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Light scattering by a fluid in a nonequilibrium steady state. I. Small gradients

T. R. Kirkpatrick[*] and E. G. D. Cohen
The Rockefeller University, New York, New York 10021

J. R. Dorfman
Institute for Physical Science and Technology, The University of Maryland,
College Park, Maryland 20742

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The equations derived in the previous paper for the unequal- and equal-time correlation functions of the microscopic densities of mass, momentum, and energy are solved and applied to light scattering for the case of a fluid subject to a small temperature gradient. The deviations of the dynamical structure factor $S(\vec{k},\omega)$ and the intensities of the Rayleigh and Brillouin lines from their equilibrium behavior are computed to first order in the temperature gradient. The shape and intensity of the Rayleigh line remains the same as in equilibrium. The shapes and the intensities of the Brillouin lines deviate from their equilibrium values by terms proportional to the temperature gradient, leading to an asymmetry in the heights and intensities of the two lines. This asymmetry in the intensities is caused by a mode-coupling effect: the coupling of two sound modes to the heat flux. Owing to restrictions on the theory, the predicted change in the shape of the Brillouin lines is too small to be detected, but the change in their integrated intensities might be observable.

I. INTRODUCTION

In the previous paper in this series (hereafter denoted as I),[1] we derived a set of hydrodynamiclike equations for the correlation functions that are needed for a description of the light scattering by a fluid in a nonequilibrium steady state. In this and the following paper we will apply those equations to determine the spectrum and intensity of the light scattered by such a fluid.

As mentioned in I, the interest in light scattering by fluids that are not in equilibrium is due to the fact that light scattering provides an experimental technique, whereby one can detect the presence of long-range correlations between the fluctuations of the microscopic densities due to nonequilibrium processes in the fluid. In fact, as we shall see, these long-range correlations are entirely due to mode-coupling effects. Thus, the detection of these long-range correlations would demonstrate that mode-coupling not only causes the anomalies in the transport coefficients near a critical point for a phase transition, but is also responsible for long-range correlations in nonequilibrium fluids.

To describe the light-scattering spectrum, one computes the dynamic structure factor $S(\vec{k},\omega)$ defined by[2]

$$S(\vec{k},\omega)=\frac{1}{T}\left[\int_V d\vec{R}\,P^2(\vec{R})\right]^{-1}\times\int_V d\vec{R}_1\int_V d\vec{R}_2\int_{-T/2}^{T/2}dt_1\int_{-T/2}^{T/2}dt_2\,P(\vec{R}_1)P(\vec{R}_2)\times\exp\{-i[\vec{k}\cdot(\vec{R}_1-\vec{R}_2)-\omega(t_1-t_2)]\}\times M_{\rho\rho}(\vec{R}_1,t_1;\vec{R}_2,t_2)\;. \tag{1.1}$$

Here $\hbar\vec{k}=\hbar(\vec{k}_f-\vec{k}_i)$ is the momentum transferred from the fluid to a photon whose incident wave vector is $\vec{k}_i$ and final wave vector is $\vec{k}_f$; $\hbar\omega=\hbar(\omega_f-\omega_i)$ is the energy transferred from the fluid to the scattered photon, V is the volume of the system, T is the duration of the experiment, $P(\vec{R})$ is a form factor that describes the fact that only a small portion of the fluid is both illuminated and

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obesrved by the optics of the system. The form factor $P(\vec{R})$ is on the order of unity inside the scattering volume and vanishes outside it.[3] The quantity $M_{\rho\rho}(\vec{R}_1,t_1;\vec{R}_2,t_2)$ defined by

$$M_{\rho\rho}(\vec{R}_1,t_1;\vec{R}_2,t_2)=\langle\delta\rho(\vec{R}_1,t_1)\delta\rho(\vec{R}_2,t_2)\rangle\ , \tag{1.2}$$

is the density-density correlation function discussed in detail in I in which $\delta\rho(\vec{R}_i,t_i)$ is the deviation of the microscopic density at $\vec{R}_i,t_i$ from its average value. The intensity of light scattered with wave-number and frequency change $\vec{k}$ and ω, respectively, is then proportional to $S(\vec{k},\omega)$.

In 1934 Landau and Placzek calculated $S(\vec{k},\omega)$ for light scattered by fluids in thermal equilibrium. In order to obtain $M_{\rho\rho}(\vec{R}_1,t_1;\vec{R}_2,t_2)$, Landau and Placzek used the Onsager-regression hypothesis which assumes that small, long-wavelength fluctuations about equilibrium decay according to the same linear laws (i.e., the linear hydrodynamic equations) that govern the decay to equilibrium of macroscopic deviations from equilibrium. Landau and Placzek found that $S(\vec{k},\omega)$ is given by[4]

$$S_{\text{eq}}(\vec{k},\omega)=\rho^2k_BT\chi_T\left[\frac{(\gamma-1)}{\gamma}\,\frac{2D_Tk^2}{\omega^2+(D_Tk^2)^2}+\frac{1}{2\gamma}\sum_{\sigma=\pm1}\frac{\Gamma_sk^2}{(\omega-\sigma ck)^2+(\Gamma_sk^2/2)}\right]. \tag{1.3}$$

Here k_B is Boltzmann's constant and ρ, T, and c are the equilibrium mass density, temperature, and adiabatic sound velocity, respectively. Also, $\chi_T=\rho^{-1}(\partial\rho/\partial p)_T$ is the isothermal compressibility, p is the pressure, $\gamma=c_p/c_v$ is the ratio of specific heats, $D_T=\lambda/\rho c_p$ is the thermal diffusivity, where λ is the coefficient of thermal conductivity, and Γ_s is the sound-damping constant,

$$\Gamma_s=(4\nu/3+\zeta/\rho)+(\gamma-1)D_T\ ,$$

with ν and ζ the kinematic viscosity and bulk viscosity, respectively.

Equation (1.3) describes a spectrum with three Lorentzian lines: one line is centered at $\omega=0$ with a width $\sim D_Tk^2$ and a height $\sim(D_Tk^2)^{-1}$. This contribution to $S(\vec{k},\omega)$ is the Rayleigh line and is due to the decay of entropy fluctuations. The other two lines are associated with the decay of pressure fluctuations and are symmetrically located with respect to the origin, i.e., centered at $\omega=\pm ck$, with widths $\sim\Gamma_sk^2$ and height $\sim(\Gamma_sk^2)^{-1}$. These are the Brillouin lines and their location at $\omega=\pm ck$ is due to Doppler shifts from propagating sound waves in the fluid. The upshifted line at $\omega=ck$ is due to sound waves moving in the $\vec{k}$ direction, while the downshifted line at $\omega=-ck$ is caused by sound waves moving in the $-\vec{k}$ direction.

A measure of the range of the correlations in an equilibrium fluid is provided by the integrated intensity of the light-scattering spectrum, since one can easily see from an examination of Eq. (1.1) that the total integrated intensity $I(\vec{k})$ defined by

$$I(\vec{k})=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}S(\vec{k},\omega) \tag{1.4}$$

is proportional to the Fourier transform in $\vec{k}$ of the equal-time density-density correlation function $M_{\rho\rho}(\vec{R}_1,t_1;\vec{R}_2,t_1)$. It is convenient to further subdivide $I(\vec{k})$ into the contribution from each of the three characteristic lines. For the σ-Brillouin line $\sigma=\pm1$, this integrated intensity is given by

$$\begin{aligned}I_{\text{eq}}^{\sigma}(\vec{k})&=\int_{-\infty}^{\infty}\frac{d\omega}{(2\pi)}\left[\frac{\rho^2k_BT\chi_T}{2\gamma}\right]\\&\quad\times\frac{\Gamma_sk^2}{(\omega-\sigma ck)^2+(\Gamma_sk^2/2)^2}\\&=\frac{\rho^2k_BT\chi_T}{2\gamma}\ ,\end{aligned} \tag{1.5a}$$

while that of the Rayleigh line is

$$\begin{aligned}I_{\text{eq}}^{H}(\vec{k})&=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\rho^2k_BT\chi_T\left[\frac{\gamma-1}{\gamma}\right]\\&\quad\times\left[\frac{2D_Tk^2}{\omega^2+(D_Tk^2)^2}\right]\\&=\rho^2k_BT\chi_T\frac{\gamma-1}{\gamma}\end{aligned} \tag{1.5b}$$

provided that the three spectral lines in $S(\vec{k},\omega)$ are well separated. It follows from Eq. (1.5a) and (1.5b) that the total intensity of the scattered light is

$$I_{\text{eq}}(\vec{k})=\rho^2k_BT\chi_T\ , \tag{1.5c}$$

a formula derived for the first time by Einstein.[4] Note that these integrated intensities are independent of $\vec{k}$. Physically, this is a consequence of the fact that the equilibrium equal-time correlation function has a short range—of the order of the size of the particles σ—for a fluid away from the gas-liquid critical point. Since the wavelength $\lambda = 2\pi/k$ in a typical light-scattering experiment is much larger than σ, it follows that light scattering cannot be used to probe these short-range correlations. As we shall see, this is not the case in a nonequilibrium fluid where the equal-time correlation functions have a long range so that the integrated intensity of the lines in the light scattering spectrum will exhibit a dependence on $\vec{k}$.

