers can be found in Ref. 12.

The outline of this paper is as follows. In Sec. II we use the kinetic theory of gases to derive general equations of motion for the $M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)$ under the circumstances that the system is in a nonequilibrium steady state, close to local equilibrium. We will introduce a local equilibrium projection operator in μ space in order to derive equations for these correlation functions, and we show that the $M_{\alpha\beta}$ satisfy a set of hydrodynamiclike equations closely related to the fluctuating hydrodynamic equations proposed by Keizer.[13] These hydrodynamiclike equations can be solved in terms of the equal-time correlation functions $M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_1)$, and in Sec. III we use kinetic theory to show that for low densities the equal-time correlation functions can be expressed explicitly in terms of the nonequilibrium one- and two-particle distribution functions. Then, using local equilibrium projection operators in μ space, we will derive a set of hydrodynamiclike equations for these equal-time correlation functions. In Sec. IV we introduce the Γ-space description of a general fluid in a nonequilibrium steady state close to local equilibrium and derive from the Liouville equation hydrodynamiclike equations for the $M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)$ for a general fluid with the aid of the Γ-space analog of the μ-space projection operator used in Sec. II. In Sec. V, we indicate how the mode-coupling method of Kadanoff and Swift[14] and of Ernst, Hauge, and van Leeuwen[15] can be used to derive a set of hydrodynamiclike equations for the equal-time correlation functions in terms of which the equations for the unequal-time correlation functions $M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)$ can be solved. The equations derived in Secs. IV and V can be seen to reduce to those derived in Secs. II and III on the basis of the kinetic theory of gases for a low-density gas. They will be applied in the next two papers to the computation of $S(\vec{k},\omega)$ of a fluid in a nonequilibrium steady state subject to a small (paper II) or a large thermal gradient (paper III). In Sec. VI a brief discussion of the results obtained in this paper is given and, in particular (cf the Appendix), the equivalence of our results and those obtained on the basis of fluctuating hydrodynamics is discussed.

II. HYDRODYNAMICLIKE EQUATIONS FOR THE UNEQUAL-TIME CORRELATION FUNCTIONS: KINETIC THEORY

A. Formulation of the problem: The basic kinetic equation

We consider a system of N identical particles of mass m, confined to a volume V. The phases of the particles will be denoted by $x_i=(\vec{r}_i,\vec{v}_i)$ where $\vec{r}_i$ and $\vec{v}_i$ are the position and velocity of particle i, respectively. It is assumed that the particles obey classical mechanics and that they interact according to a pairwise central potential $\phi(r_{ij})$, where $r_{ij}=|\vec{r}_i-\vec{r}_j|$. The Hamiltonian for the system is given by

$$H(x^N)=\sum_{i=1}^{N} m\vec{v}_i^2/2+\sum_{\substack{i<j\\1}}^{N}\phi(r_{ij}) , \tag{2.1}$$

where x^N denotes the set of phases $x_1,\ldots,x_N$ of the N particles. In the course of our calculations we will be considering a small subvolume of the system that is far from the walls, so we will neglect the direct effect of the walls on the dynamics of the particles. The walls will certainly have some effect on the system, since it is only by means of wall effects that a temperature or velocity gradient can be maintained in the system. We will comment on this point further in papers II and III.

The quantities of interest for describing the fluctuations in the system that are detectable by light-scattering experiments are connected to the time-correlation functions of the microscopic densities of conserved quantities. These time-correlation functions are defined by

$$M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)=\langle \delta a_\alpha(\vec{R}_1,t_1)\delta a_\beta(\vec{R}_2,t_2)\rangle \tag{2.2}$$

with

$$\delta a_\alpha(\vec{R},t)=\tilde{a}_\alpha(\vec{R},t)-\langle \tilde{a}_\alpha(\vec{R},t)\rangle , \tag{2.3}$$

where $\tilde{a}_\alpha(\vec{R},t)$ denotes the actual value of one of the microscopic densities of mass $\tilde{\rho}$ momentum $\tilde{\vec{g}}$, or energy $\tilde{\epsilon}$, at the position $\vec{R}$ and time t, given by

$$\tilde{\rho}(\vec{R},t)=\sum_{i=1}^{N} m\delta(\vec{r}_i(t)-\vec{R}) , \tag{2.4a}$$

$$\tilde{\vec{g}}(\vec{R},t)=\sum_{i=1}^{N} m\vec{v}_i(t)\delta(\vec{r}_i(t)-\vec{R}) , \tag{2.4b}$$

$$\tilde{\epsilon}(\vec{R},t)=\sum_{i=1}^{N} e_i(t)\delta(\vec{r}_i(t)-\vec{R}) , \tag{2.4c}$$

respectively. Here

$$e_i(t)=\tfrac{1}{2}mv_i^2(t)+\tfrac{1}{2}\sum_{j\neq i}\phi(r_{ij}(t)) , \tag{2.5}$$

$\langle \tilde{a}_\alpha(\vec{R},t)\rangle$ denotes the average value of $\tilde{a}_\alpha(\vec{R},t)$ at $\vec{R},t$ and $\vec{r}_i(t)$, $\vec{v}_i(t)$ are the position and velocity of particle i at time t, respectively. In Eqs. (2.2) and (2.3) the angular brackets denote an average over an appropriate initial ensemble. For the purpose of describing light-scattering experiments, we need to determine the density-density correlation function $M_{\rho\rho}$ and to determine this function, we will need to consider the larger set of functions $M_{\alpha\beta}$ defined above, since the equation for $M_{\rho\rho}$ is coupled to those for the other $M_{\alpha\beta}$. We remark that for dilute gases the potential-energy contributions in Eq. (2.5) will be neglected in the derivation of the hydrodynamiclike equations below, since they lead to terms of higher order in the density than the kinetic-energy terms.

To find the $M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)$ at low densities, it is convenient to introduce a microscopic μ-space density function $\tilde{F}(1,t)$ defined by

$$\tilde{F}(1,t)=\sum_{i=1}^{N}\delta(1-x_i(t)) \tag{2.6}$$

and a corresponding two-time correlation function $C(1,t_1;2,t_2)$ by

$$C(1,t_1;2,t_2)=\langle \delta F(1,t_1)\delta F(2,t_2)\rangle , \tag{2.7}$$

where $\delta F(1,t_1)=\tilde{F}(1,t_1)-\langle \tilde{F}(1,t_1)\rangle$. Here $x_i(t)=[\vec{r}_i(t),\vec{v}_i(t)]$ and "1" denotes a particular position $\vec{R}_1$ and velocity $\vec{V}_1$ in μ space. One can easily check that

$$M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)=\int d\vec{V}_1\int d\vec{V}_2 a_\alpha(\vec{V}_1)a_\beta(\vec{V}_2)\times C(1,t_1;2,t_2) , \tag{2.8}$$

where

$$a_\rho(\vec{V})=m , \tag{2.9a}$$

$$\vec{a}_{\vec{g}}(\vec{V})=m\vec{V} , \tag{2.9b}$$

$$a_\epsilon(\vec{V})=\tfrac{1}{2}mV^2 . \tag{2.9c}$$

Consequently, if we know how $C(1,t_1;2,t_2)$ depends on time, we can determine the time development of the $M_{\alpha\beta}$ by integration.

We will restrict ourselves here to a consideration of nonequilibrium steady states, where the quantities $M_{\alpha\beta}(\vec{R}_1,t_1;\vec{R}_2,t_2)$ and $C(1,t_1;2,t_2)$ are functions of time only through the difference t_1-t_2. We, therefore, consider only the quantity

$$\begin{aligned}C(1,2;t)&=C(1.t_1-t_2;2,0)\\&=\langle \delta F(1,t_1-t_2)\delta F(2,0)\rangle_{\text{ss}} ,\end{aligned} \tag{2.10}$$

with $t=t_1-t_2$, and the angular brackets denote an ensemble average with respect to a nonequilibrium steady-state (ss) distribution function. Similarly, we consider the quantities $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ defined by

$$M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)=\int d\vec{V}_1\int d\vec{V}_2 a_\alpha(\vec{V}_1)a_\beta(\vec{V}_2)\times C(1,2,t) . \tag{2.11}$$

Recently, Ernst and Cohen[16] showed how one can derive a closed kinetic equation for $C(1,2,t)$ for a dilute gas in which the particles interact with short-range central forces. Ernst and Cohen's equation is, for $t>0$,

$$\left[\frac{\partial}{\partial t}+L_0(t)\right]C(1,2,t)=\int d3\,\hat{T}(13)(1+P_{13})\times F_1(3)C(1,2,t)\;. \tag{2.12}$$

Here

$$L_0(1)=\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}\;. \tag{2.13a}$$

$\hat{T}(13)$ is a binary-collision operator defined by

$$\hat{T}(13)=\delta(\vec{R}_1-\vec{R}_3)\times\int_0^{2\pi}d\epsilon\int_0^{\sigma}b\,db\,|\vec{V}_1-\vec{V}_3|(b_\sigma-1)\;, \tag{2.13b}$$

(b,ϵ) are the impact parameter and the azimuthal angle characterizing the collision between two particles with velocities $\vec{V}_1,\vec{V}_3$, and b_σ is an operator that replaces the velocities $\vec{V}_1$ and $\vec{V}_3$ by those of the restituting collision, $\vec{V}_1',\vec{V}_3'$, given by

$$\vec{V}_1'=\vec{V}_1-(\vec{V}_{13}\cdot\hat{\sigma})\hat{\sigma}\;, \tag{2.14a}$$

$$\vec{V}_3'=\vec{V}_3+(\vec{V}_{13}\cdot\hat{\sigma})\hat{\sigma}\;, \tag{2.14b}$$

where $\hat{\sigma}$ is a unit vector in the direction of the apse line of the $(\vec{V}_1,\vec{V}_3)$ collision $\vec{V}_{13}=\vec{V}_1-\vec{V}_3$, and σ is the range of the forces. For any function $h(\vec{V}_1,\vec{V}_3)$

$$b_\sigma h(\vec{V}_1,\vec{V}_3)=h(\vec{V}_1',\vec{V}_3')=h(\vec{V}_1-(\vec{V}_{13}\cdot\hat{\sigma})\hat{\sigma},\vec{V}_3+(\vec{V}_{13}\cdot\hat{\sigma})\hat{\sigma})\;. \tag{2.15}$$

Further, P_{13} is a permutation operator that permutes particle indices 1 and 3 and $F_1(3)$ is the single-particle distribution function in the nonequilibrium steady state

$$F_1(3)=\langle\tilde{F}(3)\rangle_{\mathrm{ss}}\;. \tag{2.16}$$

To determine $C(1,2,t)$ for $t<0$, we can use the steady-state condition $C(1,2,t)=C(2,1;-t)$ and again apply Eq. (2.12) with particle indices 1 and 2 interchanged. In both cases the solution of Eq. (2.12) is determined in terms of the equal-time correlation function $C(1,2;0)$. In Sec. II B we will show how $C(1,2;0)$ can be computed.

B. Derivation of hydrodynamiclike equations for the unequal-time correlation functions

Equation (2.12) will be the starting point for our calculations of $M_{pp}(\vec{R}_1,\vec{R}_2,t)$. We will assume that the fluid is in a steady state, which is close to a state of local equilibrium with a local temperature $T(\vec{R})$, local (number) density $n(\vec{R})$, and local velocity $\vec{u}(\vec{R})$. Under these circumstances, the single-particle distribution function at low densities, is a solution of the steady-state nonlinear Boltzmann equation

$$L_0(1)F_1(1)=J(F_1F_1)=\int d3\,\hat{T}(13)F_1(1)F_1(3)\;. \tag{2.17}$$

A solution of this Boltzmann equation that describes a steady state near local equilibrium can be obtained by applying the Chapman-Enskog method to Eq. (2.17).[17] Thus, we write

$$F(1)=F_l(1)(1+\Phi_1+\Phi_2+\cdots)\;, \tag{2.18}$$

where $F_l(1)$ is the local equilibrium distribution function

$$F_l(1)=n(\vec{R}_1)\left[\frac{\beta(\vec{R}_1)m}{2\pi}\right]^{3/2}\times\exp\left[-\frac{\beta(\vec{R}_1)m}{2}C_1^2(\vec{R}_1)\right]\;, \tag{2.19a}$$

$$\equiv n(\vec{R}_1)\phi_l(1)\;, \tag{2.19b}$$

with $\beta(\vec{R}_1)=[k_BT(\vec{R}_1)]^{-1}$, where k_B is Boltzmann's constant and $\vec{C}_1(\vec{R}_1)=\vec{V}_1-\vec{u}(\vec{R}_1)$. The quantities Φ_1,Φ_2, are of first, second, etc. order in the gradients of the hydrodynamic variables $n(\vec{R})$, $T(\vec{R})$, and $\vec{u}(\vec{R})$, respectively. $\Phi_1(1)$ is given by

$$\Phi_1(1)=A_i(1)\frac{\partial\ln T}{\partial R_{1i}}+\beta mB_{ij}(1)\frac{\partial u_i}{\partial R_{1j}}\;, \tag{2.20}$$

where the superscripts (i,j) denote (x,y,z) and summation convention is used. $A_i(1)$ and $B_{ij}(1)$ are solutions of the inhomogeneous, linearized Boltzmann equations

$$\Lambda_l(1)F_l(1)A_i(1)=C_{1i}\left[\frac{\beta m}{2}C_1^2-\frac{5}{2}\right]F_l(1)\;, \tag{2.21a}$$

$$\Lambda_l(1)F_l(1)B_{ij}(1)=\left[C_{1i}C_{1j}-\frac{\delta_{ij}}{3}C_1^2\right]F_l(1)\;, \tag{2.21b}$$

where δ_{ij} is Kronecker delta function, and $\Lambda_l(1)$ is the linearized Boltzmann collision operator defined for an arbitrary function $g(1)$ by

$$\Lambda_l(1)F_l(1)g(1)=\int d3\,\hat{T}(13)(1+P_{13}) \times F_l(1)F_l(3)g(1)\ . \tag{2.22}$$

Further, $A_i(1)$ also satisfies the additional constraint that

$$(\vec{C}_1\,|\,A_i(1))_l=0,\quad i=x,y,z \tag{2.23}$$

where we have defined the inner product of two functions of velocity by

$$(h(\vec{C}_1)\,|\,g(\vec{C}_1))_l=\int d\vec{V}_1 h(\vec{C}_1)g(\vec{C}_1)\phi_l(1) \tag{2.24}$$

with $\phi_l(1)$ given by Eq. (2.19b).