As mentioned in the Introduction of paper I, the theory for light scattering from fluids not in equilibrium was developed by Procaccia *et al.*,[5] Kirkpatrick *et al.*,[6] Tremblay *et al.*,[7] Ronis and Putterman,[8] and Dufty,[9] and van der Zwan *et al.*[10] All of the original calculations were done for the case of small steady gradients; for example, a small but steady temperature gradient maintained by confining the fluid between two plates held at constant, but different temperatures. By using perturbation theory about a state of total equilibrium all of these authors found that the analog of Eq. (1.3) for a fluid with a small temperature gradient is given by

$$S(\vec{R}_0,\vec{k},\omega)=\rho^2 k_B T \chi_T \left[\frac{(\gamma-1)}{\gamma}\frac{2D_T k^2}{\omega^2+(D_T k^2)^2}+\frac{1}{2\gamma}\sum_{\sigma=\pm 1}\Gamma_s k^2 \frac{1-\sigma y_\sigma(\vec{k},\omega)c\hat{k}\cdot\vec{\nabla}T/(\Gamma_s k^2 T)}{(\omega-\sigma c k)^2+(\Gamma_s k^2/2)^2}\right], \tag{1.6a}$$

where

$$y_\sigma(\vec{k},\omega)=1+\frac{[(\Gamma_s k^2/2)^2-(\omega-\sigma c k)^2]}{[(\Gamma_s k^2/2)^2+(\omega-\sigma c k)^2]} . \tag{1.6b}$$

Here $\vec{\nabla}T$ is the temperature gradient, $\hat{k}$ is a unit vector in the direction of $\vec{k}$, and all hydrodynamic and thermodynamic quantities are to be evaluated at the center of the scattering volume $\vec{R}_0$. As in equilibrium, Eq. (1.6) describes three lines. The central line is unaffected by the small thermal gradient, but the Brillouin lines, although at the same positions as before (i.e., at $\omega = \pm ck$), are now asymmetric in that the line caused by sound waves moving in the direction of the heat flow has a larger height and intensity than the line caused by sound waves moving in the direction opposite to the heat flow. These results for the line shapes are valid only under rather restrictive conditions on the size of the scattering volume, and of the temperature gradients [cf. below Eq. (4.2)].

While the intensity of the Rayleigh line is the same as in equilibrium [cf. Eq. (1.3)], the intensities of the Brillouin lines change. They are given by

$$I^\sigma(\vec{R}_0,\vec{k})=\frac{\rho^2 k_B \chi_T}{2\gamma}\left[1-\frac{\sigma c\hat{k}\cdot\vec{\nabla}T}{\Gamma_s k^2 T}\right] . \tag{1.7}$$

That is, the integrated intensities differ from their equilibrium values by terms proportional to $(\hat{k}\cdot\vec{\nabla}T)/k^2$. This k^{-2} dependence implies that the equal-time momentum density-mass density correlation function has a long range, since it decays in configuration space as R_{12}^{-1}, at least over a range of $|R_{12}|$. The total intensity of all the lines is still given by Eq. (1.5c).

Kirkpatrick, Cohen, and Dorfman[6] obtained the Eqs. (1.6) and (1.7) by means of two different methods. One method valid for dilute gases, used the kinetic theory of gases to compute $S(\vec{k},\omega)$ and $I^\sigma(\vec{k})$, while the other method, valid for more general fluids, used a hydrodynamic method to compute these quantities. Procaccia *et al.*[5] and Machta and Oppenheim[11] obtained identical results using a nonequilibrium steady-state (ss) response[5] or mode-coupling theory[11] for calculating fluctuations. Tremblay *et al.*,[7] Ronis and Putterman,[8] and van der Zwan *et al.*[10] have derived Eq. (1.6) using fluctuating hydrodynamics.[12] Dufty[9] has derived Eq. (1.6) by using the explicit form of the N-particle distribution function given in I [cf. Eq. (I.5.2)] to obtain an expression for $M_{\rho\rho}(\vec{R}_1,\vec{R}_2,t)$ that was then evaluated using kinetic theory.

Finally, we mention that Kirkpatrick[13] has presented elsewhere a calculation of the light scattering for both small and large temperature gradients based purely on the kinetic theory of gases. Kirkpatrick's method differs from that presented here in that it is based on an analysis of the unequal- and equal-time correlation functions in terms of the so-called hydrodynamic modes of the kinetic operator $L(i)$ [cf. Eq. (I.2.34)], rather than on the derivation of hydrodynamiclike equations that those correlation functions satisfy. Both methods are completely equivalent and Kirkpatrick's results for the case of dilute gases are identical with those obtained here using hydrodynamic equations.

In this paper, we will consider the theory for light scattering from a fluid subject to a small constant temperature gradient. We remark that we have developed a similar theory to calculate the light scattering from a fluid subject to a constant velocity gradient.[6,13] These calculations are not given here, however, since the effects due to a typical velocity gradient are much smaller than those due to a typical temperature gradient. For example, in the case of a shear flow given by $\vec{u}(\vec{R}_1)=x_1X\hat{y}$, where X is the magnitude of the velocity gradient, $\sigma c\hat{k}\cdot\vec{\nabla}T/\Gamma_s k^2 T$ in Eq. (1.7) is replaced by $\hat{k}_x\hat{k}_y X/\Gamma_s k^2$, where a circumflex denotes a unit vector. For typical gradients we have the inequality $|c\hat{k}\cdot\vec{\nabla}T/T| \gg |X|$.

We will base our calculations on the hydrodynamiclike equations for $M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t)$ and for $M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t=0)$ derived in paper I to compute the dynamic structure factor and the integrated intensities of the various lines.

The plan of this paper is as follows. In Sec. II we derive the basic equations for the unequal-time correlation functions for the case of a small steady temperature gradient from the general equations given in paper I. We then expand the $M_{\alpha\beta}$ in a power series in the temperature gradient and keep only the zeroth- and first-order terms in the gradients. To complete the calculation of the unequal-time correlation function to first order in the gradient, we must also compute the equal-time correlation functions to first order in the temperature gradient. This is carried out in Sec. III and we present the explicit expressions for both the unequal- and equal-time correlation functions correct to first order in the gradient. In Sec. IV we compute the dynamical structure factor and the integrated intensities of the Rayleigh and Brillouin lines to first order in the gradient, thereby deriving Eqs. (1.6) and (1.7), given above. In Sec. V we make some comments on the results obtained in this paper. Finally, we discuss what effect the finite size of the light-scattering cell could have on the results of this paper, and we comment on some recent calculations of Satten and Ronis[14] on this point.

II. BASIC EQUATIONS FOR TIME-CORRELATION FUNCTIONS

In this section we will use the general equations for $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ and $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ derived in Secs. IV and V of the previous paper for a fluid of arbitrary density, to obtain equations for these correlation functions in the case the fluid is subject to a small steady temperature gradient. Thus, we consider the fluid in a nonequilibrium steady state with a temperature gradient in the x direction, but without a macroscopic flow (i.e., no convection), and consequently, with no pressure gradient.

The quantity needed in particular to compute $S(\vec{k},\omega)$ is $M_{\rho\rho}(\vec{R}_1,\vec{R}_2,t)$ the time-dependent density-density correlation function. In paper I we showed that $M_{\rho\rho}(\vec{R}_1,\vec{R}_2,t)$ is determined by the solution of a set of five coupled hydrodynamic equations of the form

$$\frac{\partial}{\partial t}M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t)=H_{\alpha\gamma}(\vec{R}_1)M_{\gamma\rho}(\vec{R}_1,\vec{R}_2,t)\ , \tag{2.1}$$

where $H_{\alpha\gamma}(\vec{R}_1)$ is the evolution matrix defined by Eqs. (I.4.21a)–(I.4.21c) and summation convention is used. The explicit form for the $H_{\alpha\gamma}$ can be obtained by linearizing the nonlinear Navier-Stokes equations about a steady state. The time-dependent correlation functions $M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t)$ are defined by

$$M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t)=\langle \delta a_\alpha(\vec{R}_1,t)\delta\rho(\vec{R}_2,0)\rangle_{\text{ss}}\ . \tag{2.2}$$

Here the average is taken over a stationary-state ensemble, and the quantities $\delta a_\alpha(\vec{R}_1,t)$ and $\delta\rho(\vec{R}_2,0)$ are defined by Eqs. (I.2.3) and (I.2.4) where the quantities $\delta a_\alpha(\vec{R}_1,t)$ represent, for $\alpha=1,2,\ldots,5$, microscopic fluctuations in the local mass, momentum, and energy densities at $\vec{R}_1$ at time t. For the case of a temperature gradient in the x direction and no macroscopic flow these equations are

$$\frac{\partial}{\partial t}M_{\rho\rho}+\frac{\partial}{\partial R_{1i}}M_{g_i\rho}=0\ , \tag{2.3a}$$

$$\frac{\partial}{\partial t}M_{g_i\rho}+\frac{\partial}{\partial R_{1i}}\left[\left(\frac{\partial p}{\partial\rho}\right)_{\epsilon}M_{\rho\rho}+\left(\frac{\partial p}{\partial\epsilon}\right)_{\rho}M_{\epsilon\rho}\right]
=\frac{\partial}{\partial R_{1j}}\left[(\eta\Delta_{ij,kl}+\zeta\delta_{ij}\delta_{kl})\frac{\partial}{\partial R_{1k}}\frac{M_{g_l\rho}}{\rho}\right]\ , \tag{2.3b}$$

$$\begin{aligned}\frac{\partial}{\partial t}M_{\epsilon\rho}+\frac{\partial}{\partial R_{1i}}\frac{h}{\rho}M_{g_i\rho}
&=\frac{\partial}{\partial R_{1i}}\left\{\lambda\frac{\partial}{\partial R_{1i}}\left[\left(\frac{\partial T}{\partial\rho}\right)_{\epsilon}M_{\rho\rho}+\left(\frac{\partial T}{\partial\epsilon}\right)_{\rho}M_{\epsilon\rho}\right]\right.\\
&\qquad\left.+\left[\left(\frac{\partial\lambda}{\partial\rho}\right)_{\epsilon}M_{\rho\rho}+\left(\frac{\partial\lambda}{\partial\epsilon}\right)_{\rho}M_{\epsilon\rho}\right]\frac{\partial T}{\partial R_{1i}}\right\}\ .\end{aligned} \tag{2.3c}$$

In Eqs. (2.3a)–(2.3c), the subscripts i, j, k, l represent x, y, z coordinates and again summation convention is used. The quantities p, ρ, h, T, ϵ, η, ζ, and λ are, respectively, the pressure, mass density, enthalpy density, temperature, energy density, and coefficient of shear viscosity, bulk viscosity, and thermal conductivity. Owing to the presence of the temperature gradient, all of these quantities except p depend on $\vec{R}_1$. The solution to Eqs. (2.3) are determined by the initial conditions $M_{\alpha\rho}(t=0)$, i.e., by the equal-time correlation functions

$$M_{\alpha\rho}(\vec{R}_1,\vec{R}_2)\equiv M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t=0)\ ,$$

which in turn are given by

$$M_{\alpha\rho}(\vec{R}_1,\vec{R}_2)=A_{\alpha\rho}(\vec{R}_1,\vec{R}_2)+D_{\alpha\rho}(\vec{R}_1,\vec{R}_2)\ , \qquad (2.4)$$

where $A_{\alpha\rho}(\vec{R}_1,\vec{R}_2)$ is the local equilibrium contribution to $M_{\alpha\rho}$;

$$A_{\alpha\rho}(\vec{R}_1,\vec{R}_2)=\langle \delta a_\alpha(\vec{R}_1)\delta\rho(\vec{R}_2)\rangle_{L,\mathrm{ss}}\ , \qquad (2.5)$$

and $\langle\ \rangle_{L,\mathrm{ss}}$ denotes a local equilibrium steady-state ensemble average [cf. (I.4.9)]. The quantities $D_{\alpha\rho}(\vec{R}_1,\vec{R}_2)$ are proportional to the gradients and satisfy the equation [cf. (I.5.7)]

$$\begin{aligned}H_{\alpha\gamma}(\vec{R}_1)D_{\gamma\beta}(\vec{R}_1,\vec{R}_2)+H_{\beta\gamma}(\vec{R}_2)D_{\alpha\gamma}(\vec{R}_1,\vec{R}_2)\\ =\delta(\vec{R}_{12})(\delta a_{\alpha T}\delta a_{\beta T}S_{x,T})_{0,\vec{R}_1}\beta\\ \times\frac{\partial \ln T(R_{1x})}{\partial R_{1x}}\ ,\end{aligned} \qquad (2.6)$$

where $\vec{R}_{12}=\vec{R}_1-\vec{R}_2$, $\delta a_{\alpha T}=\int_V d\vec{R}_1\delta a_\alpha(\vec{R}_1)$ is the microscopic fluctuation of the total mass, momentum, or energy in the volume V of the system, and $S_{x,T}$ is the total microscopic heat current in the x direction which is defined in the Eqs. (I.4.23) and the discussion below it, as well as by the condition that $\vec{u}=0$. The ensemble average appearing on the right-hand side of Eq. (2.6) is defined by Eqs. (I.4.24) and (I.5.8), and is an equilibriumlike ensemble average with uniform temperature and chemical potential, whose values are set equal to the local values of these quantities of the point $\vec{R}_1$.

The dynamic structure factor $S(\vec{k},\omega)$ is defined in the Introduction in terms of $M_{\rho\rho}(\vec{R}_1,\vec{R}_2,t)$ by Eq. (1.1), and in this and Sec. III we will compute $M_{\rho\rho}$ to first order in the temperature gradient. To find $M_{\rho\rho}(\vec{R}_1,\vec{R}_2,t)$, we need to find all of the $M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t)$ to first order in the temperature gradient. It is convenient to consider the $M_{\alpha\rho}$, not as functions of $\vec{R}_1$ and $\vec{R}_2$, but as functions of the relative coordinates $\vec{R}_{12}=\vec{R}_1-\vec{R}_2$ and the center-of-mass coordinates $\vec{R}=\frac{1}{2}(\vec{R}_1+\vec{R}_2)$. For a fluid in equilibrium, the $M_{\alpha\rho}$ will depend only on $\vec{R}_{12}$, but when a gradient is present these quantities will depend on the location of the center of mass $\vec{R}$, as well, because of the variation of the local thermodynamic and hydrodynamic quantities with position.[15] Similarly, the equal-time correlation functions will also depend on the center of mass $\vec{R}$ as well as on the relative coordinates $\vec{R}_{12}$ for a fluid with a temperature gradient.

Considering then the $M_{\alpha\rho}$ as functions of the variables $\vec{R}$ and $\vec{R}_{12}$, it is convenient to introduce the Fourier transform of $M_{\alpha\rho}$ with respect to $\vec{R}_{12}$, as well as the Laplace transform in time; that is, we define $M_{\alpha\rho}(\vec{R},\vec{q},\omega)$ by

$$\begin{aligned}M_{\alpha\rho}(\vec{R},\vec{q},\omega)=\int_0^\infty dt\int d\vec{R}_{12}e^{i\omega t-i\vec{q}\cdot\vec{R}_{12}}\\ \times M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t)\ .\end{aligned} \qquad (2.7)$$

For later use we remark that the dynamical structure factor $S(\vec{k},\omega)$ is then given, with Eq. (2.7), in terms of $M_{\rho\rho}(\vec{R},\vec{q},\omega)$ by

$$\begin{aligned}S(\vec{k},\omega)=2\,\mathrm{Re}\left[\int d\vec{R}\,P^2(\vec{R})\right]^{-2}\\ \times\int d\vec{R}\,P^2(\vec{R})\int\frac{d\vec{q}}{(2\pi)^3}P^2_{\vec{k}-\vec{q}}\\ \times M_{\rho\rho}(\vec{R},\vec{q},\omega)\ .\end{aligned} \qquad (2.8)$$

Here Re denotes the real part of the expression and $P_{\vec{k}-\vec{q}}$ is the Fourier transform of the function $P(\vec{R})$. We have also used that $P(\vec{R})$ is a Gaussian,[3] and we note for later use that $P_{\vec{k}-\vec{q}}$ sharply peaks about $\vec{k}=\vec{q}$ if $kL\gg 1$, where L is the size of the scattering volume.

To obtain an expression for $M_{\alpha\rho}(\vec{R},\vec{q},\omega)$ correct to first order in the temperature gradient, we express the hydrodynamic matrix elements $H_{\alpha\beta}(\vec{R}_1)$ in relative and center-of-mass coordinates, then expand $H_{\alpha\beta}$ in powers of the temperature gradient at $\vec{R}$, and take the Fourier transform with respect to the relative coordinates $\vec{R}_{12}$. This procedure leads to the equation

$$\begin{aligned}-i\omega M_{\alpha\rho}(\vec{R},\vec{q},\omega)=M_{\alpha\rho}(\vec{R},\vec{q},t=0)\\ +\bar{H}_{\alpha\gamma}(\vec{R},\vec{q})M_{\gamma\rho}(\vec{R},\vec{q},\omega)\ ,\end{aligned} \qquad (2.9)$$

where we have introduced the Fourier transform of the equal-time correlation function $M_{\alpha\rho}(\vec{R},\vec{q},t=0)$ by

$$\begin{aligned}M_{\alpha\rho}(\vec{R},\vec{q},t=0)\\ =\int d\vec{R}_{12}e^{-i\vec{q}\cdot\vec{R}_{12}}M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,t=0)\\ =A_{\alpha\rho}(\vec{R},\vec{q})+D_{\alpha\rho}(\vec{R},\vec{q})\ .\end{aligned} \qquad (2.10)$$

The elements $\bar{H}_{\alpha\beta}(\vec{R},\vec{q})$ are obtained from Eqs. (2.3a)–(2.3c) by rewriting these equations in terms of the center-of-mass coordinate $\vec{\mathrm{R}}$, and the relative coordinate $\vec{\mathrm{R}}_{12}$. After carrying out the Fourier transform with respect to the relative coordinate $\vec{\mathrm{R}}_{12}$, we find that $\bar{H}_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}})$ can be expressed as a gradient expansion in the form

$$\bar{H}_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}})=\bar{H}_{\alpha\beta,0}(\vec{\mathrm{R}},\vec{\mathrm{q}})+\Delta\bar{H}_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}}) \; . \tag{2.11a}$$