The low-density value of the (local) coefficient of shear viscosity $\eta_B(\vec{R}_1)$, and the low-density value of the (local) coefficient of thermal conductivity $\lambda_B(\vec{R}_1)$, can be expressed in terms of $B_{ij}(\vec{C}_1)$ and $A_i(\vec{C}_1)$, respectively, as

$$\frac{\rho m}{k_B T}\left[C_{1i}C_{1j}-\frac{\delta_{ij}}{3}C_1^2\,|\,B_{kl}(\vec{C}_1)\right]_l=-\eta_B(\vec{R}_1)\Delta_{ij,kl} \tag{2.25a}$$

and

$$nk_B\left[C_{1i}\left[\frac{\beta(\vec{R}_1)m}{2}C_1^2-\frac{5}{2}\right]\middle|A_j(\vec{C}_1)\right] =-\lambda_B(\vec{R}_1)\delta_{ij}\ , \tag{2.25b}$$

where

$$\Delta_{ij,kl}=\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}-\tfrac{2}{3}\delta_{ij}\delta_{kl}\ . \tag{2.26}$$

Now the quantities $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ are obtained as follows. The $M_{\alpha\beta}$ are directly related to $C(1,2,t)$ by means of the velocity integrations indicated in Eq. (2.8). The correlation function $C(1,2,t)$ satisfies Eq. (2.12), which has the structure of a Boltzmann equation linearized about a nonequilibrium steady-state distribution function $F_1(\vec{R}_1,\vec{V}_1)$. Thus, after solving this Boltzmann equation for F_1, equations of motion for $C(1,2,t)$ and subsequently for the $M_{\alpha\beta}$ can be derived. For the case of interest here, when the system is close to a local equilibriums state, either the Chapman-Enskog method, or a method based on Zwanzig's projection operators[18] can be used. Here we will use the latter method since this method is analogous to the one we will employ later for a general fluid, in Sec. IV. In Zwanzig's projection-operator method, a projection operator $P(1)$ is introduced that projects a function of $\vec{R}_1$, $\vec{V}_1$ onto a space spanned by the conserved variables $a_\alpha(\vec{V}_1)$ defined by Eqs. (2.9a)–(2.9c). For convenience we rearrange those functions somewhat to facilitate the carrying out of the velocity integrals in the local equilibrium state. That is, instead of the set $a_\alpha(\vec{V}_1)$, we define a more convenient but equivalent set of function $\psi_\alpha(\vec{C}_1)$, $\alpha=1,2,\ldots,5$, by

$$\begin{gathered}\psi_1=m,\quad \psi_2=mC_{1x}(\vec{R}_1),\quad \psi_3=mC_{1y}(\vec{R}_1)\ ,\\ \psi_4=mC_{1z}(\vec{R}_1)\ ,\\ \psi_5=\left[\frac{\beta(\vec{R}_1)m}{2}\vec{C}_1^2(\vec{R}_1)-\frac{3}{2}\right]\end{gathered} \tag{2.27}$$

with $\vec{C}_1(\vec{R}_1)$ given below Eq. (2.19).

The projection operator we use is the local equilibrium operator defined by

$$P(1)=\sum_{\alpha=1}^{5}\frac{|\,\psi_\alpha(1))_l(\psi_\alpha(1)\,|}{(\psi_\alpha(1)\,|\,\psi_\alpha(1))_l}\ , \tag{2.28}$$

where the l in $|\,\psi_\alpha(1))_l$ indicates that the weight function $\phi_l(1)$ of the inner product defined by Eq. (2.24) is in the ket vector. The relation between $C(1,2,t)$ and the $M_{\alpha\beta}$ is then obtained through one between $P(1)C(1,2,t)$ and the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$, which can be derived with the help of the Eqs. (2.27) and (2.28), and can be written in the form

$$\begin{aligned}\int d\vec{V}_2 a_\beta(\vec{V}_2)P(1)C(1,2,t)={}&m^{-2}\,|\,\psi_1)_l M_{\rho\beta}(\vec{R}_1,\vec{R}_2,t)\\ &+m^{-1}\beta(\vec{R}_1)\,|\,\psi_i)_l[M_{g_i\beta}(\vec{R}_1,\vec{R}_2,t)-u_i(\vec{R}_1)M_{\rho\beta}(\vec{R}_1,\vec{R}_2,t)]\\ &+\tfrac{2}{3}\,|\,\psi_5)_l\left[\beta(\vec{R}_1)M_{\epsilon'\beta}(\vec{R}_1,\vec{R}_2,t)-\frac{3}{2m}M_{\rho\beta}(\vec{R}_1,\vec{R}_2,t)\right]\ ,\end{aligned} \tag{2.29}$$

where

$$M_{\epsilon'\beta}=M_{\epsilon\beta}-u_i(\vec{R}_1)M_{g_i\beta}+\frac{\vec{u}^2(\vec{R}_1)}{2}M_{\rho\beta}\ . \tag{2.30}$$

In Eqs. (2.29) and (2.30) we have used summation convention; $g_i=g_x$, g_y, and g_z for $i=2$, 3, and 4, respectively. It is important to note that neither the projection operator $P(1)$ nor the operators appearing in Eq. (2.12) act on the variables with particle index 2. By means of Eq. (2.29), we will be able to convert an equation for $P(1)C(1,2,t)$ directly into an equation for $M_{\alpha\beta}$ by multiplying by

$$\int d\vec{V}_1 \int d\vec{V}_2 a_\alpha(\vec{V}_1) a_\beta(\vec{V}_2) .$$

To derive an equation for $P(1)C(1,2,t)$, we write

$$C(1,2,t)=P(1)C(1,2,t)+P_\perp(1)C(1,2,t) , \tag{2.31}$$

where $P_\perp(1)=1-P(1)$, is the projection operator onto the space of variables orthogonal to the ψ_α's. We now use Eq. (2.12) to derive a pair of simultaneous equations for PC and $P_\perp C$. To do this, it is convenient to consider the Laplace transform of Eq. (2.12) which we write as

$$[z+L(1)]\hat{C}(1,2,z)=C(1,2,t=0) , \tag{2.32}$$

where $\hat{C}(1,2,z)$ is the Laplace transform of $C(1,2,t)$ defined by

$$\hat{C}(1,2,z)=\int_0^\infty dt\, e^{-zt} C(1,2,t) \tag{2.33}$$

with the circumflex denoting a Laplace transformed quantity, and

$$L(1)=L_0(1)-\int d3\, \hat{T}(13)(1+P_{13})F_1(3) . \tag{2.34}$$

After multiplying Eq. (2.32) by $P(1)$ and $P_\perp(1)$, and using Eq. (2.31), we obtain

$$[z+PL(1)P]P\hat{C}=PC(1,2,0)-PLP_\perp\hat{C} \tag{2.35a}$$

and

$$[z+P_\perp L(1)P_\perp]P_\perp\hat{C}=P_\perp C(1,2,0)-P_\perp LP\hat{C} . \tag{2.35b}$$

By using Eq. (2.35b) to eliminate $P_\perp\hat{C}$, we obtain the following equation for $P\hat{C}$:

$$\{z+PL(1)P-PL(1)P_\perp[z+P_\perp L(1)P_\perp]^{-1}P_\perp L(1)P\}P\hat{C}(1,2,z)$$
$$=PC(1,2,0)-PL(1)P_\perp[z+P_\perp L(1)P_\perp]^{-1}P_\perp C(1,2,0) . \tag{2.36}$$

In order to proceed beyond the formal result for $P\hat{C}$ given above, we will need to use that the system is in a steady state close to local equilibrium. We recall that the Chapman-Enskog solution of the Boltzmann equation describes a state of a gas with two well-separated characteristic length scales; one, denoted by l, is the mean-free path of a gas particle while the other is the length scale L_∇, over which the hydrodynamic variables ρ, $\vec{u}$, and β vary. It is assumed in the Chapman-Enskog solution that $l \ll L_\nabla$. It is this separation of microscopic and macroscopic length scales that permits a derivation of the hydrodynamic equations from the Boltzmann transport equation. We will consider fluids with gradients such that this applies to the case of interest here, and use this separation of lengths scales to simplify the equation for $P\hat{C}(1,2,z)$, Eq. (2.36). To do this, we note that the linearized Boltzmann collision operator appearing in $L(1)$, Eq. (2.34), is of the order or magnitude cl^{-1}, where c is a characteristic average velocity, the velocity of sound, for example, and l is the mean-free path $\sim(n\sigma^2)^{-1}$, while the gradient term $L_0(1)$, in Eq. (2.34), is of order cL_∇^{-1} when it acts on a hydrodynamic variable and is, therefore, much smaller than the collision operator. Consequently, we will be able to expand $P_\perp L(1)P_\perp$ in powers of the gradient operator $L_0(1)$. To be specific, we first write the collision operator

$$\int d3\, \hat{T}(13)(1+P_{13})F_1(3)=\Lambda_l(1)+\Lambda_{\nabla_1}(1) + \cdots , \tag{2.37}$$

$$\Lambda_l(1)=\int d3\, \hat{T}(13)(1+P_{13})F_l(3) , \tag{2.38a}$$

$$\Lambda_{\nabla_1}(1)=\int d3\, \hat{T}(13)(1+P_{13})F_l(3)\Phi_1(3) , \tag{2.38b}$$

and so on, where F_l is given by Eq. (2.19a), and Φ_1 by Eq. (2.20). Unless Λ_l acts on a function of the form $F_l(1)\psi_i(1)$ when it gives zero, it is of the order of magnitude $\sim cl^{-1}$, while Λ_{∇_1} is of order cL_∇^{-1}. Further, for the light-scattering experiments we want to describe, we will only be interested in variations of the correlation functions $M_{\alpha\beta}$ over hydrodynamic time scales, $t_H \approx L_\nabla/c$, long compared to the mean-free time, so we consider the Laplace variable z to be of order $\sim c/L_\nabla$, also.

If we now apply these remarks to the operator $P_\perp[z+P_\perp L(1)P_\perp]^{-1}P_\perp$ appearing in Eq. (2.36), we see that it has an expansion in powers of l/L_∇,

$$P_\perp[z+P_\perp L(1)P_\perp]^{-1}P_\perp=-P_\perp\Lambda_l^{-1}P_\perp-P_\perp\Lambda_l^{-1}P_\perp[z+P_\perp L_0(1)P_\perp-P_\perp\Lambda_{\nabla_1}P_\perp]P_\perp\Lambda_l^{-1}P_\perp+\cdots\ . \tag{2.39}$$

Here we have used that $P_\perp\Lambda_l P_\perp=\Lambda_l$, since $P(1)$ projects onto the space of eigenfunctions of $\Lambda_l(1)$ with zero eigenvalue, and that $P_\perp\Lambda_l^{-1}P_\perp$ is a well-defined operator, since $P_\perp$ projects onto a subspace that is orthogonal to that of the zero eigenfunctions of $\Lambda_l(1)$. Upon inserting this expansion Eq. (2.39) into Eq. (2.36), and collecting terms, we find that $P\hat{C}(1,2,z)$ satisfies the equation

$$\left[z+P\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}P+P\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}P_\perp\Lambda_l^{-1}P_\perp\left[\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}-\Lambda_{\nabla_1}\right]P+\cdots\right]P\hat{C}=PC(1,2,0)+\cdots\ , \tag{2.40}$$

where we used that $\Lambda_l P\hat{C}=0$. On the left-hand side of Eq. (2.40) we have retained only the terms of order cL_∇^{-1} and of order $cL_\nabla^{-1}(lL_\nabla^{-1})$, neglecting terms of order $cL_\nabla^{-1}(lL_\nabla^{-1})^2$ and higher. On the right-hand side we have neglected all the terms proportional to $P_\perp C(1,2,0)$. These are of order lL_∇^{-1} and higher since $PL(1)\sim O(L_\nabla^{-1})$ and $[z+P_\perp L(1)P_\perp]^{-1}\sim O(l)$. Although it is not yet obvious at this point why these various terms can be neglected, we will show in paper II, Appendix B, subsection II that they lead to less important contributions to the light-scattering spectrum than the terms we retain.

It is now a straightforward matter, albeit a lengthy one, to convert Eq. (2.4) for $P\hat{C}$ to a set of five coupled equations for $\hat{M}_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$, i.e., the Laplace transform of $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$. To do this, one uses the Laplace transform of Eq. (2.29) to obtain a relation between $P\hat{C}$ and $\hat{M}_{\alpha\beta}$, and then takes the inner product of Eq. (2.40) with respect to the five a_α or equivalently the five ψ_α's defined by Eq. (2.27). Using the relations

$$P_\perp(1)\,|\,1)_l=P_\perp(1)\,|\,C_{1i})_l=P_\perp(1)\left[\frac{\beta mC_1^2}{2}-\frac{3}{2}\right]_l=0\ , \tag{2.41a}$$

$$P_\perp(1)\,|\,C_{1i}C_{1j})_l=\left|\left[C_{1i}C_{1j}-\delta_{ij}\frac{C_1^2}{3}\right]\right)_l\ , \tag{2.41b}$$

$$P_\perp(1)\left|C_{1i}\left[\frac{\beta mC_1^2}{2}-\frac{3}{2}\right]\right)_l=\left|C_{1i}\left[\frac{\beta mC_1^2}{2}-\frac{5}{2}\right]\right)_l\ , \tag{2.41c}$$

$$\left[\left[C_{1i}C_{1j}-\delta_{ij}\frac{C_1^2}{3}\right]\Big|A_k\right]_l=\left[C_{1i}\left[\frac{\beta mC_1^2}{2}-\frac{5}{2}\right]\Big|B_{jk}\right]_l=0\ , \tag{2.41d}$$

the derivation of equations for $\hat{M}_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$ is straightforward. We merely quote the results.

The equations for $\hat{M}_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$ are as follows.

(a) For $\alpha=\rho$:

$$z\hat{M}_{\rho\beta}+\frac{\partial}{\partial R_{1i}}\hat{M}_{g_i\beta}=M_{\rho\beta}(\vec{R}_1,\vec{R}_2,t=0)\ ; \tag{2.42a}$$

(b) for $\alpha=g_i$:

$$z\hat{M}_{g_i\beta}+\frac{\partial}{\partial R_{1j}}\left[\left[\frac{\partial p}{\partial\epsilon}\right]_\rho\delta_{ij}\hat{M}_{\epsilon'\beta}+\rho u_i\hat{M}_{u_j\beta}+u_j\hat{M}_{g_i\beta}\right]$$

$$=M_{g_i\beta}(\vec{R}_1,\vec{R}_2,t=0)+\frac{\partial}{\partial R_{1j}}\eta_B\Delta_{ij,kl}\frac{\partial}{\partial R_{1k}}\hat{M}_{u_l\beta}+\frac{\partial}{\partial R_{1j}}\left[\left[\frac{\partial\eta_B}{\partial\epsilon}\right]_\rho\hat{M}_{\epsilon'\beta}+\left[\frac{\partial\eta_B}{\partial\rho}\right]_\epsilon\hat{M}_{\rho\beta}\right]2\left[D_{ij}-\frac{\delta_{ij}}{3}D_{ll}\right]\ ; \tag{2.42b}$$

(c) for $\alpha=\epsilon'$:

$$z\hat{M}_{\epsilon'\beta}+u_i\frac{\partial}{\partial R_{1i}}\hat{M}_{\epsilon'\beta}+\left[\frac{\partial h}{\partial \epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}\left[\frac{\partial u_i}{\partial R_{1i}}\right]+\hat{M}_{u_i\beta}\frac{\partial \epsilon}{\partial R_{1i}}+h\frac{\partial}{\partial R_{1i}}\hat{M}_{u_i\beta}$$
$$=M_{\epsilon'\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t=0)+\frac{\partial}{\partial R_{1i}}\lambda_B\frac{\partial}{\partial R_{1i}}\left[\left[\frac{\partial T}{\partial \epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}+\left[\frac{\partial T}{\partial \rho}\right]_{\epsilon}\hat{M}_{\rho\beta}\right]$$
$$+\frac{\partial}{\partial R_{1i}}\left[\left[\frac{\partial \lambda_B}{\partial \epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}+\left[\frac{\partial \lambda_B}{\partial \rho}\right]_{\epsilon}\hat{M}_{\rho\beta}\right]\frac{\partial T}{\partial R_{1i}}$$
$$+4\eta_B\left[D_{ij}-\frac{\delta_{ij}}{3}D_{ll}\right]\frac{\partial}{\partial R_{1i}}\hat{M}_{u_j\beta}+2D_{ij}\left[\left[\frac{\partial \eta_B}{\partial \rho}\right]_{\epsilon}\hat{M}_{\rho\beta}+\left[\frac{\partial \eta_B}{\partial \epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}\right]\left[D_{ij}-\frac{\delta_{ij}}{3}D_{ll}\right]. \tag{2.42c}$$

Here we have defined $\hat{M}_{u_i\beta}$ by

$$\hat{M}_{u_i\beta}=\frac{1}{\rho(\vec{\mathrm{R}}_1)}[\hat{M}_{g_i\beta}-u_i(\vec{\mathrm{R}}_1)\hat{M}_{\rho\beta}] \tag{2.43a}$$

and used the notation

$$D_{ij}=\frac{1}{2}\left[\frac{\partial u_i}{\partial R_{1j}}+\frac{\partial u_j}{\partial R_{1i}}\right]. \tag{2.43b}$$

The subscripts $i,j,k,l,$ represent x,y,z coordinates and summation convention has been used. The thermodynamic quantities appearing in Eqs. (2.42a) – (2.42c) are the local pressure $p(\vec{\mathrm{R}}_1)=n(\vec{\mathrm{R}}_1)k_BT(\vec{\mathrm{R}}_1)$, the local energy density

$$\epsilon(\vec{\mathrm{R}}_1)=\tfrac{3}{2}n(\vec{\mathrm{R}}_1)k_BT(\vec{\mathrm{R}}_1)\ ,$$

and the local enthalpy density $h(\vec{\mathrm{R}}_1)=\epsilon(\vec{\mathrm{R}}_1)+p(\vec{\mathrm{R}}_1)$. These quantities depend on position as indicated. The transport coefficients appearing in Eqs. (2.42b) and (2.42c) are given by Eqs. (2.25a) and (2.25b).

The (average) hydrodynamic variables ρ, $\vec{u}$, and T occurring in the Eqs. (2.42) are determined by the Navier-Stokes equations as follows from our assumption that the Chapman-Enskog solution of the Boltzmann equation describes the nonequilibrium steady state.

C. Discussion of Eqs. (2.42)

The hydrodynamic equations for the $\hat{M}_{\alpha\beta}$ given by Eqs. (2.42a) – (2.42c) can be put in a simple matrix form as

$$z\hat{M}_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,z)=H_{\alpha\gamma}(\vec{\mathrm{R}}_1)\hat{M}_{\gamma\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,z)+M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t=0)\ , \tag{2.44}$$

where $H_{\alpha\gamma}(\vec{\mathrm{R}}_1)$ is an evolution matrix defined by Eqs. (2.42a) – (2.42c). We note that Eq. (2.44) is linear in the $\hat{M}_{\alpha\beta}$ but the elements of the matrix of coefficients $H_{\alpha\gamma}(\vec{\mathrm{R}}_1)$ are not simply gradients with constant coefficients, but gradients with coefficients proportional to local thermodynamic functions, transport coefficients, and their various derivatives that all depend on the point $\vec{\mathrm{R}}_1$. In order to interpret Eqs. (2.42) or (2.44), we note that small macroscopic deviations $\delta\rho$, $\delta\vec{g}$, $\delta\epsilon$ of the mass, momentum, and energy densities from their nonequilibrium steady-state values satisfy equations that can be derived from the nonlinear Navier-Stokes equations by linearizing these equations about the steady state. These linearized equations read

$$\frac{\partial}{\partial t}\delta a_\alpha(\vec{\mathrm{R}}_1t)=H_{\alpha\gamma}(\vec{\mathrm{R}}_1)\delta a_\gamma(\vec{\mathrm{R}}_1t)\ , \tag{2.45}$$

where the $\delta a_\alpha(\vec{\mathrm{R}}_1t)=(\delta\rho,\delta\vec{g},\delta\epsilon)$. Thus, both the small deviations of hydrodynamic variables about their nonequilibrium steady-state values, and the correlations of fluctuations about steady-state values described by $M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t)$, satisfy the *same* set of hydrodynamic equations with the same evolution matrix $H_{\alpha\gamma}(\vec{\mathrm{R}}_1)$. This may be regarded as a generalization of the Onsager regression principle to nonequilibrium steady states. By *assuming* the validity of this generalized Onsager principle, Keizer[13] obtained a set of Langevin equations for the fluctuations of hydrodynamic variables about their nonequilibrium steady-state values, which have a form *identical* to Eq. (2.45) except that there is an additional "fluctuating force" term on the right-hand side of Keizer's equations and the $H_{\alpha\gamma}(\vec{\mathrm{R}}_1)$ given in this section is the low-density limit of Keizer's evolution matrix. In Sec. IV we will sketch a derivation of this evolution matrix for a more general fluid which gives a result identical to that postulated by Keizer.[19]

Now, having derived the equations of motion for the $\hat{M}_{\alpha\beta}$ that we need for a dilute gas, we turn our attention to the calculations of the equal-time correlation function $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t=0)$ in the nonequilibrium steady state that is needed for the solution of Eq. (2.44).

III. HYDRODYNAMICLIKE EQUATIONS FOR THE EQUAL-TIME CORRELATION FUNCTIONS: KINETIC THEORY

A. Relation to nonequilibrium distribution functions

The equal-time values of the $M_{\alpha\beta}$ are defined by

$$M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t=0)=\int d\vec{V}_1\int d\vec{V}_2 a_\alpha(\vec{V}_1)a_\beta(\vec{V}_2)\times C(1,2,t=0)\ , \tag{3.1}$$

where $C(1,2,0)$ is the equal-time correlation function defined by Eq. (2.10) with $t=0$. That is,

$$C(1,2,0)=\langle\delta F(1,0)\delta F(2,0)\rangle_{\text{ss}}\ . \tag{3.2}$$

We can relate $C(1,2,0)$ to the one- and two-particle distribution functions in the steady state by means of Eqs. (2.7) and (2.16) as

$$\begin{aligned}C(1,2,0)&=\langle[\tilde{F}(1)-\langle\tilde{F}(1)\rangle_{\text{ss}}]\times[\tilde{F}(2)-\langle\tilde{F}(2)\rangle_{\text{ss}}]\rangle_{\text{ss}}\\&=\delta(1-2)F_1(1)+G_2(1,2)\ .\end{aligned} \tag{3.3}$$

where G_2 is the pair-correlation function

$$G_2(1,2)=F_2(1,2)-F_1(1)F_1(2)\ , \tag{3.4}$$

and $F_2(1,2)$ is the two-particle distribution function defined by

$$F_2(1,2)=\left\langle\sum_{i\neq j}\delta(1-x_i)\delta(2-x_j)\right\rangle_{\text{ss}}\ . \tag{3.5}$$

The equal-time value of the $M_{\alpha\beta}$ can then be expressed as

$$M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,0)=A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)+D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)\ , \tag{3.6}$$

where

$$A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)=\delta(\vec{R}_1-\vec{R}_2)\times\int d\vec{V}_1 a_\alpha(\vec{V}_1)a_\beta(\vec{V}_1)F_1(1) \tag{3.7a}$$

and

$$D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)=\int d\vec{V}_1\int d\vec{V}_2 a_\alpha(\vec{V}_1)a_\beta(\vec{V}_2)\times G_2(1,2)\ . \tag{3.7b}$$

To determine the $A_{\alpha\beta}$, we expand $F_1(1)$ in powers of the gradients by using the Chapman-Enskog solution of the Boltzmann equation given by Eq. (2.18). This leads to

$$A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)=A_{\alpha\beta,l}(\vec{R}_1,\vec{R}_2)+A_{\alpha\beta,\nabla_1}(\vec{R}_1,\vec{R}_2)+\cdots \tag{3.8}$$

with

$$A_{\alpha\beta,l}=\delta(\vec{R}_1-\vec{R}_2)\times\int d\vec{V}_1 a_\alpha(\vec{V}_1)a_\beta(\vec{V}_1)F_l(1)\ , \tag{3.9a}$$

$$A_{\alpha\beta,\nabla_1}=\delta(\vec{R}_1-\vec{R}_2)\times\int d\vec{V}_1 a_\alpha(\vec{V}_1)a_\beta(\vec{V}_1)F_l(1)\Phi_1(1)\ , \tag{3.9b}$$

and so on. For $D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ one needs $G_2(1,2)$.

B. Kinetic equation for the pair-correlation function

The nonequilibrium pair-correlation function $G_2(1,2)$ has been studied by a number of authors using the techniques of the kinetic theory of gases.[11,16,20,21] If the density of the gas is sufficiently low, and if we are interested in determining $G_2(1,2)$ for $R_{12}\gg\sigma$, then $G_2(1,2)$ satisfies the equation

$$[L(1)+L(2)]G_2(1,2)=T(12)F_1(1)F_1(2)\ , \tag{3.10}$$

where the binary-collision operator $T(12)$ is defined by Eq. (2.13b), and $L(1)$ by Eq. (2.34). Equation (3.10) takes into account that for low densities particle correlations are established by means of binary collisions among the particles, as described by the $T(12)F_1F_1$ term on the right-hand side of Eq. (3.10). These correlations are propagated in the fluid by the free-streaming of the colliding pair of particles as described by the $L_0(1)$ and $L_0(2)$ operators on the left-hand side of Eq. (3.10), and by random collisions of the particles 1 and 2 with other particles in the fluid, described by the collision operator contributions to $L(1)$ and $L(2)$.