The matrix elements $\bar{H}_{\alpha\beta,0}(\vec{\mathrm{R}},\vec{\mathrm{q}})$ are zeroth order in the temperature gradient and are obtained from $\bar{H}_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}})$ by neglecting all terms that contain derivatives with respect to $\vec{\mathrm{R}}$. The correction $\Delta\bar{H}_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}})$ is proportional to first and higher derivatives of the thermodynamic quantities, transport coefficient, or the $M_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}},\omega)$ with respect to $\vec{\mathrm{R}}$. The elements $\Delta\bar{H}_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}})$ in turn have a gradient expansion given by

$$\Delta\bar{H}_{\alpha\beta}(\vec{\mathrm{R}},\vec{\mathrm{q}})=\Delta\bar{H}_{\alpha\beta,1}(\vec{\mathrm{R}},\vec{\mathrm{q}})+\Delta\bar{H}_{\alpha\beta,2}(\vec{\mathrm{R}},\vec{\mathrm{q}})+\cdots \; , \tag{2.11b}$$

where $\Delta\bar{H}_{\alpha\beta,1}$, $\Delta\bar{H}_{\alpha\beta,2}$, etc., contain first, second, etc., derivatives, respectively, with respect to $\vec{\mathrm{R}}$. The matrix elements $\bar{H}_{\alpha\beta,0}(\vec{\mathrm{R}},\vec{\mathrm{q}})$ are given by

$$\bar{H}_{\rho\rho,0}=\bar{H}_{\rho\epsilon,0}=0 \; , \tag{2.12a}$$

$$\begin{aligned}
&\bar{H}_{\rho g_i,0}=-iq_i,\ \bar{H}_{g_i\rho,0}=-iq_iA_1(\vec{\mathrm{R}}) \; ,\\
&\bar{H}_{g_i\epsilon,0}=-iq_iA_2(\vec{\mathrm{R}}),\ \ \bar{H}_{\epsilon g_i,0}=-iq_iA_3(\vec{\mathrm{R}}) \; ,\\
&\bar{H}_{\epsilon\rho,0}=-\lambda(\vec{\mathrm{R}})A_4(\vec{\mathrm{R}})q^2 \; ,\\
&\bar{H}_{\epsilon\epsilon,0}=-\lambda(\vec{\mathrm{R}})A_5(\vec{\mathrm{R}})q^2 \; ,\\
&\bar{H}_{g_ig_j,0}=-\nu(\vec{\mathrm{R}})q^2\delta_{ij}-\left[\tfrac{1}{3}\nu(\vec{\mathrm{R}})+\frac{\zeta(\vec{\mathrm{R}})}{\rho(\vec{\mathrm{R}})}\right]q_iq_j \; .
\end{aligned} \tag{2.12b}$$

The first-order corrections in the temperature gradient to these matrix elements are given by

$$\Delta\bar{H}_{\rho\rho,1}=\Delta\bar{H}_{\rho\epsilon,1}=0 \; , \tag{2.13a}$$

$$\begin{aligned}
&\Delta\bar{H}_{\rho g_i,1}=-\tfrac{1}{2}\delta_{ix}\frac{\partial}{\partial R_x} \; , \quad \Delta\bar{H}_{g_i\rho,1}=-\frac{1}{2}\left[\delta_{ix}\frac{\partial}{\partial R_x}\right]A_1+\frac{1}{2}\left[\frac{\partial A_1}{\partial R_x}\right]q_i\frac{\partial}{\partial q_x} \; ,\\
&\Delta\bar{H}_{g_i\epsilon,1}=-\frac{1}{2}\left[\delta_{ix}\frac{\partial}{\partial R_x}\right]A_2+\frac{1}{2}\left[\frac{\partial A_2}{\partial R_x}\right]q_i\frac{\partial}{\partial q_x} \; ,\\
&\Delta\bar{H}_{\epsilon g_i,1}=-\frac{1}{2}\left[\delta_{ix}\frac{\partial}{\partial R_x}\right]A_3+\frac{1}{2}\left[\frac{\partial A_3}{\partial R_x}\right]q_i\frac{\partial}{\partial q_x} \; ,
\end{aligned} \tag{2.13b}$$

$$\begin{aligned}
\Delta\bar{H}_{g_ig_j,1}=&\left[\frac{1}{2}\left[\frac{\partial\nu}{\partial R_x}\right]q^2\frac{\partial}{\partial(iq_x)}+iq_x\nu\frac{\partial}{\partial R_x}-iq_x\nu\frac{\partial\ln\rho}{\partial R_x}\right]\delta_{ij}\\
&+\left\{\frac{1}{2}\left[\frac{\partial}{\partial R_x}\left[\frac{\nu}{3}+\frac{\zeta}{\rho}\right]\right]q_iq_j\frac{\partial}{\partial(iq_x)}+\frac{i}{2}\left[\frac{\nu}{3}+\frac{\zeta}{\rho}\right](\delta_{jx}q_i+\delta_{ix}q_j)\frac{\partial}{\partial R_x}\right\}\\
&-\left[\frac{\partial\ln\rho}{\partial R_x}\right]\left[i\nu\delta_{ix}q_j-\frac{2\nu}{3}iq_i\delta_{jx}+iq_i\delta_{jx}\frac{\zeta}{\rho}\right]\\
&+\tfrac{1}{2}(\delta_{jx}iq_i-\delta_{ix}iq_j)\left[\frac{5}{3}\frac{\partial\nu}{\partial R_x}-\frac{\partial}{\partial R_x}\left[\frac{\zeta}{\rho}\right]\right] \; ,
\end{aligned} \tag{2.13c}$$

$$\Delta\bar{H}_{\epsilon\rho,1}=iq_x\left[\frac{\partial\lambda}{\partial\rho}\right]_{\epsilon}\frac{\partial T}{\partial R_x}+iq_x\lambda\left[\frac{\partial A_4}{\partial R_x}\right]+iq_xA_4\frac{\partial}{\partial R_x}-\frac{iq^2}{2}\frac{\partial(A_4\lambda)}{\partial R_x}\frac{\partial}{\partial q_x} \; , \tag{2.13d}$$

$$\Delta\bar{H}_{\epsilon\epsilon,1}=iq_x\left[\frac{\partial\lambda}{\partial\epsilon}\right]_{\rho}\left[\frac{\partial T}{\partial R_x}\right]+iq_x\lambda\left[\frac{\partial A_5}{\partial R_x}\right]+iq_x\lambda A_5\frac{\partial}{\partial R_x}-\frac{iq^2}{2}\frac{\partial(\lambda A_5)}{\partial R_x}\frac{\partial}{\partial q_x} \; . \tag{2.13e}$$

In Eqs. (2.12) and (2.13) $A_1=(\partial p/\partial\rho)_{\epsilon}$, $A_2=(\partial p/\partial\epsilon)_{\rho}$, $A_3=h/\rho$, $A_4=(\partial T/\partial\rho)_{\epsilon}$, $A_5=(\partial T/\partial\epsilon)_{\rho}$, $\nu=\eta/\rho$, and all quantities depend on the center-of-mass variable $\vec{\mathrm{R}}$. In Sec. III we will use the Eqs. (2.9)–(2.13) to obtain explicit expressions for the $M_{\alpha\rho}$.

III. SOLUTIONS FOR THE $M_{\alpha\rho}$

Since we intend in this section to compute the $M_{\alpha\rho}$ to first order in the temperature gradient, we make the following gradient expansions of the $M_{\alpha\rho}$:

$$M_{\alpha\rho}(\vec{R},\vec{q},\omega)=M_{\alpha\rho,0}(\vec{R},\vec{q},\omega)+M_{\alpha\rho,1}(\vec{R},\vec{q},\omega) + \cdots , \tag{3.1a}$$

$$M_{\alpha\rho}(\vec{R},\vec{q},t=0)=M_{\alpha\rho,0}(\vec{R},\vec{q},t=0) +M_{\alpha\rho,1}(\vec{R},\vec{q},t=0)+ \cdots , \tag{3.1b}$$

where $M_{\alpha\rho,i}$ denotes the contributions to $M_{\alpha\rho}$ that are proportional to the ith power of the temperature gradient. Then using Eqs. (2.9), (2.11), and (3.1), we can write the equations that determine $M_{\alpha\rho,0}$ and $M_{\alpha\rho,1}$ as

$$-i\omega M_{\alpha\rho,0}(\vec{R},\vec{q},\omega)=M_{\alpha\rho,0}(\vec{R},\vec{q},t=0) +\bar{H}_{\alpha\gamma,0}(\vec{R},\vec{q})M_{\gamma\rho,0}(\vec{R},\vec{q},\omega) \tag{3.2a}$$

and

$$-i\omega M_{\alpha\rho,1}(\vec{R},\vec{q},\omega)=M_{\alpha\rho,1}(\vec{R},\vec{q},t=0) +\bar{H}_{\alpha\gamma,0}M_{\gamma\rho,1}(\vec{R},\vec{q},\omega) +\Delta\bar{H}_{\alpha\gamma,1}M_{\gamma\rho,0}(\vec{R},\vec{q},\omega) . \tag{3.2b}$$

If we then first solve Eq. (3.2a) for $M_{\alpha\rho,0}$ and substitute the solution into Eq. (3.2b), we will have a set of equations for $M_{\alpha\rho,1}(\vec{R},\vec{q},\omega)$ which can then be solved in terms of the equal-time correlation functions.