If we now combine Eqs. (3.3) and (3.10), we see that the equal-time correlation function $C(1,2,0)$ is given at low densities by the equation

$$C(1,2,0)=\delta(1-2)F_1(1)+[L(1)+L(2)]^{-1}\times\hat{T}(12)F_1(1)F_1(2)\ . \qquad (3.11)$$

The second term on the right-hand side of Eq. (3.11) cannot, in general, be neglected compared to the first, even at low densities, since one can show that for the case of interest here the two terms are of the same order of magnitude.[1,16] In fact, in these papers we will see that the most important correction to the equilibrium dynamic structure factor for small wave numbers k, comes from the nonequilibrium pair-correlation function $G_2(1,2)$.

C. Hydrodynamiclike equations from the kinetic equation for $G_2(1,2)$

Having obtained an expression for the pair-correlation function $G_2(1,2)$, we now turn our attention to the calculation of $D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ given by Eq. (3.7b). Since $D_{\alpha\beta}$ is simply a projection of $G_2(1,2)$ onto the hydrodynamic subspace defined by the $\{\psi_\alpha\}$, given by Eq. (2.27), we can adopt the same projection-operator method to determine the $D_{\alpha\beta}$ as we did for the $M_{\alpha\beta}$. However, we now need to consider projection operators acting on both particle indices 1 and 2, since two dynamical operators, $L(1)$ and $L(2)$, appear in Eq. (3.10) for $G_2(1,2)$. This is in contrast to Eq. (2.32) for $\hat{C}(1,2,z)$ where only $L(1)$ appears. We are, therefore, forced to consider a set of four simultaneous equations for the quantities $P(1)P(2)G_2(1,2)$, $P_\perp(1)P(2)G_2(1,2)$, $P(1)P_\perp(2)G_2(1,2)$, and $P_\perp(1)P_\perp(2)G_2(1,2)$. These equations can be derived by applying the products $P(1)P(2)$, $P(1)P_\perp(2)$, $P_\perp(1)P(2)$, and $P_\perp(1)P_\perp(2)$ successively to Eq. (3.10) for G_2, and by writing G_2 in the form

$$G_2(1,2)=P(1)P(2)G_2(1,2)+P(1)P_\perp(2)G_2(1,2)+P_\perp(1)P(2)G_2(1,2)+P_\perp(1)P_\perp(2)G_2(1,2)\ . \qquad (3.12)$$

We then solve three of these simultaneous equations so as to express $P(1)P_\perp(2)G_2$, $P_\perp(1)P(2)G_2$, and $P_\perp(1)P_\perp(2)G_2(1,2)$ in terms of $P(1)P(2)G_2(1,2)$. These expressions are then inserted in the equation for $P(1)P(2)G_2$ to obtain a closed equation for this function in terms of $T(12)F_1(1)F_1(2)$. As for the case discussed in the previous section, we order this equation in powers of the gradients (or l/L_∇) and keep only the terms of order cL_∇^{-1} and $cL_\nabla^{-1}(l/L_\nabla)$. The resulting equation for $P(1)P(2)G(1,2)$ is then found to be

$$(1+P_{12})\left[P(1)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}+P(1)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}P_\perp(1)\Lambda_l^{-1}(1)P_\perp(1)\left[\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}-\Lambda_{\nabla_1}(1)\right]\right]P(1)P(2)G_2(1,2)$$
$$=P(1)P(2)\hat{T}(12)(1+P_{12})F_l(1)F_l(2)\Phi_1(1)\ . \qquad (3.13)$$

The right-hand side of Eq. (3.13) is obtained by using the Chapman-Enskog expansion of F_1, Eq. (2.18), the relation $T(12)F_l(1)F_l(2)=0$ and retaining only the terms proportional to lL_∇^{-1} in the expansion of F_1. In paper II we will show (see Appendix B, subsection II) that the higher-order terms in this expansion can be neglected.

We can convert Eq. (3.13) into a set of hydrodynamical equations for the $D_{\alpha\beta}$ by multiplying this equation by $\psi_\alpha(1)\psi_\beta(2)$ and integrating over $\vec{V}_1$ and $\vec{V}_2$. In so doing, we will need the identity

$$\int d\vec{V}_1\int d\vec{V}_2\psi_\alpha(1)\psi_\beta(2)T(12)(1+P_{12})F_l(1)F_l(2)\Phi_1(1)$$
$$=-\delta(\vec{R}_1-\vec{R}_2)\int d\vec{V}_1\psi_\alpha(1)\psi_\beta(1)\Lambda_l(1)F_l(1)\Phi_1(1)\ , \qquad (3.14)$$

which may easily be proved using that the $\{\psi_\alpha\}$ are conserved quantities in binary collisions.[21] Using also Eqs. (3.14), (2.37), (2.38a), and (2.38b), we obtain the following equation for $P(1)P(2)G_2(1,2)$:

$$\int d\vec{V}_1\int d\vec{V}_2\psi_\alpha(1)\psi_\beta(2)(1+P_{12})\left[P(1)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}+P(1)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}P_\perp(1)\Lambda_l^{-1}P_\perp(1)\left[\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}-\Lambda_{\nabla_1}\right]\right]$$
$$\times P(1)P(2)G_2(1,2)=-n(R_1)\delta(\vec{R}_1-\vec{R}_2)\left[\left[\psi_\alpha(1)\psi_\beta(1)\middle|C_{1i}\left[\frac{\beta mC_1^2}{2}-\frac{5}{2}\right]\right]_l\frac{\partial\ln T}{\partial R_{1i}}\right.$$
$$\left.+\left(\psi_\alpha(1)\psi_\beta(1)\,|\,\beta m(C_{1i}C_{1j}-\tfrac{1}{3}\delta_{ij}C_1^2)\right)_l\frac{\partial u_i}{\partial R_{1j}}\right|\ . \qquad (3.15)$$

The operators on the left-hand side of Eq. (3.15) are, apart from the permutation operator P_{12}, identical to those appearing on the left-hand side of Eq. (2.40) for $P\hat{C}$. Therefore, the analysis of Eq. (3.15) can proceed in the same way as that for Eq. (2.40): one has to carry out all the indicated innerproduct integrals, and relate some to thermodynamic quantities and others to expressions for transport coefficients as given by Eqs. (2.25a) and (2.25b). As a result, we can immediately write the hydrodynamic equations for $D_{\alpha\beta}$ as

$$H_{\alpha\gamma}(\vec{R}_1)D_{\gamma\beta}(\vec{R}_1,\vec{R}_2)+H_{\beta\gamma}(\vec{R}_2)D_{\alpha\gamma}(\vec{R}_1,\vec{R}_2)$$

$$=n(\vec{R}_1)\delta(\vec{R}_1-\vec{R}_2)\left[\left[a_\alpha(1)a_\beta(1)\middle|C_{1i}\left[\frac{\beta mC_1^2}{2}-\frac{5}{2}\right]\frac{\partial\ln T}{\partial R_{1i}}\right]_l+\left[a_\alpha(1)a_\beta(1)\middle|\beta m(C_{1i}C_{1j}-\tfrac{1}{3}\delta_{ij}C_1^2)\frac{\partial u_i}{\partial R_{1j}}\right]_l\right] . \quad (3.16)$$

Here $\underline{H}$ is the evolution matrix defined by Eq. (2.44) with matrix elements given by Eqs. (2.42a)–(2.42c).

Equations (2.44), (3.7a), (3.7b), and (3.16), together with the definitions of the $H_{\alpha\beta}$ in Eq. (2.42), provide us with a complete description of the hydrodynamic fluctuations for a dilute gas maintained in a nonequilibrium steady state. In the following sections we will generalize the ideas and methods used here to derive a set of equations that are valid for a fluid of arbitrary density and that reduce to those given here in the limit of low densities.

IV. HYDRODYNAMICLIKE EQUATIONS FOR THE UNEQUAL-TIME CORRELATIONS FUNCTIONS: GENERAL FLUID

A. Formulation of the problem

In this section we will show that the hydrodynamic equations obtained in Sec. II for $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ for dilute gases, Eq. (2.42), apply to a fluid of arbitrary density as well. The only difference between the equations in Secs. II and IV is that for a general fluid the bulk-viscosity coefficient is not zero and that the other transport coefficients and the thermodynamic quantities have to be replaced by their values for a general fluid. This implies then that also for a general fluid the Onsager regression hypothesis can be generalized to nonequilibrium steady states (cf. Sec. II), i.e., the equations of motion for $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ can be obtained by a linearization of the Navier-Stokes equations about the steady state.

As before, we consider the fluid to be in a nonequilibrium steady state close to local equilibrium. We will apply the idea of the Chapman-Enskog method, used in μ space to construct solutions of the Boltzmann equation, to obtain a similar solution of the Liouville equation in Γ space. That is, we will expand the N-particle distribution function $F_N(x^N)$, which satisfies the Liouville equations, about its value at local equilibrium in powers of the gradients of the hydrodynamic variables. The resulting distribution function will be used to compute ensemble averages in the nonequilibrium steady state. Then using a projection-operator method similar to that used in Sec. II, we will be able to derive equations of motion for the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$.

We begin by defining the Liouville operator L_N for the system (neglecting interactions of the particles of the system with the walls) as

$$L_N(x^N)=\sum_{i=1}^{N}L_0(i)-\sum_{\substack{i<j\\1}}^{N}\theta_{ij} , \quad (4.1)$$

with

$$L_0(i)=\vec{v}_i\cdot\vec{\nabla}_{\vec{r}_i} , \quad (4.2a)$$

and

$$\theta_{ij}=\frac{1}{m}\frac{\partial\phi(r_{ij})}{\partial\vec{r}_i}\cdot\left[\frac{\partial}{\partial\vec{v}_i}-\frac{\partial}{\partial\vec{v}_j}\right] . \quad (4.2b)$$

In general, the distribution function for the system $F_N(x_1,\ldots,x_N,t)$ satisfies Liouville's equation

$$\frac{\partial F_N(x_1,\ldots,x_N,t)}{\partial t}+L_N(x_1,\ldots,x_N)F_N(x_1,\ldots,x_N,t)=0, \quad (4.3)$$

while any function of the phase variables $\tilde{a}(x_1,\ldots,x_N,t)$ satisfies the equation of motion

$$\frac{d\tilde{a}(x_1,\ldots,x_N,t)}{dt}=L_N\tilde{a}(x_1,\ldots,x_N,t) , \quad (4.4a)$$

with formal solution

$$\tilde{a}(x_1,x_2,\ldots,x_N,t)=e^{tL_N}\tilde{a}(x_1,\ldots,x_N,t=0)=\tilde{a}(x_1(t),x_2(t)\ldots,x_N(t),t=0)\ . \tag{4.4b}$$

Here the time evolution operator e^{tL_N} acts on the phases x^N in the function behind it and replaces them with their values a time t later. In the nonequilibrium steady state, the N-particle distribution function $F_N^{\mathrm{ss}}(x_1,\ldots,x_N)$ is independent of time and the correlation functions $M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t)$ defined in general by Eq. (2.2), can be expressed as

$$\begin{aligned}M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t)\equiv M_{\alpha\beta}(\vec{\mathrm{R}}_1,t;\vec{\mathrm{R}}_2,0)&=\int d\Gamma\, F_N^{\mathrm{ss}}(x^N)\delta a_\beta(\vec{\mathrm{R}}_2)e^{tL_N}\delta a_\alpha(\vec{\mathrm{R}}_1)\\ &=\int d\Gamma\,\delta a_\alpha(\vec{\mathrm{R}}_1)e^{-tL_N}F_N^{\mathrm{ss}}(x^N)\delta a_\beta(\vec{\mathrm{R}}_2)\ ,\end{aligned} \tag{4.5}$$

where $d\Gamma=\sum_N (N!)^{-1}dx_1\cdots dx_N$, i.e., we consider grand-canonical-ensemble averages where only the average number of particles is fixed. In writing the second equality in Eq. (4.5), we used Liouville's theorem, neglected interactions of the walls with the fluid and denoted $\delta a_\alpha(\vec{\mathrm{R}}_i,t=0)$ by $\delta a_\alpha(\vec{\mathrm{R}}_i)$. We assume that the system is close to local equilibrium and the distribution function $F_N^{\mathrm{ss}}(x^N)$ can be expanded in powers of the gradients of the hydrodynamic variables as

$$F_N^{\mathrm{ss}}(x^N)=F_L^{\mathrm{ss}}(x^N)+F_{\nabla_1}^{\mathrm{ss}}(x^N)+\cdots\ . \tag{4.6}$$

Here $F_L^{\mathrm{ss}}(x^N)$ is the Γ-space local equilibrium distribution function in the steady-state ensemble, and $F_{\nabla_1}^{\mathrm{ss}}$ is the first correction in the expansion of F_N^{ss} in terms of the spatial gradients in the system. In the next section we will discuss the explicit structure of $F_{\nabla_1}^{\mathrm{ss}}$, but this is not needed for the calculations in this section.