A. M, A, and D to zeroth order in the gradient

We will regard the quantities $\Delta\bar{H}_{\alpha\beta,1}$ as small perturbations to $\bar{H}_{\alpha\beta,0}$. Since the combinations $\bar{H}_{\alpha\gamma,0}M_{\gamma\beta,i}$ appear in the Eqs. (3.2) for $i=0,1$, it is convenient to expand the quantities $M_{\alpha\rho,i}$ in terms of the eigenfunctions of the matrix $\bar{H}_{\alpha\beta,0}$. These eigenfunctions are the well-known hydrodynamic modes, and we discuss them as well as their associated eigenvalues in Appendix A. One can see by inspection of Eq. (2.12) that the matrix elements $\bar{H}_{\alpha\beta,0}$ have the general form $Aq+Bq^2$, where the term Aq represents the Euler terms and the term Bq^2 the dissipative Navier-Stokes terms in the linearized hydrodynamic equations. In principle, there are higher terms of order q^3, q^4, and so on, due to Burnett, and higher-order terms in the linearized hydrodynamic equations. However, this expansion can be terminated at order q^2 provided that q satisfies the condition

$$ql \ll 1 , \tag{3.3}$$

where l is a characteristic microscopic length on the order of a mean-free path for a gas or on the order of the range of the forces for a liquid.[16] If Eq. (3.3) is satisfied, then one can expand the hydrodynamic modes and their associated eigenvalues in powers of q, or rather ql, and one can construct combinations of the $M_{\alpha\rho,i}$ that are approximate eigenfunctions of $\bar{H}_{\alpha\beta,0}$ as shown in Appendix A. These approximate eigenfunctions of $\bar{H}_{\alpha\beta,0}$ differ from the exact eigenfunctions by terms of order $(qM_{\alpha\rho,i})$, as discussed below Eq. (A11e). They consist of a heat mode given by

$$M_{H\rho,i}=\frac{A_2}{c^2}(A_3M_{\rho\rho,i}-M_{\epsilon\rho,i}) , \tag{3.4a}$$

two sound modes

$$M_{\sigma\rho,i}=\frac{1}{2c^2}(A_1M_{\rho\rho,i}+A_2M_{\epsilon\rho,i} +\sigma c\hat{q}_jM_{g_j\rho,i}) \quad (\sigma=\pm 1) \tag{3.4b}$$

and two shear modes[17]

$$M_{\eta_j\rho,i}=\frac{1}{c}\hat{q}_{\perp k}^{(j)}M_{g_k\rho,i} \quad (j=1,2) . \tag{3.4c}$$

Here $\hat{q}_{\perp}^{(1)}$, $\hat{q}_{\perp}^{(2)}$, and $\hat{q}$ form a set of three mutually orthogonal unit vectors and summation convention has been used in Eqs. (3.4b) and (3.4c).

The quantities $M_{\alpha\rho,i}$ $(\alpha=\rho,g,\epsilon)$ appearing in Eqs. (3.2a) and (3.2b) can in turn be expressed in terms of $M_{H\rho,i}$, $M_{\sigma\rho,i}$, and $M_{\eta_j\rho,i}$ by

$$M_{\rho\rho,i}=M_{+\rho,i}+M_{-\rho,i}+M_{H\rho,i} , \tag{3.5a}$$

$$M_{\epsilon\rho,i}=A_3(M_{+\rho,i}+M_{-\rho,i}) + \left[A_3-\frac{c^2}{A_2}\right]M_{H\rho,i} , \tag{3.5b}$$

$$M_{g_j\rho,i}=c\hat{q}_j(M_{+\rho,i}-M_{-\rho,i})+c\hat{q}_{\perp j}^{(1)}M_{\eta_1\rho,i} +c\hat{q}_{\perp j}^{(2)}M_{\eta_2\rho,i} . \tag{3.5c}$$

To distinguish between these two sets of functions, we will use Greek subscripts on M, and subsequently on A and D to represent the indices ρ, $\vec{g}$, and ϵ, and Latin subscripts a, b, c, etc., to represent the indices H, σ, and η_i. By using the Eqs. (3.4), we can obtain from the Eq. (3.2a) for the $M_{\alpha\rho,0}$ a set of five equations for the $M_{\alpha\rho,0}(\vec{R},\vec{q},\omega)$ that read as follows:

$$(-i\omega+D_T q^2)M_{H\rho,0}(\vec{R},\vec{q},\omega) -D_T q^2(\gamma-1)(M_{+\rho,0}+M_{-\rho,0})=A_{H\rho,0}\ , \tag{3.6a}$$

$$(-i\omega+\omega_\sigma)M_{\sigma\rho,0}(\vec{R},\vec{q},\omega) -\tfrac{1}{2}[D_l-D_T(\gamma-1)]q^2 M_{-\sigma\rho,0}-\frac{D_T}{2}q^2 M_{H\rho,0} =A_{\sigma\rho,0}, \tag{3.6b}$$

and

$$(-i\omega+\nu q^2)M_{\eta_i\rho,0}(\vec{R},\vec{q},\omega) =A_{\eta_i\rho,0}\quad (i=1,2) \tag{3.6c}$$

where $D_l=\frac{4}{3}\nu+\zeta/\rho$; $\omega_\sigma=i\sigma c q+\frac{1}{2}\Gamma_s q^2$, and $\Gamma_s=D_l+(\gamma-1)D_T$. In deriving Eqs. (3.6a)–(3.6c), we have used the gradient expansions

$$A_{\alpha\rho}(\vec{R},\vec{q})=A_{\alpha\rho,0}(\vec{R},\vec{q})+A_{\alpha\rho,1}(\vec{R},\vec{q})+\cdots \tag{3.7a}$$

and

$$D_{\alpha\rho}(\vec{R},\vec{q})=D_{\alpha\rho,1}(\vec{R},\vec{q})+\cdots\ , \tag{3.7b}$$

where $D_{\alpha\rho,0}$ vanishes since the $D_{\alpha\rho}$ are proportional to the temperature gradient as follows from Eq. (2.6). Further, the $A_{\alpha\rho,i}$ and $D_{\alpha\rho,i}$ are defined in terms of $A_{\alpha\rho,i}$ and $D_{\alpha\rho,i}$ by equations identical to Eq. (3.4). For small q, such that $ql \ll 1$, the quantities $A_{H\rho,0}$, $A_{\sigma\rho,0}$, and $A_{\eta_i\rho,0}$ can be easily calculated[18] with the result that

$$\begin{aligned} A_{H\rho,0}&=\rho^2\frac{k_BT}{\gamma}(\gamma-1)\chi_T\ ,\\ A_{\sigma\rho,0}&=\rho^2\frac{k_BT}{2\gamma}\chi_T,\quad A_{\eta_i\rho,0}=0\ , \end{aligned} \tag{3.8}$$

where all quantities in Eqs. (3.8) are to be evaluated at the point $\vec{R}$.

Equations (3.6a)–(3.6c) can now be solved for the $M_{\alpha\rho,0}$ by iteration. The resulting expressions are given by a series in powers of q as[19]

$$M_{H\rho,0}(\vec{R},\vec{q},\omega)=\frac{A_{H\rho,0}}{(-i\omega+D_Tq^2)}+\frac{q^2D_T(\gamma-1)}{(-i\omega+D_Tq^2)}\left[\frac{A_{+\rho,0}}{(-i\omega+\omega_+)}+\frac{A_{-\rho,0}}{(-i\omega+\omega_-)}\right]+\cdots\ , \tag{3.9a}$$

$$M_{\sigma\rho,0}(\vec{R},\vec{q},\omega)=\frac{A_{\sigma\rho,0}}{(-i\omega+\omega_\sigma)}+\frac{D_Tq^2}{2(-i\omega+\omega_\sigma)}\frac{A_{H\rho,0}}{(-i\omega+D_Tq^2)}+\frac{q^2[D_l-D_T(\gamma-1)]}{2(-i\omega+\omega_\sigma)}\frac{A_{-\sigma\rho,0}}{(-i\omega+\omega_{-\sigma})}+\cdots\ , \tag{3.9b}$$

and

$$M_{\eta_i\rho,0}=\frac{A_{\eta_i\rho,0}}{-i\omega+\nu q^2}=0 \tag{3.9c}$$

with the $A_{\alpha\rho,0}$ given by Eqs. (3.8). Equations (3.9a) and (3.9b) can be used to compute the Landau-Placzek expression for the dynamic structure factor for a fluid in equilibrium. To do this, we use the expressions for $M_{H\rho,0}$ and $M_{\sigma\rho,0}$ given by Eqs. (3.9a) and (3.9b) together with Eq. (3.5a) to obtain an expansion of $M_{\rho\rho,0}(\vec{R},\vec{q},\omega)$ in powers of q. Neglecting then the $\vec{R}$ dependence of $M_{\rho\rho}(\vec{R},\vec{q},\omega)$ since an equilibrium fluid is homogeneous, inserting the resulting expansion of $M_{\rho\rho,0}(\vec{R},\vec{q},\omega)$ in Eq. (2.8) for $S(\vec{k},\omega)$, and carrying out the $\vec{R}$ and $\vec{q}$ integrals, one obtains Eq. (1.3) for $S_{\text{eq}}(\vec{k},\omega)$ provided that $kL \gg 1$, and $c/(\Gamma_s k^2 L) \ll 1$. We will discuss these conditions in more detail in Sec. IV. We note that when a gradient is present, and the fluid is in a nonequilibrium steady state, there is an $\vec{R}$ dependence in $M_{\rho\rho,0}(\vec{R},\vec{q},\omega)$ that must be taken into account explicitly in the calculation of $S(\vec{k},\omega)$. If the above conditions together with other restrictions to be discussed in Sec. IV are satisfied then from $M_{\rho\rho,0}(\vec{R},\vec{q},\omega)$ one can derive an equilibriumlike expression for the dynamic structure factor denoted by $S_0(\vec{R}_0,\vec{k},\omega)$ that has the form of Eq. (1.3), but where all the thermodynamic and hydrodynamic quantities are evaluated at the center of the scattering volume $\vec{R}_0$ [cf. Eq. (1.6)]. We also remark that although the second terms on the right-hand side of Eqs. (3.9a) and (3.9b) make only negligible contributions to (1.3), they have to be kept for consistency in the calculations to be discussed below.

B. $M(\vec{R},\vec{q},\omega)$ to first order in the temperature gradient

Now we turn our attention to the determination of the quantities $M_{\alpha\rho,1}(\vec{R},\vec{q},\omega)$ in the gradient expansion of the $M_{\alpha\rho}(\vec{R},\vec{q},\omega)$, Eq. (3.1a). The

$M_{\alpha\rho,1}(\vec{R},\vec{q},\omega)$ can be found from Eq. (3.2b) by expressing them in terms of the quantities $M_{\alpha\rho,0}(\vec{R},\vec{q},\omega)$, using Eqs. (3.9) and (3.5), and the equal-time correlation functions $A_{\alpha\rho,1}(\vec{R},\vec{q})$ and $D_{\alpha\rho,1}(\vec{R},\vec{q})$. As in the zeroth-order calculation, a simplification occurs if one expresses the $M_{\alpha\rho,1}$ in terms of approximate eigenfunctions of the matrix $\bar{H}_{\alpha\beta,0}$. Therefore, we define the quantities $M_{H\rho,1}$, $M_{\sigma\rho,1}$, and $M_{\eta_i\rho,1}$ in terms of the $M_{\alpha\rho,1}$ through Eqs. (3.4) with $i=1$.

By taking the appropriate linear combinations of Eqs. (3.2b), we can transform them into a set of equations for the $M_{\alpha\rho,1}(\vec{R},\vec{q},\omega)$. These equations are such that $M_{H\rho,1}$ satisfies an equation of the form

$$\begin{aligned}(-i\omega+D_Tq^2)M_{H\rho,1}(\vec{R},\vec{q},\omega)+\left[X^TR_{HH}^{(1)}+X^TR_{HH}^{(2)}q\frac{\partial}{\partial q_x}+R_{HH}^{(3)}\frac{\partial}{\partial R_x}\right]M_{H\rho,0}\\ -\sum_{\sigma=\pm1}\left[q^2D_T(\gamma-1)M_{\sigma\rho,1}(\vec{R},\vec{q},\omega)+\left[X^TR_{H\sigma}^{(1)}+X^TR_{H\sigma}^{(2)}q\frac{\partial}{\partial q_x}+R_{H\sigma}^{(3)}\frac{\partial}{\partial R_x}\right]M_{\sigma\rho,0}(\vec{R},\vec{q},\omega)\right]\\ +(X^TR_{H\eta_1}^{(1)}M_{\eta_1\rho,0}+X^TR_{H\eta_2}^{(1)}M_{\eta_2\rho,0})=A_{H\rho,1}+D_{H\rho,1}\,, \qquad (3.10\text{a})\end{aligned}$$

while $M_{\sigma\rho,1}$ satisfies an equation of the form

$$\begin{aligned}[-i\omega+\omega_\sigma]M_{\sigma\rho,1}+\left[X^TR_{\sigma,\sigma}^{(1)}+X^TR_{\sigma,\sigma}^{(2)}q\frac{\partial}{\partial q_x}+R_{\sigma,\sigma}^{(3)}\frac{\partial}{\partial R_x}\right]M_{\sigma\rho,0}\\ -\left[\frac{D_lq^2}{2}-\frac{D_T(\gamma-1)}{2}q^2\right]M_{-\sigma\rho,1}+\left[X^TR_{\sigma,-\sigma}^{(1)}+X^TR_{\sigma,-\sigma}^{(2)}q\frac{\partial}{\partial q_x}+R_{\sigma,-\sigma}^{(3)}\frac{\partial}{\partial R_x}\right]M_{-\sigma\rho,0}\\ -\frac{D_Tq^2}{2}M_{H\rho,1}+\left[X^TR_{\sigma,H}^{(1)}+X^TR_{\sigma,H}^{(2)}q\frac{\partial}{\partial q_x}+R_{\sigma,H}^{(3)}\frac{\partial}{\partial R_x}\right]M_{H\rho,0}\\ +\sum_{i=1,2}\left[X^TR_{\sigma\eta_i}^{(2)}q\frac{\partial}{\partial q_x}+R_{\sigma\eta_i}^{(3)}\frac{\partial}{\partial R_x}\right]M_{\eta_i\rho,0}=A_{\sigma\rho,1}+D_{\sigma\rho,1}\,. \qquad (3.10\text{b})\end{aligned}$$

(3.10b)

We will not give the corresponding equations for $M_{\eta_i\rho,1}$ here, since they are not needed for the computation of $M_{\rho\rho,1}$. Further, as we have already shown that $M_{\eta_i\rho,0}(\vec{R},\vec{q},\omega)=0$, Eq. (3.9c), we can drop the terms proportional to $M_{\eta_i\rho,0}$ in Eqs. (3.10a) and (3.10b). In paper III we will consider the contribution of these shear modes further, since they do contribute to the light scattering for large gradients. In Eqs. (3.10a) and (3.10b) the quantities $A_{\alpha\rho,1}$ and $D_{\alpha\rho,1}$ are defined in terms of the $A_{\alpha\rho,1}$ and $D_{\alpha\rho,1}$ by equations identical to Eq. (3.4) and we have defined the quantity X^T by $X^T=T^{-1}\partial T/\partial R_x$.

We will not need the explicit forms of the $R_{ab}^{(i)}$ yet, but only that they depend on $\vec{R}$ and $\vec{q}$ and have a q expansion of the form

$$R_{ab}^{(i)}=R_{ab,0}^{(i)}+qR_{ab,1}^{(i)}+q^2R_{ab,2}^{(i)}+\cdots\,. \qquad (3.11)$$

Now we turn to the solution of Eqs. (3.10a) and (3.10b) with the shear-mode contributions set equal to zero. In Appendix B we discuss the terms $R_{ab}^{(i)}$ and show that the $M_{\alpha\rho,1}$ contain three types of corrections to $M_{\alpha\rho,0}$ that are distinguished by their orders of magnitude.

(1) The largest correction term in the $M_{\alpha\rho,1}$ for small q are of order

$$(cX^T/\Gamma_sq^2)\cdot(cq/\Gamma_sq^2)\approx O(X^T/q^3)$$

compared to $M_{\alpha\rho,0}$. All terms of this order of magnitude eventually cancel and do not contribute to $S(\vec{k},\omega)$ to order X^T. We remark that the presence of these terms of $O(X^T/q^3)$ implies that at this stage of the calculation the second terms on the right-hand sides of Eqs. (3.9a) and (3.9b) have to be retained. For, the $O(q)$ corrections to the $M_{\alpha\rho,0}$ lead to terms of $O(X^T/q^2)$ in $M_{\alpha\rho,1}$ that should be kept. It turns out, however, at the end of our calculations that this class of terms of $O(X^T/q^2)$ that has been generated by the $O(X^T/q^3)$ terms also cancels.

(2) The most dominant nonvanishing contributions to the $M_{\alpha\rho,1}$ are of relative order $cX^T/\Gamma_s q^2$, for small q.

(3) The remaining terms are of relative order $X^T/q = (cX^T/\Gamma_s q^2)\cdot(\Gamma_s q^2/cq)$. These terms are smaller than those listed above by a factor of $\Gamma_s q^2/cq$. Since we have imposed the restriction $\Gamma_s q^2/cq \ll 1$, the most important correction to $M_{\alpha\rho,0}$ will be of order $cX^T/\Gamma_s q^2$, and we will neglect the terms of order X^T/q. Therefore, in Appendix B we retain only those terms in the $R_{ab}^{(i)}$ that lead to contributions to $M_{\alpha\rho,1}$ that are at least of relative order $cX^T/\Gamma_s q^2$. This procedure yields in a straightforward, but lengthy manner, the following equations for $M_{H\rho,1}(\vec{R},\vec{q},\omega)$ and $M_{\sigma\rho,1}(\vec{R},\vec{q},\omega)$:

$$(-i\omega + D_T q^2) M_{H\rho,1} - q^2 D_T(\gamma-1)(M_{+\rho,1} + M_{-\rho,1}) - \frac{1}{2}\frac{\partial \ln\rho}{\partial R_x} cq \frac{\partial}{\partial q_x}(M_{+\rho,0} - M_{-\rho,0}) = A_{H\rho,1} + D_{H\rho,1} \tag{3.12a}$$

and

$$\begin{aligned}(-i\omega+\omega_\sigma)M_{\sigma\rho,1} + \Bigg[&\frac{1}{2}\frac{\partial\omega_\sigma}{\partial(iq_x)}\frac{\partial}{\partial R_x} - \frac{1}{2}\frac{\partial}{\partial R_x}\left[i\sigma qc + \frac{D_l q^2}{2}\right]\frac{\partial}{\partial(iq_x)} \\ &- \frac{A_2 q^2}{4c^2}\left[\frac{\partial(\lambda A_4)}{\partial R_x} + A_3 \frac{\partial(\lambda A_5)}{\partial R_x}\right]\frac{\partial}{\partial(iq_x)} + \sigma\hat{q}_x \frac{3}{4}\frac{\partial c}{\partial R_x} - \frac{\sigma\hat{q}_x c}{4}\frac{\partial \ln\rho}{\partial R_x}\Bigg] M_{\sigma\rho,0} \\ - \frac{D_T q^2}{2} M_{H\rho,1} - \frac{-i\sigma qc}{4c^2}&\left[\frac{\partial A_1}{\partial R_x} + \left[A_3 - \frac{c^2}{A_2}\right]\frac{\partial A_2}{\partial R_x}\right]\frac{\partial}{\partial(iq_x)} M_{H\rho,0} - \left[\frac{D_l q^2}{2} - D_T\frac{(\gamma-1)}{2}q^2\right] M_{-\sigma\rho,1} \\ - \left[\frac{i\sigma q}{2}\frac{\partial c}{\partial R_x}\frac{\partial}{\partial iq_x} + \frac{i\sigma cq}{2}\frac{\partial\ln\rho}{\partial R_x}\frac{\partial}{\partial iq_x}\right]& M_{-\sigma\rho,0} = A_{\sigma\rho,1} + D_{\sigma\rho,1}\ .\end{aligned} \tag{3.12b}$$

To derive these equations, we have used the thermodynamic identities given by Eqs. (A9) in Appendix A as well as the relation

$$A_2(\partial A_3/\partial R_x) = -\left[\frac{c^2}{\rho}\right]\left[\frac{\partial p}{\partial R_x}\right]_p$$

which follows directly from thermodynamics by using the expressions for A_2 and A_3 given below Eq. (2.13).