As was the case with the low-density theory developed in Secs. II and III, the properties of the local equilibrium distribution function will be used extensively in deriving the equations for the $M_{\alpha\beta}$ for a general fluid. The local equilibrium distribution function for a system of N particles is given by

$$F_L^{\mathrm{ss}}(x^N)=\frac{e^{y_\alpha * \tilde{a}_\alpha}}{\int d\Gamma\, e^{y_\alpha * \tilde{a}_\alpha}}\ . \tag{4.7a}$$

Here the $\tilde{a}_\alpha$'s are given by Eqs. (2.4a)–(2.4c) with $t=0$, summation convention is used, and the quantity $y_\alpha^* \tilde{a}_\alpha$ is defined by

$$y_\alpha * \tilde{a}_\alpha=\int d\vec{\mathrm{R}}\, y_\alpha(\vec{\mathrm{R}})\tilde{a}_\alpha(\vec{\mathrm{R}})\ . \tag{4.7b}$$

The y_α are the thermodynamic variables conjugate to the $\langle \tilde{a}_\alpha\rangle$. If we denote the set $\{\tilde{a}_\alpha\}$ by $(\tilde{\rho},\tilde{\vec{\mathrm{g}}},\tilde{\epsilon})$ then the set of conjugate (local) variables $\{y_\alpha\}$ is given by $\{\beta\mu-\beta u^2/2,\beta\vec{\mathrm{u}},-\beta\}$,[22] where μ is the local chemical potential. The values of the y_α are determined by the condition[23]

$$\langle \tilde{a}_\alpha(\vec{\mathrm{R}})\rangle=\langle \tilde{a}_\alpha(\vec{\mathrm{R}})\rangle_{L,\mathrm{ss}}\ , \tag{4.8}$$

where $\langle \tilde{a}_\alpha(\vec{\mathrm{R}})\rangle_{L,\mathrm{ss}}$ is the average of $\tilde{a}_\alpha(\vec{\mathrm{R}})$ in the steady-state local equilibrium ensemble with distribution function given by Eq. (4.7a). For the case of interest here, with the $\tilde{a}_\alpha(\vec{\mathrm{R}})$ given by Eq. (2.4) and the corresponding $y_\alpha(\vec{\mathrm{R}})$ given above, the local equilibrium distribution function has the explicit form

$$F_L^{\mathrm{ss}}(x^N)=\frac{e^{\beta_\mu * \tilde{\rho}-\beta * \tilde{\epsilon}'}}{\int d\Gamma\, e^{\beta_\mu * \tilde{\rho}-\beta * \tilde{\epsilon}'}}\ , \tag{4.9}$$

where

$$\tilde{\epsilon}'(\vec{\mathrm{R}})=\tilde{\epsilon}(\vec{\mathrm{R}})-\vec{\mathrm{u}}(\vec{\mathrm{R}})\cdot\tilde{\vec{\mathrm{g}}}(\vec{\mathrm{R}})+\tfrac{1}{2}\tilde{\rho}(\vec{\mathrm{R}})\vec{\mathrm{u}}^2(\vec{\mathrm{R}})\ . \tag{4.10}$$

This is clearly a generalization of an equilibrium ensemble to the case where there is a position-dependent temperature, chemical potential, and nonzero flow velocity in the fluid.

B. Γ-space projection operator

As was the case in the low-density theory in Sec. II, we will construct equations of motion for the $M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t)$ from a fundamental dynamical equation, which is in this case closely related to the Liouville equation, by means of a suitably chosen projection operator that directly relates the $M_{\alpha\beta}$ to the solution of the dynamical equation. For the case of low densities, the basic dynamic equation is the Eq. (2.12) for the time-correlation function $C(1,2,t)$. The relation between the $M_{\alpha\beta}$ and $C(1,2,t)$ is given by Eq. (2.11), and the appropriate projection operator that is used to convert Eq. (2.12) to an equation for the $M_{\alpha\beta}$ is defined by Eq. (2.28).

For the general case of interest here, it is convenient to start with the dynamical equation for the quantity $e^{-tL_N}F_N^{\mathrm{ss}}\delta a_\beta(\vec{\mathrm{R}}_2)$ since it appears in Eq. (4.5). The Laplace transform of $e^{-tL_N}F_N^{\mathrm{ss}}\delta a_\beta(\vec{\mathrm{R}}_2)$ given by

$$F_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=\int_0^\infty dt\, e^{-zt}e^{-tL_N}F_N^{\mathrm{ss}}(x^N)\delta a_\beta(\vec{\mathrm{R}}_2) \tag{4.11}$$

yields the basic equation

$$(z+L_N)F_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=F_N^{\mathrm{ss}}\delta a_\beta(\vec{\mathrm{R}}_2)\ . \tag{4.12}$$

We now introduce a Γ-space local equilibrium projection operator P that projects an arbitrary function $F_L^{\mathrm{ss}}h(x^N)$ onto the space of conserved densities $\tilde{a}_\alpha$. This projection operator is the Γ-space analog of the μ-space projection operator used in Sec. II and is defined as[10]

$$PF_L^{\mathrm{ss}}h(x^N)=F_L^{\mathrm{ss}}\langle h(x^N)\rangle_{L,\mathrm{ss}}+F_L^{\mathrm{ss}}\delta a_\alpha(\vec{\mathrm{R}})*\frac{\delta y_\alpha(\vec{\mathrm{R}})}{\delta\langle\tilde{a}_\beta(\vec{\mathrm{R}}')\rangle_{L,\mathrm{ss}}}*\langle\delta a_\beta(\vec{\mathrm{R}}')h(x^N)\rangle_{L,\mathrm{ss}}\ . \tag{4.13}$$

Here summation convention is used and $\delta y_\alpha(\vec{\mathrm{R}})/\delta\langle\tilde{a}_\beta(\vec{\mathrm{R}}')\rangle_{L,\mathrm{ss}}$ denotes a functional differentiation. One can check that P is a projection operator, i.e., that $P^2=P$, by using the identity

$$\frac{\delta\langle\tilde{a}_\beta(\vec{\mathrm{R}})\rangle_{L,\mathrm{ss}}}{\delta y_\alpha(\vec{\mathrm{R}}')}=\langle\delta a_\beta(\vec{\mathrm{R}})\delta a_\alpha(\vec{\mathrm{R}}')\rangle_{L,\mathrm{ss}} \tag{4.14}$$

that can easily be proved using Eq. (4.7). Further, from Eq. (4.14), it follows that $\delta y_\alpha(\vec{\mathrm{R}})/\delta\langle\tilde{a}_\beta(\vec{\mathrm{R}}')\rangle_{L,\mathrm{ss}}$ in Eq. (4.13) is just the normalizing factor $\langle\delta a_\alpha(\vec{\mathrm{R}}')\delta a_\beta(\vec{\mathrm{R}})\rangle_{L,\mathrm{ss}}^{-1}$.

In order to proceed with the derivation of equations for $M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t)$, we first note the following relation between the projection operator and the Laplace transform of $M_{\alpha\beta}$:

$$PF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=F_L^{\mathrm{ss}}\delta a_\alpha(\vec{\mathrm{R}})*\frac{\delta y_\alpha(\vec{\mathrm{R}})}{\delta\langle\tilde{a}_\gamma(\vec{\mathrm{R}}')\rangle_{L,\mathrm{ss}}}*\hat{M}_{\gamma\beta}(\vec{\mathrm{R}}',\vec{\mathrm{R}}_2,z)\ , \tag{4.15}$$

where $\hat{M}_{\gamma\beta}(\vec{\mathrm{R}}',\vec{\mathrm{R}}_2,z)$ is the Laplace transform of $M_{\gamma\beta}(\vec{\mathrm{R}}',\vec{\mathrm{R}}_2,t)$. In giving Eq. (4.15), we have used Eq. (4.13) and that

$$\int d\Gamma\, F_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=0\ .$$

Equation (4.15) and the relation

$$\int d\Gamma\,\delta a_\gamma(\vec{\mathrm{R}}_1)PF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=\hat{M}_{\gamma\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,z) \tag{4.16}$$

together with the projection operator P will be used next to derive hydrodynamiclike equations for $\hat{M}_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,z)$.

To develop the projection-operator equation for $PF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}$, we apply P and $P_\perp=(1-P)$ successively to Eq. (4.12). This leads to the two equations

$$zPF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)+PL_NPF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)+PL_NP_\perp F_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=PF_N^{\mathrm{ss}}\delta a_\beta(\vec{\mathrm{R}}_2) \tag{4.17a}$$

and

$$zP_\perp F_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)+P_\perp L_NP_\perp F_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)+P_\perp L_NPF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=P_\perp F_N^{\mathrm{ss}}\delta a_\beta(\vec{\mathrm{R}}_2)\ . \tag{4.17b}$$

After solving Eq. (4.17b) for $P_\perp F_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}$ in terms of $PF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}$ and inserting the result into Eq. (4.17a), we obtain an equation for $PF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}$, similar to Eq. (2.36), of the form

$$\begin{aligned}[z+PL_NP-PL_NP_\perp(z+P_\perp L_NP_\perp)^{-1}P_\perp L_NP]PF_N^{\mathrm{ss}}\delta\hat{a}_{\beta z}(\vec{\mathrm{R}}_2)=&\,PF_N^{\mathrm{ss}}\delta a_\beta(\vec{\mathrm{R}}_2)\\&-PL_NP_\perp(z+P_\perp L_NP_\perp)^{-1}P_\perp F_N^{\mathrm{ss}}\delta a_\beta(\vec{\mathrm{R}}_2)\ .\end{aligned} \tag{4.18}$$

As in the low-density case, we order the terms appearing in Eq. (4.18) in powers of (lL_∇^{-1}) where l is a length that characterizes the range of the microscopic correlations between the particles in the fluid. To obtain explicit equations for the $\hat{M}_{\alpha\beta}$, we multiply Eq. (4.18) by $\int d\Gamma\,\delta a_\alpha(\vec{\mathrm{R}}_1)$ and use Eqs. (4.15) and (4.16), and $\langle\delta a_\alpha(\vec{\mathrm{R}}_1)\rangle_{L,\mathrm{ss}}=0$ to obtain

$$z\hat{M}_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,z)+E_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,z)-N_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,z)=M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t=0)\ , \tag{4.19}$$

where

$$E_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t)=\left[\int d\Gamma\,\delta a_\alpha(\vec{\mathrm{R}}_1)L_N\delta a_\sigma(\vec{\mathrm{R}}_3)F_L^{\mathrm{ss}}(x^N)\right]*\frac{\delta y_\sigma(\vec{\mathrm{R}}_3)}{\delta\langle\tilde{a}_\gamma(\vec{\mathrm{R}}_4)\rangle_{L,\mathrm{ss}}}*\hat{M}_{\gamma\beta}(\vec{\mathrm{R}}_4,\vec{\mathrm{R}}_2,z) \tag{4.20a}$$

and

$$N_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z) = -\left[\int d\Gamma[P_\perp^\dagger L_N \delta a_\alpha(\vec{R}_1)](z+P_\perp L_N P_\perp)^{-1}P_\perp L_N F_L^{ss}\delta a_\sigma(\vec{R}_3)\right] * \frac{\delta y_\sigma(\vec{R}_3)}{\delta\langle\tilde{a}_\gamma(\vec{R}_4)\rangle_{L,ss}} * \hat{M}_{\gamma\beta}(\vec{R}_4,\vec{R}_2,z) \; . \tag{4.20b}$$

Here we have used that the adjoint of P is $P^\dagger=(F_L^{ss})^{-1}PF_L^{ss}$ and we have neglected the second term on the right-hand side of Eq. (4.18), which is a gradient dependent correction to the initial condition term $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t=0)$ that can be dropped for reasons to be discussed in paper II. The terms $E_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$ are proportional to the first power of the spatial gradients acting on $\hat{M}_{\alpha\beta}$ and represent the nondissipative, or Euler, contributions to the hydrodynamic equations for the $\hat{M}_{\alpha\beta}$, while the terms $N_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$ are proportional to the second powers of the spatial gradients acting on $\hat{M}_{\alpha\beta}$ and represent the dissipative or Navier-Stokes terms in the hydrodynamic equations for the $\hat{M}_{\alpha\beta}$. To see this, one need only use that

$$L_N\delta a_\alpha(\vec{R}) = -\left[\frac{\partial}{\partial R_i}\right]\tilde{J}_{\alpha i}(\vec{R}) \; ,$$

where the $\tilde{J}_{\alpha i}(\vec{R})$ are microscopic fluxes. For the explicit expressions of $\tilde{J}_{\alpha i}(R)$ we refer to the literature.[24] As an example, we quote:

$$L_N\delta\rho(\vec{R}) = -\left[\frac{\partial}{\partial R_i}\right]\tilde{g}_i(\vec{R}) \; ,$$

where $\tilde{\vec{g}}(\vec{R})$ is the mass flux.

C. Hydrodynamiclike equations for the unequal-time correlation functions

To obtain explicit equations for $\hat{M}_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$ from the formal equations given by Eqs. (4.19) and (4.20), one orders the terms in Eq. (4.19) in powers of (lL_{∇}^{-1}). Provided we consider fluids that are not close to their critical points, l will be on the order of the range of the forces for a liquid, while for a gas, l is on the order of a mean-free path. Since the calculations to $O(l)$ are straightforward and can be found in the literature[24] for the special case of an equilibrium fluid, we will not give the details here but merely quote the results.[25]

The equations for $\hat{M}_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$ are as follows.