C. A and D to first order in the gradient

To obtain explicit expressions for the $M_{\alpha\rho,1}$, we need to compute $A_{\alpha\rho,1}$ and $D_{\alpha\rho,1}$ appearing on the right-hand sides of Eqs. (3.12a) and (3.12b). We consider first $A_{\alpha\rho,1}$ and begin with the expression for $A_{\alpha\rho,1}(\vec{R},\vec{q})$ given in terms of the $A_{\alpha\rho,1}$ by equations identical to the Eqs. (3.4). Considering the gradient expansion of $A_{\alpha\rho}(\vec{R},\vec{q})$ defined by Eqs. (2.5) and (2.10), we obtain with the use of an expansion of the local stationary-state distribution function about the reference ensemble defined in Sec. IV of paper I

$$\begin{aligned}A_{\alpha\rho}(\vec{R},\vec{q}) &\equiv \int d\vec{R}_{12} e^{-i\vec{q}\cdot\vec{R}_{12}} \langle \delta a_\alpha(\vec{R}_1)\delta\rho(\vec{R}_2)\rangle_{L,\mathrm{ss}} \\ &= \int d\vec{R}_{12} e^{-i\vec{q}\cdot\vec{R}_{12}} \langle \delta a_\alpha(\vec{R}_1)\delta\rho(\vec{R}_2)\rangle_{0,\vec{R}} \\ &\quad + \int d\vec{R}_{12} e^{-i\vec{q}\cdot\vec{R}_{12}} \int d\vec{R}' \langle \delta a_\alpha(\vec{R}_1)\delta\rho(\vec{R}_2)\delta a_\gamma(\vec{R}')\rangle_{0,\vec{R}} \cdot (\vec{R}'-\vec{R})\cdot\vec{\nabla} y_\gamma(\vec{R}) + O((X^T)^2) \\ &= A_{\alpha\beta,0} + A_{\alpha\beta,1} + O((X^T)^2)\ .\end{aligned} \tag{3.13}$$

The first term on the right-hand side of Eq. (3.13) is the quantity $A_{\alpha\rho,0}(\vec{R},\vec{q})$ which was used earlier to compute the $A_{\alpha\rho,0}$ appearing on the right-hand side of Eq. (3.2a) for $M_{\alpha\rho,0}$. The second term on the right-hand side of (3.13) can be neglected since it does not lead to corrections of order $cX^T/\Gamma_s q^2$ that are of interest here. To see this, one only needs to note that the equilibriumlike three-point correlation function has a range in the variables $\vec{R}_1-\vec{R}$ and $\vec{R}'-\vec{R}$, that is, on the order of the microscopic correlation length l, which is small away from the critical point. Therefore, for small q, this term can be neglected. Thus, to this order, we can set $A_{\alpha\rho}(\vec{R},\vec{q})=A_{\alpha\rho,0}(\vec{R},\vec{q})$.

The quantities $D_{\alpha\rho,1}$ appearing in Eqs. (3.12a) and (3.12b) are the first nonvanishing terms in the gradient expression of the D's, and are defined in terms of the $D_{\alpha\rho,1}$ by equations of the form (3.4). The $D_{\alpha\rho,1}$ are in turn given by the solution of Eq. (2.6) when suitably Fourier transformed. Up to terms of first order in X^T, the $D_{\alpha\beta,1}(\vec{R},\vec{q})$ satisfy the equations

$$\bar{H}_{\alpha\gamma,0}(\vec{R},\vec{q})D_{\gamma\beta,1}(\vec{R},\vec{q})+\bar{H}_{\beta\gamma,0}(\vec{R},-\vec{q})D_{\alpha\gamma,1}(\vec{R},\vec{q})$$
$$=(\delta a_{\alpha T}\delta a_{\beta T}S_{xT})_{0,\vec{R}}\beta X^T\ . \tag{3.14}$$

Here the $\bar{H}_{\alpha\beta,0}(\vec{R},\pm\vec{q})$ are defined by the Eqs. (2.12). To determine the $D_{\alpha\beta,1}$ most easily, it is convenient to express them in terms of the quantities $D_{ab,1}$ that approximately diagonalize $\bar{H}_{\alpha\beta,0}(\vec{R},\vec{q})$ or $\bar{H}_{\alpha\beta,0}(\vec{R},-\vec{q})$. As mentioned above, the quantities $D_{a\beta,1}(\vec{R},\vec{q})$ defined by [cf. Eqs. (3.4)]

$$D_{H\beta,1}(\vec{R},\vec{q})=\frac{A_2}{c^2}(A_3D_{\rho\beta,1}-D_{\epsilon\beta,1})\ , \tag{3.15a}$$

$$D_{\sigma\beta,1}(\vec{R},\vec{q})=\frac{1}{2c^2}(A_1D_{\rho\beta,1}+A_2D_{\epsilon\rho,1}$$
$$+\sigma c\hat{q}_iD_{g_i\beta,1})\ , \tag{3.15b}$$

$$D_{\eta_i\beta,1}(\vec{R},\vec{q})=\frac{1}{c}\hat{q}^{(i)}_{\perp,j}D_{g_j\beta,1}\ , \tag{3.15c}$$

are approximate eigenfunctions of $\bar{H}_{\alpha\gamma,0}(\vec{R},\vec{q})$. Similarly, one may apply the methods of Appendix A to construct approximate eigenfunctions of $\bar{H}_{\beta\gamma,0}(\vec{R},-\vec{q})$. In Appendix A we show that the quantities $D_{ab,1}(\vec{R},\vec{q})$ defined by

$$D_{\alpha H,1}(\vec{R},\vec{q})=\frac{A_2}{c^2}(A_3D_{\alpha\rho,1}-D_{\alpha\epsilon,1})\ , \tag{3.16a}$$

$$D_{\alpha\sigma,1}(\vec{R},\vec{q})=\frac{1}{2c^2}(A_1D_{\alpha\rho,1}+A_2D_{\alpha\epsilon,1}$$
$$-\sigma c\hat{q}_iD_{\alpha g_i,1})\ , \tag{3.16b}$$

$$D_{\alpha\eta_i,1}(\vec{R},\vec{q})=\frac{1}{c}(-\hat{q})^{(i)}_{\perp,j}D_{\alpha g_j,1}\ , \tag{3.16c}$$

are approximate eigenfunctions of $\bar{H}_{\beta\gamma,0}(\vec{R},-\vec{q})$ belonging to the eigenvalues $-\omega_H(q)$, $-\omega_\sigma(q)$, and $-\omega_{\eta_i}(q)$, respectively. Accordingly, we consider the equations for the quantities $D_{ab,1}(\vec{R},\vec{q})$, where both a and b denote one of the set (σ,H,η_i) obtained by a linear transformation of Eq. (3.14) from an equation for the $D_{\alpha\beta,1}$ to one for the $D_{ab,1}$. The derivation of this transformed equation is outlined in Appendix A and the result reads

$$-[\omega_a(q)+\omega_b(q)]D_{ab,1}$$
$$=(\delta a_{a,\hat{q}}\delta a_{b,-\hat{q}}S_{xT})_{0,\vec{R}}\beta X^T \tag{3.17}$$

with the ω_a and $\delta a_{a,\hat{q}}$ given by Eqs. (A7a), (A8a), and (A12) of Appendix A.