(a) For $\alpha=\rho$:

$$z\hat{M}_{\rho\beta}+\frac{\partial}{\partial R_{1i}}\hat{M}_{g_i\beta}=M_{\rho\beta}(\vec{R}_1,\vec{R}_2,t=0) \; ; \tag{4.21a}$$

(b) for $\alpha=g_i$:

$$z\hat{M}_{g_i\beta}+\frac{\partial}{\partial R_{1j}}\left[\delta_{ij}\left[\frac{\partial p}{\partial\rho}\right]_\epsilon\hat{M}_{\rho\beta}+\delta_{ij}\left[\frac{\partial p}{\partial\epsilon}\right]_\rho\hat{M}_{\epsilon'\beta}+\rho u_i\hat{M}_{u_j\beta}+u_j\hat{M}_{g_i\beta}\right]$$

$$=M_{g_i\beta}(\vec{R}_1,\vec{R}_2,t=0)+\frac{\partial}{\partial R_{1j}}(\eta\Delta_{ij,kl}+\zeta\delta_{ij}\delta_{kl})\frac{\partial}{\partial R_{1k}}\hat{M}_{u_l\beta}$$

$$+2\frac{\partial}{\partial R_{1j}}\left[\left[\frac{\partial\eta}{\partial\rho}\right]_\epsilon\hat{M}_{\rho\beta}+\left[\frac{\partial\eta}{\partial\epsilon}\right]_\rho\hat{M}_{\epsilon'\beta}\right]\left[D_{ij}-\frac{\delta_{ij}}{3}D_{ll}\right]$$

$$+\frac{\partial}{\partial R_{1j}}\left[\left[\frac{\partial\zeta}{\partial\epsilon}\right]_\rho\hat{M}_{\rho\beta}+\left[\frac{\partial\zeta}{\partial\epsilon}\right]_\rho\hat{M}_{\epsilon'\beta}\right]\delta_{ij}D_{ll} \; ; \tag{4.21b}$$

(c) for $\alpha=\epsilon'$:

$$
\begin{aligned}
z\hat{M}_{\epsilon'\beta}+u_i\frac{\partial}{\partial R_{1i}}\hat{M}_{\epsilon'\beta}+\left[\frac{\partial h}{\partial\rho}\right]_{\epsilon}\hat{M}_{\rho\beta}\frac{\partial u_i}{\partial R_{1i}}+\left[\frac{\partial h}{\partial\epsilon}\right]_{\rho}\hat{M}_{\epsilon'\rho}\frac{\partial u_i}{\partial R_{1i}}+\hat{M}_{u_i\beta}\frac{\partial\epsilon}{\partial R_{1i}}+h\frac{\partial}{\partial R_{1i}}\hat{M}_{u_i\beta}\\
=M_{\epsilon'\beta}(\vec{R}_1,\vec{R}_2,t=0)+\frac{\partial}{\partial R_{1i}}\lambda\frac{\partial}{\partial R_{1i}}\left[\left[\frac{\partial T}{\partial\rho}\right]_{\epsilon}\hat{M}_{\rho\beta}+\left[\frac{\partial T}{\partial\epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}\right]\\
+\frac{\partial}{\partial R_{1i}}\left[\left[\frac{\partial\lambda}{\partial\rho}\right]_{\epsilon}\hat{M}_{\rho\beta}+\left[\frac{\partial\lambda}{\partial\epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}\right]\frac{\partial T}{\partial R_{1i}}+2\left[2\eta\left[D_{ij}-\frac{\delta_{ij}}{3}D_{ll}\right]+\zeta\delta_{ij}D_{ll}\right]\frac{\partial}{\partial R_{1i}}\hat{M}_{u_j\beta}\\
+2D_{ij}\left[\left[\frac{\partial\eta}{\partial\rho}\right]_{\epsilon}\hat{M}_{\rho\beta}+\left[\frac{\partial\eta}{\partial\epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}\right]\left[D_{ij}-\frac{\delta_{ij}}{3}D_{ll}\right]+D_{ii}\left[\left[\frac{\partial\zeta}{\partial\rho}\right]_{\epsilon}\hat{M}_{\rho\beta}+\left[\frac{\partial\zeta}{\partial\epsilon}\right]_{\rho}\hat{M}_{\epsilon'\beta}\right]D_{ll}\ .
\end{aligned}
\tag{4.21c}
$$

In these equations p, $\vec{u}$, T, ρ, ϵ, h, η, ζ, and λ are the pressure, flow velocity, temperature, mass density, energy density, enthalpy density, shear viscosity, bulk viscosity, and heat conductivity, respectively, at the point $\vec{R}_1$ and $\hat{M}_{\epsilon'\beta}$ and $\hat{M}_{u_i\beta}$ are defined by the equations [cf. Eqs. (2.30) and (2.43)]:

$$\hat{M}_{u_i\beta}(\vec{R}_1,\vec{R}_2,z)=\frac{1}{\rho(\vec{R}_1)}[\hat{M}_{g_i\beta}(\vec{R}_1,\vec{R}_2,z)-u_i(\vec{R}_1)\hat{M}_{\rho\beta}(\vec{R}_1,\vec{R}_2,z)]\ , \tag{4.22a}$$

$$\hat{M}_{\epsilon'\beta}(\vec{R}_1,\vec{R}_2,z)=\hat{M}_{\epsilon\beta}(\vec{R}_1,\vec{R}_2,z)-u_i(\vec{R}_1)\hat{M}_{g_i\beta}(\vec{R}_1,\vec{R}_2,z)+\frac{u^2}{2}(\vec{R}_1)\hat{M}_{\rho\beta}(\vec{R}_1,\vec{R}_2,z)\ . \tag{4.22b}$$

Further, local Green-Kubo expressions have been used for the transport coefficients η, ζ, and λ. Since they are used in deriving Eqs. (4.21), we give them here for reference. Denoting the set of microscopically conserved densities by $\{\tilde{\rho},\tilde{g},\tilde{\epsilon}\}$, the corresponding set of microscopic currents are $\{\tilde{g}_i,\tilde{t}_{ij},\tilde{s}_i\}$ with $\tilde{g}_i$ the mass flux, $\tilde{t}_{ij}$ the momentum flux, and $\tilde{s}_i$ the energy flux.[24] The local Green-Kubo formulas used in deriving Eqs. (4.21) are[26]

$$\frac{1}{k_BT(\vec{R}_1)}\lim_{z\to 0}\langle\hat{T}_{ki}(\vec{R}_1,z)T_{jl,T}\rangle_{0,\vec{R}_1}=\eta(\vec{R}_1)\Delta_{ik,jl}+\zeta(\vec{R}_1)\delta_{ik}\delta_{jl} \tag{4.23a}$$

$$\frac{1}{k_BT^2(\vec{R}_1)}\lim_{z\to 0}\langle\hat{S}'_i(\vec{R}_1,z)S'_{j,T}\rangle_{0,\vec{R}_1}=\lambda(\vec{R}_1)\delta_{ij} \tag{4.23b}$$

with

$$S'_i=S_i-u_jT_{ji} \tag{4.23c}$$

and

$$\langle S'_{i,T}\hat{T}_{ki}(\vec{R}_1,z)\rangle_{0,\vec{R}_1}=0\ . \tag{4.23d}$$

In Eqs. (4.23), $T_{ij}(\vec{R}_1)\equiv P^{\dagger}\tilde{t}_{ij}(\vec{R}_1)\equiv I_{g_i,j}(\vec{R}_1)$, $S_j(\vec{R}_1)\equiv P^{\dagger}\tilde{s}_j(\vec{R}_1)\equiv I_{\epsilon,j}(\vec{R}_1)$, $\hat{I}_{\alpha,j}(\vec{R}_1,z)=(z-L_N)^{-1}\times I_{\alpha,j}(\vec{R}_1)$, and

$$I_{\alpha,jT}=\int d\vec{R}_1I_{\alpha,j}(\vec{R}_1)\ .$$

Further, the angular brackets $\langle\ \rangle_{0,\vec{R}_1}$ denote an average over a position-dependent distribution function, $F_0(x^N\,|\,\vec{R}_1)$ that has the form of a total equilibrium N-particle distribution function except that the temperature, chemical potential, and mean velocity depend parametrically on the position $\vec{R}_1$ in the fluid, i.e.,

$$F_0(x^N\,|\,\vec{R}_1)=\frac{e^{y_\alpha(\vec{R}_1)a_{\alpha,T}}}{\int d\Gamma\, e^{y_\alpha(\vec{R}_1)a_{\alpha,T}}} \tag{4.24}$$

with $a_{\alpha,T}=\int d\vec{R}\ \tilde{a}_\alpha(\vec{R})$. The position-dependent distribution function $F_0(x^N\,|\,\vec{R}_1)$ appears naturally in the derivation of the hydrodynamiclike equations, Eqs. (4.21), when one expands the $y_\alpha(\vec{R})$ in the local equilibrium distribution function Eq. (4.7a), about their values at the point R_1.

Comparing Eqs. (2.42) and (4.21), it is clear that they differ only in that the values of the thermodynamic and transport quantities that appear in Eq. (4.21) are replaced by their low-density values (including $\zeta=0$) in Eq. (2.42). Equation (4.21) has also been derived by Brey,[27] who used a method based on a different projection operator.

Again, as in the low-density case, Eqs. (4.21) can be put in the general matrix form

$$z\hat{M}_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)=H_{\alpha\gamma}(\vec{R}_1)\hat{M}_{\gamma\beta}(\vec{R}_1,\vec{R}_2,z)+M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,0)\ , \qquad (4.25)$$

where the matrix $\underline{H}$ can be obtained from Eqs. (4.21). To complete our calculations of $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,z)$, we will have to solve Eq. (4.21) in terms of the equal-time correlation functions $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t=0)$, and in Sec. V we show how these functions may be computed.

V. EQUAL-TIME CORRELATION FUNCTIONS FOR A GENERAL FLUID

A. Formulation of the problem

To obtain the equal-time correlation function $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t=0)\equiv M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$, we need to determine the explicit form of the nonequilibrium steady-state distribution function $F_N^{\rm ss}(x^N)$, since $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ is given by

$$\begin{aligned}M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)&=\langle \delta a_\alpha(\vec{R}_1)\delta a_\beta(\vec{R}_2)\rangle_{\rm ss}\\&=\int d\Gamma\, \delta a_\alpha(\vec{R}_1)\delta a_\beta(\vec{R}_2)F_N^{\rm ss}(x^N)\ . \qquad (5.1)\end{aligned}$$

We shall first give a normal solution to Liouville's equation for $F_N^{\rm ss}(x^N)$ in the form of the sum of the local equilibrium distribution function $F_L^{\rm ss}$ given in the previous section and a correction term proportional to the gradients of the hydrodynamic quantities. We then indicate how one can determine the explicit form of the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ by a generalization of the mode-coupling methods developed for systems in equilibrium[14,15] to systems in a nonequilibrium steady state.[28] This will lead to a set of hydrodynamiclike equations for the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ that are the extension of Eq. (3.16) to the case of a general fluid.

The formal solution of Liouville's equation for $F_N^{\rm ss}(x^N)$ is obtained by a systematic but formal expansion in powers of l/L_∇ where l is the correlation length discussed earlier and L_∇ is a hydrodynamic gradient length. If we neglect terms of $O[(l/L_\nabla)^2]$, the $F_N^{\rm ss}(x^N)$ can be determined by a number of techniques given in the literature.[15,29] To $O[(l/L_\nabla)]$, the result is

$$F_N^{\rm ss}(x^N)=F_L^{\rm ss}(x^N)-\int_0^\infty dt\, e^{-L_N t}F_L^{\rm ss}(x^N)I_{\alpha,i} * \frac{\partial y_{\alpha,i}}{\partial R_i}\ , \qquad (5.2)$$

where $F_L^{\rm ss}$ is given by Eq. (4.7) and $I_{\alpha,i}$ below Eq. (4.23). With the aid of this expression for the distribution function, we can compute the equal-time correlation function $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$.

We begin by writing $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ as

$$M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)=A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)+D_{\alpha\beta}(\vec{R}_1,\vec{R}_2) \qquad (5.3a)$$

with

$$A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)=\langle \delta a_\alpha(\vec{R}_1)\delta a_\beta(\vec{R}_2)\rangle_{L,\rm ss} \qquad (5.3b)$$

and

$$D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)=-\int_0^\infty d\tau\langle \delta a_\alpha(\vec{R}_1,\tau)\delta a_\beta(\vec{R}_2,\tau)I_{\gamma,i}(\vec{R})\rangle_{L,\rm ss} * \frac{\partial y_{\gamma,i}(\vec{R})}{\partial R_i}\ , \qquad (5.3c)$$

where

$$\delta a_\alpha(\vec{R}_1,\tau)=e^{\tau L_N}\delta a_\alpha(\vec{R}_1)\ . \qquad (5.3d)$$

The quantities $A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ are the analogs for a general fluid of those defined by Eq. (3.7a). They may be readily computed, as they are equal-time correlation functions in a local equilibrium ensemble. In particular, one can expand $F_L^{\rm ss}$ about the reference ensemble $F_0^{\rm ss}(x^N\,|\,\vec{R}_1)$ and use this expansion to produce a gradient expansion of $A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$. As shown in the next paper, we will, in fact, only need the lowest-order term for the application to light scattering.

B. Hydrodynamiclike equations for $D_{\alpha\beta}$

Since the quantities $D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ vanish in an equilibrium ensemble, they are proportional at least to the gradients of the hydrodynamic quantities. They are the analogs of the quantities $D_{\alpha\beta}$ defined by Eq. (3.7b), and they are responsible for the long-range correlations contained in $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$. As in Sec. III, we show here that the $D_{\alpha\beta}$ satisfy a hydrodynamiclike set of equations.

First, we consider $\Gamma_{\alpha\beta\gamma}$ defined by

$$\begin{aligned}&\Gamma_{\alpha\beta\gamma}(\vec{R}_1,\vec{R}_2,\vec{R},\tau)\\&\quad=\langle \delta a_\alpha(\vec{R}_1,\tau)\delta a_\beta(\vec{R}_2,\tau)I_{\gamma,i}(\vec{R})\rangle_{L,\rm ss}\ . \qquad (5.4)\end{aligned}$$

To determine the behavior of Γ with time τ, we use a simple extension of the method of Ernst *et al.*[12,15] We will only give the results and refer to the literature for the details.

The main result that we need is that $\Gamma_{\alpha\beta\gamma}(\vec{R}_1,\vec{R}_2,\vec{R},\tau)$ is given by the expression

$$\Gamma_{\alpha\beta\gamma}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,\vec{\mathrm{R}},\tau)=\langle\{[e^{\tau\underline{H}(\vec{\mathrm{R}}_1)}]_{\alpha\delta}\delta a_\delta(\vec{\mathrm{R}}_1)\}\{[e^{\tau\underline{H}(\vec{\mathrm{R}}_2)}]_{\beta\epsilon}\delta a_\epsilon(\vec{\mathrm{R}}_2)\}\hat{I}_{\gamma,i}(\vec{\mathrm{R}})\rangle_{L,\mathrm{ss}}\ , \tag{5.5}$$

where $\underline{H}(\vec{\mathrm{R}})$ is the hydrodynamic evolution matrix defined by Eq. (4.21). It is worth noting that this result of mode-coupling theory is equivalent to the replacement of the exact microscopic value of $\delta a_\alpha(\vec{\mathrm{R}},\tau)$,

$$\delta a_\alpha(\vec{\mathrm{R}},\tau)=(\exp\tau L_N)\delta a_\alpha(\vec{\mathrm{R}})$$

by a hydrodynamic approximation

$$\delta a_\alpha(\vec{\mathrm{R}},\tau)\approx[\exp\tau\underline{H}(\vec{\mathrm{R}})]_{\alpha\beta}\delta a_\beta(\vec{\mathrm{R}})\ .$$

Such a replacement can only be understood if one replaces the exact values of the microscopic densities at point $\vec{\mathrm{R}}_1$ by suitably defined coarse-grained densities. Then one can reasonably assume that although the microscopic densities evolve in time according to the microscopic dynamics, their coarse-grained counterparts evolve through hydrodynamic processes. The method of Ernst *et al.*[15] is designed to provide a plausible foundation for the replacement of microscopic evolution by hydrodynamic evolution in the computation of time-correlation functions like those discussed here.

To obtain the desired hydrodynamic equations for $D_{\alpha\beta}$, we differentiate Eq. (5.4) with respect to time (τ), and multiply the resulting expression by

$$\left[-\int_0^\infty d\tau * \frac{\partial y_\gamma(\vec{\mathrm{R}})}{\partial R_i}\right]$$

so as to obtain

$$\begin{aligned}H_{\alpha\gamma}(\vec{\mathrm{R}}_1)D_{\gamma\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2)+H_{\beta\gamma}(\vec{\mathrm{R}}_2)D_{\alpha\gamma}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2)\\=\langle\delta a_\alpha(\vec{\mathrm{R}}_1)\delta a_\beta(\vec{\mathrm{R}}_2)\hat{I}_{\gamma,i}(\vec{\mathrm{R}})\rangle_{L,\mathrm{ss}}\\ *\frac{\partial y_\gamma(\vec{\mathrm{R}})}{\partial R_i}\ .\end{aligned} \tag{5.6}$$

Consistent with our Navier-Stokes approximation for F_N^{ss}, we can expand the local equilibrium steady-state average on the right-hand side of Eq. (5.6) about the reference ensemble, $F_0^{\mathrm{ss}}(x^N\mid\vec{\mathrm{R}}_1)$. In the same approximation we can replace $\hat{I}_{\gamma,i}(\vec{\mathrm{R}})*\partial y_\gamma/\partial R_i$ by $I_{\gamma,iT}\partial y_\alpha(\vec{\mathrm{R}}_1)/\partial R_{1i}$ where $I_{\gamma,iT}$ is defined below Eq. (4.23) and we replace

$$\langle\delta a_\alpha(\vec{\mathrm{R}}_1)\delta a_\beta(\vec{\mathrm{R}}_2)I_{\gamma,iT}\rangle_{0,\vec{\mathrm{R}}_1}$$

by

$$V^{-1}\delta(\vec{\mathrm{R}}_1-\vec{\mathrm{R}}_2)\langle\delta a_{\alpha T}\delta a_{\beta T}I_{\gamma,iT}\rangle_{0,\vec{\mathrm{R}}_1}+O(\nabla^2)\ .$$

The quantities $\delta a_{\alpha T}$ and $\delta a_{\beta T}$ are defined in a manner similar to that for $I_{\gamma,iT}$. The resulting equation for $D_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2)$ is then

$$\begin{aligned}H_{\alpha\gamma}(\vec{\mathrm{R}}_1)D_{\gamma\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2)+H_{\beta\gamma}(\vec{\mathrm{R}}_2)D_{\alpha\gamma}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2)\\=\delta(\vec{\mathrm{R}}_1-\vec{\mathrm{R}}_2)(\delta a_{\alpha T}\delta a_{\beta T}I_{\gamma,iT})_{0,\vec{\mathrm{R}}_1}\frac{\partial y_\gamma(\vec{\mathrm{R}}_1)}{\partial R_{1i}}\\=\delta(\vec{\mathrm{R}}_1-\vec{\mathrm{R}}_2)\left[(\delta a_{\alpha T}\delta a_{\beta T}S'_{iT})_{0,\vec{\mathrm{R}}_1}\beta\frac{\partial\ln T(\vec{\mathrm{R}}_1)}{\partial R_{1i}}+(\delta a_{\alpha T}\delta a_{\beta T}T_{i,jT})_{0,\vec{\mathrm{R}}_1}\beta\frac{\partial u_i(\vec{\mathrm{R}}_1)}{\partial R_{ij}}\right]\ ,\end{aligned} \tag{5.7}$$

where

$$(\delta a_{\alpha T}\delta a_{\beta T}I_{\gamma,iT})_{0,\vec{\mathrm{R}}_1}=\frac{1}{V}\langle\delta a_{\alpha T}\delta a_{\beta T}I_{\gamma,iT}\rangle_{0,\vec{\mathrm{R}}_1}\ , \tag{5.8}$$

and we have used that $\{I_{\gamma,iT}\}=\{0,T_{ijT},S_{iT}\}$ is defined below Eq. (4.23) and S'_{iT} by Eq. (4.23c).

We remark that Eq. (5.7) is the analog for a general fluid of Eq. (3.16) derived for a dilute gas using the kinetic equation (3.10) for the pair-correlation function $G_2(1,2)$. Equation (5.7) has also been derived by Ronis *et al.*[30] and by Machta[31] using different methods.

VI. DISCUSSION

We conclude this paper with a number of remarks.

(1) We have derived hydrodynamic equations for the time-correlation functions $M_{\alpha\beta}(\vec{\mathrm{R}}_1,\vec{\mathrm{R}}_2,t)$ and for the equal-time correlation functions $M_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{R}}_2)$ by two methods: by kinetic theory, for dilute gases, and by nonequilibrium ensemble methods, for general fluids. The advantage of the kinetic-theory method is that a partial justification of the validity of the basic Eqs. (2.12) and (3.10) for C and G_2, respectively, can be given. In fact, one can show that some contributions due to higher-order col-

lisions, such as triple collisions, ring collisions, etc., can indeed be neglected in these equations, since they lead to effects of higher order in the density than kept here. However, it should be stressed that a complete justification based on kinetic theory is not available at present even in this relatively simple case. In spite of this limitation, what can be accomplished in kinetic theory is still more concrete and trustworthy than the purely formal hydrodynamic derivations presented in Secs. III and IV. Since the hydrodynamic results reduce in the low-density case to the kinetic ones, it seemed worthwhile to give the kinetic derivation also in order to support the use of the more general but formal hydrodynamic results in the next two papers.

(2) Equations equivalent to those for the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ derived in Sec. IV have been obtained by a number of authors using a variety of methods. These methods may be grouped into two categories. One method is similar to that followed here. Starting from the Liouville equation, one constructs an ensemble distribution function that describes the nonequilibrium steady state in terms of which both equal- and unequal-time correlation functions can be computed. This method has been used by Oppenheim, Procaccia, Ronis and co-workers,[2,30,31] and by Brey[27] to derive a set of equations for the various time-correlation functions needed to compute $S(\vec{k},\omega)$. While the techniques differ, the results obtained for the correlation functions agree to first order in the gradients of the hydrodynamic variables.

The other method that has been used in this connection seems, at first glance, to be completely different in spirit, and is based on fluctuating hydrodynamics. In this method one assumes that the fluctuations of the microscopic densities $\delta a_\alpha(\vec{R},t)$ obey a set of Langevin-type hydrodynamic equations, which are the Navier-Stokes equations linearized about the steady state, to which a fluctuating stress tensor and heat-flow vector have been added, as suggested by Landau and Lifshitz.[32] The relevant Langevin-type hydrodynamic equations for the nonequilibrium states were first postulated by Keizer,[13] together with the prescription that the correlations of the fluctuating terms are to be computed by assuming that these correlations have the same form as given by Landau and Lifshitz, except that the temperature, velocity, transport coefficients, and other thermodynamic variables are replaced by their local values in the nonequilibrium steady state. Furthermore, in this approach one does not have to evaluate the equal-time correlation functions $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t=0)$, separately, since they too are determined by the correlations of the fluctuating stress tensor and heat-flow vector. This method was used by Tremblay, Siggia, and Arai,[3] van der Zwan, Bedeaux and Mazur,[5] and by Ronis and Putterman.[4] The explicit results obtained by these authors for $S(\vec{k},\omega)$ are in agreement with the ensemble methods used here to first order in the gradients.

It may seem surprising that these two methods—ensemble theory and fluctuating hydrodynamics—should give identical results, especially so since the ensemble method has to resort to mode-coupling theory to compute equal-time correlation functions, while these correlations seem to follow directly from the Langevin assumption in the fluctuating hydrodynamic equations. It is, therefore, worth spending some time to illustrate the connection between these two methods. This is done in the Appendix. For the sake of simplicity and brevity we consider the case of a dilute gas so that the methods of kinetic theory can be employed. In the Appendix we outline a method by means of which one can show that both the unequal- and equal-time correlation functions determined by fluctuating hydrodynamics are completely consistent with those obtained from the ensemble theory. The source of the agreement is that both methods agree on some crucial features of a certain equal-time correlation function, and on the form of the hydrodynamiclike equations for the time-dependent correlation functions.

(3) We have emphasized in the Introduction that in a fluid in a nonequilibrium steady state, correlations between fluctuations extend over a much larger range than in fluids in equilibrium, and that these long-range correlations are closely related to the appearance of "long-time tails" in the equilibrium time-correlation functions that determine transport coefficients. These points will be clarified in more detail in the following papers, where we apply the formalism developed here to the case of a system with a temperature gradient and explicitly compute the relevant correlation functions.

(4) In our derivation of the equations for $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ and $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,,t=0)$, we regularly made gradient expansions and neglected, without detailed argument, both higher-order terms in the gradient expansions, and corrections to initial condition terms that appeared in our equations. In the next paper we will introduce the various expansion parameters that appear when these equations are solved to compute the $S(\vec{k},\omega)$ and we will show there (cf. Appendix I B, subsection II), how one can justify the approximations made here.

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APPENDIX

In this appendix we give a brief outline of the connection between the hydrodynamic equations derived from the kinetic theory presented in Secs. II and III and the hydrodynamic Langevin approach discussed by Keizer.

I. Fluctuating hydrodynamic equations from the fluctuating Boltzmann equation

As a first step, we derive Keizer's fluctuating hydrodynamic equations for the fluctuations δa_α from a kinetic equation for the fluctuation of the single-particle distribution function $\delta F(1,t) = \tilde{F}(1,t) - \langle \tilde{F}(1,t) \rangle_{ss}$, defined below Eq. (2.7). We assume that the fluctuations in a dilute gas are described by a Boltzmann equation linearized around the average state $F_1(1) = \langle \tilde{F}(1,t) \rangle_{ss}$ with a random force $\tilde{S}(1,t)$ added. The equation of motion for the fluctuations is then,

$$\left[\frac{\partial}{\partial t} + L(1)\right] \delta F(1,t) = \tilde{S}(1,t) . \tag{A1}$$

Here $L(1)$ is given by Eq. (2.34). The random force $\tilde{S}(1,t)$ is assumed to have the following properties:

$$\langle \tilde{S}(1,t) \rangle_{ss} = 0 , \tag{A2a}$$

$$\langle \tilde{S}(1,t) \tilde{S}(2,t') \rangle_{ss} = \Gamma(1,2) \delta(t-t') , \tag{A2b}$$

$$\langle \tilde{S}(1,t) \delta F(2,0) \rangle_{ss} = 0 \quad \text{for } t > 0 , \tag{A2c}$$

where $\Gamma(1,2)$ is as yet undetermined. We fix $\Gamma(1,2)$ by requiring that Eqs. (A1) and (A2) give the same equal-time correlation function as Eqs. (3.3), (3.4), and (3.10) of the text. By formally solving Eq. (A1) and requiring that its solution gives the correct equal-time correlation function, it is straightforward to show that[1,16]

$$\begin{aligned}\Gamma(1,2) = &-[\Lambda_l(1) + \Lambda_\nabla(1) + \Lambda_l(2) + \Lambda_\nabla(2)] \delta(1-2) F_1(1) \\ &+ \hat{T}(12) F_1(1) F_1(2) + \delta(1-2) \int d3\, \hat{T}(13) F_1(1) F_1(3) .\end{aligned} \tag{A3}$$

Here the notation is identical to that used in Sec. II, and we write $\Lambda_\nabla(1) = \Lambda_{\nabla_1}(1) + \Lambda_{\nabla_2}(1) + \cdots$.

Using the μ-space projection operator given in Sec. II, we can derive the fluctuating hydrodynamic equations that are associated with Eq. (A1). The derivation proceeds in a manner identical to that used in Sec. II for $C(1,2,t)$ and will not be duplicated here. The resulting equations are to Navier-Stokes order, in matrix notation:

$$\frac{\partial}{\partial t} \delta a_\alpha(\vec{R}_1,t) = H_{\alpha\gamma}(\vec{R}_1) \delta a_\gamma(\vec{R}_1,t) + \tilde{\sigma}_\alpha(\vec{R}_1,t) . \tag{A4}$$

Here δa_α is the column vector whose components are $\delta\rho$, δg_x, δg_y, δg_z, and $\delta\epsilon'$, and $\tilde{\vec{\sigma}}$ is a column vector representing the hydrodynamic "fluctuating forces" with components

$$\tilde{\vec{\sigma}} = (0, \partial \tilde{P}_{xi}/\partial R_{1i}, \partial \tilde{P}_{yi}/\partial R_{1i}, \partial \tilde{P}_{zi}/\partial R_{1i}, \partial \tilde{Q}_i/\partial R_{1i}) ,$$

where $\underline{\tilde{P}}$ is the fluctuating stress tensor and $\underline{\tilde{Q}}$ is the fluctuating heat flux defined by

$$\tilde{P}_{ij}(\vec{R}_1,t) = m \int d\vec{V}_1 C_{1i} C_{1j} P_\perp(1) \times \frac{1}{\Lambda_l(1)} P_\perp(1) \tilde{S}(1,t) ,$$

$$\tilde{Q}_i(\vec{R}_1,t) = \frac{1}{\beta} \int d\vec{V}_1 C_{1i} \left[\frac{\beta m C_1^2}{2} - \frac{3}{2}\right] P_\perp(1) \times \frac{1}{\Lambda_l(1)} P_\perp(1) \tilde{S}(1,t) . \tag{A5}$$

In Eq. (A4), $\underline{H}$ is the evolution matrix discussed in Secs. II and III and in deriving Eq. (A4) we have used that

$$\langle [P(1)\tilde{S}(1,t)] \tilde{S}(2,t') \rangle_{ss} = \langle \tilde{S}(1,t) [P(2)\tilde{S}(2,t')] \rangle_{ss} = 0 , \tag{A6}$$

which can be obtained from Eqs. (A2) and (A3), and the property that the ψ_α are conserved in a binary collision.

Since in $\tilde{\sigma}$ both $\underline{\tilde{Q}}$ and $\underline{\tilde{P}}$ are preceded by a spatial derivative, it follows that $\langle \tilde{\sigma} \tilde{\sigma} \rangle$ is at least of $O(\nabla^2)$ for Navier-Stokes fluctuating hydrodynamics. Examining $\Gamma(1,2)$ [cf. Eq. (A3)], we see that all one needs of $\Gamma(1,2)$ to compute the correlation of the random force to this order is

$$\Gamma_{\text{eff}}(1,2)=-[\Lambda_l(1)+\Lambda_l(2)]\,\delta(1-2)F_l(1)\ . \tag{A7}$$

Using Eqs. (2.25a), (2.25b), and (A7), the correlations between the fluctuating forces can be easily computed with the result

$$\langle \tilde{P}_{ij}(\vec{R}_1,t)\tilde{P}_{kl}(\vec{R}_2,t')\rangle_{ss} =2k_B T(\vec{R}_1)\eta_B(\vec{R}_1)\delta(t-t')\,\delta(\vec{R}_1-\vec{R}_2)\Delta_{ij,kl}\ , \tag{A8a}$$

$$\langle \tilde{P}_{ij}(\vec{R}_1,t)\tilde{Q}_k(\vec{R}_2,t')\rangle_{ss}=0\ , \tag{A8b}$$

$$\langle \tilde{Q}_i(\vec{R}_1,t)\tilde{Q}_j(\vec{R}_2,t')\rangle_{ss} =2k_B T^2(\vec{R}_1)\lambda_B(\vec{R}_1)\delta_{ij}\,\delta(t-t')\delta(\vec{R}_1-\vec{R}_2)\ . \tag{A8c}$$

The correlations given by Eq. (A8) are a local version of those given by Landau and Lifshitz for fluctuations around total equilibrium.[33] Equations (A4) and (A8) are identical to those given by Keizer for fluctuations in a nonequilibrium steady state, when Keizer's equations are applied to gases at low densities.

Finally, one can easily show that Eq. (A4) leads to Eqs. (2.42) for the quantities $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$. To do this, one need only multiply Eq. (A4) by $\delta a_\beta(\vec{R}_2,0)$, average over the fluctuations, and use $\langle \delta a_\beta(\vec{R}_2,0)\tilde{\sigma}_\alpha(\vec{R}_1,t)\rangle_{ss}=0$.

II. Equal-time correlation functions from the fluctuating Boltzmann equation

Next we show that Keizer's fluctuating hydrodynamic equations, i.e., Eqs. (A4)–(A8) lead to equal-time correlation functions $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ identical to those derived in Sec. III. In order to do this, we use Eq. (A1) but, instead of the full correlation between the fluctuating forces given by Eq. (A3) we will use the effective correlation given by Eq. (A7), which is equivalent to that used in a local Landau-Lifshitz theory. Using Eqs. (A1), (A2), and (A7), we formally solve Eq. (A1) and compute the equal-time correlation function $\langle \delta F(1,t)\delta F(2,t)\rangle_{ss}$ in the stationary state. The result is

$$\langle \delta F(1,t)\delta F(2,t)\rangle_{ss}=e^{-[L(1)+L(2)]t}\langle \delta F(1)\delta F(2)\rangle_{ss} -\int_0^t d\tau\, e^{-[L(1)+L(2)](t-\tau)}[\Lambda_l(1)+\Lambda_l(2)]\delta(1-2)F_l(1)\ . \tag{A9}$$

Owing to the steady-state assumption, we can carry out the time integral in Eq. (A9), so that

$$\langle \delta F(1,t)\delta F(2,t\rangle_{ss}=\langle \delta F(1)\delta F(2)\rangle_{ss}=-\frac{1}{[L(1)+L(2)]}[\Lambda_l(1)+\Lambda_l(2)]\delta(1-2)F_l(1)\ . \tag{A10}$$

By using Eqs. (2.34) and (2.37), we can write

$$\langle \delta F(1)\delta F(2)\rangle_{ss}=\frac{1}{[L(1)+L(2)]}(1+P_{12})L(1)\delta(1-2)F_l(1) -\frac{1}{[L(1)+L(2)]}\left[\delta(1-2)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}F_l(1)-[\Lambda_\nabla(1)+\Lambda_\nabla(2)]\delta(1-2)F_l(1)\right] \tag{A11}$$

or

$$\langle \delta F(1)\delta F(2)\rangle_{ss}=\delta(1-2)F_l(2)-\frac{1}{[L(1)+L(2)]}\left[\delta(1-2)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}F_l(1)-[\Lambda_\nabla(1)+\Lambda_\nabla(2)]\delta(1-2)F_l(1)\right] =A'(1,2)+D'(1,2)\ . \tag{A12}$$

We now show that the quantities $A'(1,2)$ and $D'(1,2)$ in Eq. (A12) are closely related to the matrices $A_{\alpha\beta}$ and $D_{\alpha\beta}$ defined in Sec. III. To see this, we use Eq. (A12) to compute the hydrodynamic correlation functions $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ defined by Eq. (3.1). The term due to $A'(1,2)$ is easily shown to lead to $A_{\alpha\beta,l}(\vec{R}_1,\vec{R}_2)$ defined by Eq. (3.9a). The D' term in Eq. (A12) obeys the equation

$$[L(1)+L(2)]D'(1,2)=-\delta(1-2)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}F_l(1)+[\Lambda_\nabla(1)+\Lambda_\nabla(2)]\delta(1-2)F_l(1)\;. \tag{A13}$$

The second source term $[\Lambda_\nabla(1)+\Lambda_\nabla(2)]\delta(1-2)F_l(1)$ in Eq. (A13) vanishes to Navier-Stokes order when Eq. (A13) is projected onto the hydrodynamic subspace, i.e., $P(1)P(2)\Lambda_\nabla(1)=P(1)P(2)\Lambda_\nabla(2)=0$ as may be shown using that $\psi_\alpha(j)$ is conserved in a binary collision. Using this property, an effective equation for $D'(1,2)$ is

$$[L(1)+L(2)]D'(1,2)=-\delta(1-2)\vec{V}_1\cdot\frac{\partial}{\partial\vec{R}_1}F_l(1)\;. \tag{A14}$$

Since $\vec{V}_1\cdot(\partial/\partial\vec{R}_1)F_l(1)=\Lambda_l(1)F_l(1)\Phi_1(1)$ in the steady state, and because of the identity given by Eq. (3.14), we see that the equation for $D'(1,2)$ and the equation for the pair-correlation function $G_2(1,2)$ are identical in the hydrodynamic subspace. Thus, the equal-time correlation functions given by the local Landau-Lifshitz fluctuating forces are equivalent, in the hydrodynamic subspace, to those given in Sec. III. This equivalence also implies that fluctuating hydrodynamics, with local Landau-Lifshitz correlations functions given by the Eqs. (A8), contain the same long-range correlations due to the mode-coupling effects as are found in the next two papers on the basis of the equations for the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ derived in Secs. II – V of this paper.

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[1] T. Kirkpatrick, E. G. D. Cohen, and J. R. Dorfman, Phys. Rev. Lett. 42, 862 (1979); 44, 472 (1980); T. Kirkpatrick and E. G. D. Cohen, Phys. Lett. 78A, 350 (1980).

[2] I. Procaccia, D. Ronis, and I. Oppenheim, Phys. Rev. Lett. 42, 287 (1979); D. Ronis, I. Procaccia, and I. Oppenheim, Phys. Rev. A 19, 1324 (1979).

[3] A. Tremblay, E. Siggia, and M. Arai, Phys. Lett. 76A, 57 (1980); Phys. Rev. A 23, 1451 (1981).

[4] D. Ronis and S. Putterman, Phys. Rev. A 22, 733 (1980).

[5] G. van der Zwan, D. Bedeaux, and P. Mazur, Physica (Utrecht) 107A, 491 (1981).

[6] J. Dufty, in *Spectral Line Shapes*, edited by B. Wende (de Gruyter, Berlin, 1981), p. 1143.

[7] See, for example, J. R. Dorfman and E. G. D. Cohen, Phys. Rev. A 6, 786 (1972).

[8] See, for example, J. R. Dorfman and E. G. D. Cohen, J. Math. Phys. 8, 282 (1967).

[9] G. Ludwig, Physica (Utrecht) 28, 841 (1962).

[10] K. Kawasaki, Prog. Theor. Phys. 51, 1064 (1974).

[11] A. Onuki, J. Stat. Phys. 18, 475 (1978).

[12] T. Kirkpatrick, Ph.D. thesis, The Rockefeller University, New York, 1981 (unpublished).

[13] J. Keizer, Phys. Fluids 21, 198 (1978).

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

[15] M. Ernst, E. Hauge, and J. M. J. van Leeuwen, J. Stat. Phys. 15, 7 (1976).

[16] M. Ernst and E. G. D. Cohen, J. Stat. Phys. 25, 153 (1981). See also, E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, New York, 1981), pp. 79 – 88.

[17] For a recent view of the kinetic theory of gases see, J. R. Dorfman and H. van Beijeren, in *Statistical Mechanics Part B: Time Dependent Processes*, edited by B. Berne (Plenum, New York, 1977), p. 65.

[18] R. Zwanzig, Phys. Rev. 124, 983 (1961).

[19] In discussing the relation of our equations and those of fluctuating hydrodynamics, we will assume throughout this paper that ensemble averages and averages over the fluctuations are equivalent.

[20] M. Ernst, B. Cichocki, J. R. Dorfman, J. Sharma, and H. van Beijeren, J. Stat. Phys. 18, 237 (1978).

[21] M. Ernst and J. R. Dorfman, Physica (Utrecht) 61, 157 (1972).

[22] See, for example, D. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974).

[23] A similar condition is used when solving the Boltzmann equation with the Chapman-Enskog solution method.

[24] M. Ernst and J. R. Dorfman, J. Stat. Phys. 12, 311 (1975).

[25] For the nonequilibrium case considered here the reader is referred to Ref. 12 for the complete derivation.

[26] For a detailed discussion of the relation between Eq. (4.23) and the Green-Kubo formulas, see Ref. 12.

[27] J. Brey, in *Systems Far from Equilibrium*, edited by L. Garrido (Springer, Berlin, 1980), p. 244.

[28] An alternative method was used by Kawasaki, See Ref. 10.

[29] C. Wong, J. McLennan, M. Lindenfeld, and J. Dufty, J. Chem. Phys. 68, 1563 (1978).

[30] D. Ronis, I. Procaccia, and J. Machta, Phys. Rev. A 22, 714 (1980).

[31] J. Machta, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1980 (unpublished); J. Machta and I. Oppenheim, Physica (Utrecht) A (in press).

[32] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1959), Chap. XVII.

[33] M. Bixon and R. Zwanzig, Phys. Rev. 187, 267 (1969), and R. F. Fox and G. E. Uhlenbeck, Phys. Fluids 13,

2881 (1970), have shown that for a fluid in equilibrium $\Gamma_{eq}(1,2)$ is given by $\Gamma_{eq}(1,2)=-[\Lambda_{eq}(1)+\Lambda_{eq}(2)]\delta(1-2)F_{eq}(1)$. From this, these authors have derived Landau-Lifshitz's fluctuating hydrodynamics for a fluid in equilibrium. Because Eq. (A7) is a local equilibrium version of $\Gamma_{eq}(1,2)$, it is not surprising that $\Gamma_{eff}(1,2)$ leads to a local equilibrium version of Landau-Lifshitz's fluctuating hydrodynamics.