We are only interested in the leading contributions to $D_{ab,1}(\vec{R},\vec{q})$ for small q, i.e., those that lead to corrections to $M_{\alpha\rho,0}$ of relative order X^T/q^2. Contributions of this order are obtained only for the combinations $(a,b)=(H,H)$, $(\sigma,-\sigma)$, (η_i,H), (H,η_i), and (η_i,η_j) since only for these combinations of hydrodynamic modes is $[\omega_a(q)+\omega_b(q)]$ in Eqs. (3.17) of $O(q^2)$. As we discussed earlier, the shear-mode contributions to M_{ab} may be neglected so that the only combinations of interest to use are $D_{HH,1}(\vec{R},\vec{q})$ and $D_{\sigma-\sigma,1}(\vec{R},\vec{q})$, which are given with Eq. (3.17) by

$$D_{HH,1}(\vec{R},\vec{q})=\frac{-(\delta a_{H,\hat{q}}\delta a_{H,-\hat{q}}S_{xT})_{0,\vec{R}}\beta X^T}{2D_Tq^2} \tag{3.18a}$$

and

$$D_{\sigma-\sigma,1}(\vec{R},\vec{q})=-\frac{(\delta a_{\sigma,\hat{q}}\delta a_{-\sigma,-\hat{q}}S_{xT})_{0,\vec{R}}}{\Gamma_sq^2}\beta X^T\ , \tag{3.18b}$$

respectively. The quantities $(\delta a_{H,\hat{q}}\delta a_{H,-\hat{q}}S_{xT})_{0,\vec{R}}$ and $(\delta a_{\sigma,\hat{q}}\delta a_{-\sigma,-\hat{q}}S_{xT})_{0,\vec{R}}$ are typical mode-coupling amplitudes, and their values can be found in the literature.[18] They are

$$(\delta a_{H,\hat{q}}\delta a_{H,-\hat{q}}S_{xT})_{0,\vec{R}}=0\ , \tag{3.19a}$$

$$(\delta a_{\sigma,\hat{q}}\delta a_{-\sigma,-\hat{q}}S_{xT})_{0,\vec{R}}=\frac{\sigma\rho c\hat{q}_x}{2c^2\beta^2}\ . \tag{3.19b}$$

Finally, we need $D_{H\rho,1}$ and $D_{\sigma\rho,1}$ to complete the calculation of $M_{H\rho,1}$ and $M_{\sigma\rho,1}$. These quantities can be obtained by solving the Eqs. (3.15) and (3.16) and are given by

$$D_{H\rho,1}=D_{H+,1}(\vec{R},\vec{q})+D_{H-,1}(\vec{R},\vec{q})+D_{HH,1}(\vec{R},\vec{q})$$
$$\approx D_{HH,1}(\vec{R},\vec{q}) \tag{3.20a}$$

and

$$D_{\sigma\rho,1}=D_{\sigma H,1}(\vec{R},\vec{q})+D_{\sigma\sigma,1}(\vec{R},\vec{q})+D_{\sigma-\sigma,1}(\vec{R},\vec{q})$$
$$\approx D_{\sigma-\sigma,1}(\vec{R},\vec{q})\ , \tag{3.20b}$$

where only terms of $O(X^T/q^2)$ are retained in the second (approximate) equality in Eqs. (3.20a) and (3.20b). Combining Eqs. (3.20a) and (3.20b) with (3.18) and (3.19), we find

$$D_{H\rho,1}(\vec{R},\vec{q})\approx 0 \tag{3.21a}$$

and

$$D_{\sigma\rho,1}(\vec{R},\vec{q})=-\rho^2\frac{k_BT\chi_T}{2\gamma}\frac{\sigma c\hat{q}_x}{\Gamma_s q^2}X^T\ . \tag{3.21b}$$

IV. CALCULATION OF $S(\vec{k},\omega)$ and $I(\vec{k})$

We have now assembled all the pieces necessary for the calculation of $M_{\rho\rho}(\vec{R},\vec{q},\omega)$. Using the Eqs. (3.13) and (3.21) on the right-hand side of Eqs. (3.12), iterating these equations around $X^T=0$, using Eqs. (A9) and consistently keeping only those terms that are of order X^T/q^2 when compared with $M_{H\rho,0}(\vec{R},\vec{q},\omega)$ and $M_{\sigma\rho,0}(\vec{R},\vec{q},\omega)$, leads after a lengthy calculation to the result

$$\begin{aligned}M_{\rho\rho}(\vec{R},\vec{q},\omega)&=M_{\rho\rho,0}(\vec{R},\vec{q},\omega)+M_{\rho\rho,1}(\vec{R},\vec{q},\omega)+O((X^T)^2)\\&=(M_{H\rho}+M_{\sigma\rho}+M_{-\sigma\rho})_0+(M_{H\rho}+M_{\sigma\rho}+M_{-\sigma\rho})_1+O((X^T)^2)\\&\approx\rho^2\frac{k_BT}{\gamma}\chi_T\frac{(\gamma-1)}{(-i\omega+D_Tq^2)}\\&\quad+\rho^2\frac{k_BT}{2\gamma}\chi_T\sum_{\sigma=\pm1}\left[\frac{(1-\sigma c\hat{q}_xX^T/\Gamma_sq^2)}{(-i\omega+i\sigma cq+\frac{1}{2}\Gamma_sq^2)}\right.\\&\qquad\left.-\frac{1}{2}\frac{\sigma c\hat{q}_xX^T}{(-i\omega+i\sigma cq+\frac{1}{2}\Gamma_sq^2)^2}\right]\ .\end{aligned}\tag{4.1}$$

The dynamical structure factor as well as the integrated intensities of the Rayleigh and Brillouin lines can now be computed to order X^T. To compute the dynamical structure factor, we insert the expression for $M_{\rho\rho}(\vec{R},\vec{q},\omega)$ in Eq. (2.8). Then if we use that the form factors $P(\vec{R})$ are sharply peaked around the point $\vec{R}_0$, and have a spatial extent L, we can carry out the $\vec{R}$ and $\vec{q}$ integrals appearing in Eq. (2.8). If the following conditions are satisfied:

$$kL\gg 1,\quad \frac{c}{\Gamma_sk^2L}\ll 1,\quad L\,|X^T|\ll 1\ ,$$

and

$$\frac{L\,|\vec{\nabla}c\,|\,k}{\Gamma_sk^2}\ll 1\ , \tag{4.2}$$

one obtains Eqs. (1.6a) and (1.6b) for the dynamical structure factor $S(\vec{R}_0,\vec{k},\omega)$, where $\vec{R}_0$ indicates that all thermodynamic and hydrodynamic quantities are to be evaluated at the point $\vec{R}_0$ in the fluid.

The first two inequalities in Eq. (4.2) have been mentioned below Eq. (3.9) since they must be satisfied in order to obtain the equilibrium Landau-Placzek result given by Eq. (1.3). The condition $kL\gg 1$ pertains to both the central and Brillouin lines and states that the wavelength $\lambda=2\pi/k$ must be much less than the size of the scattering volume. The condition c/Γ_sk^2L is required only for the Brillouin-line contributions to $S(\vec{k},\omega)$ and expresses that the uncertainty in the location of the sound peaks, due to the finite size of the scattering volume $\Delta\omega=c\Delta k\sim c/L$, should be much less than their natural linewidth Γ_sk^2. The nonequilibrium condition $L\,|X^T|\ll 1$ is used to restrict the gradient expansion of $S(\vec{k},\omega)$ to first order in powers of X^T and simply states that the length over which the gradients change, $L_\nabla=|X^T|^{-1}=T/|\vec{\nabla}T|$, must be much larger than the size of the scattering volume L. Similarly, the condition $(L\,|\vec{\nabla}c\,|\,k)/\Gamma_sk^2\ll 1$ requires that the uncertainty in the location of the sound peaks due to the thermal gradient $\Delta\omega=Lk\,|\vec{\nabla}c\,|$ is much less than the natural linewidth Γ_sk^2. Of the four conditions listed in Eq. (4.2), the most restrictive are the second and the fourth that refer to the effects due to the finite size of the scattering volume L and of the gradient length L_∇ on the shapes of the Brillouin lines.

We remark that the integrated intensities of the Rayleigh and the Brillouin lines in $S(\vec{R}_0,\vec{k},\omega)$ can be obtained in two ways. The first method uses the explicit expression for $S(\vec{R}_0,\vec{k},\omega)$ given by Eqs. (1.6). If we use Eqs. (1.6) and identify the parts of $S(\vec{R}_0,\vec{k},\omega)$ that are peaked around $\omega=\sigma ck$ and $\omega=0$, respectively, and integrate these contributions over all frequencies, we obtain for the integrated intensity of the σ-Brillouin line

$$\begin{aligned} I^\sigma(\vec{R}_0,\vec{k}) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\rho^2\frac{k_BT}{2\gamma}\chi_T\Gamma_s k^2 \\ &\quad\times\frac{[1-\sigma y_\sigma(\vec{k},\omega)c\hat{k}_x X^T/\Gamma_s k^2]}{(\omega-\sigma ck)^2+(\Gamma_s k^2/2)^2} \\ &=\rho^2\frac{k_BT}{2\gamma}\chi_T\left[1-\frac{\sigma c\hat{k}_x X^T}{\Gamma_s k^2}\right] \end{aligned} \tag{4.3a}$$

and for the integrated intensity of the central or Rayleigh line

$$\begin{aligned} I^H(\vec{R}_0,\vec{k}) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\rho^2 k_BT\chi_T\frac{(\gamma-1)}{\gamma} \\ &\quad\times\frac{2D_Tk^2}{\omega^2+(D_Tk^2)^2} \\ &=\rho^2k_BT\chi_T\frac{(\gamma-1)}{\gamma}\,, \end{aligned} \tag{4.3b}$$

where all thermodynamic and hydrodynamic quantities are evaluated at $\vec{R}_0$. If the above method is used to obtain the integrated intensities, then the expansion parameters that determine the validity of Eqs. (4.3) appear to be those given by Eqs. (4.2) since these inequalities were needed to derive Eq. (1.6). However, one can see that these results hold under less restrictive conditions by using an alternative method to obtain $I^\sigma(\vec{R}_0,\vec{k})$ and $I^H(\vec{R}_0,\vec{k})$.

In this method we use Eq. (2.8), the general expression for $S(\vec{R}_0,\vec{k},\omega)$, and integrate first over all frequencies to obtain the total integrated intensity $I(\vec{R}_0,\vec{k})$. If this is done, then one finds an expression for $I(\vec{R}_0,\vec{k})$ that depends on $M_{\rho\rho}(\vec{R},\vec{q},t=0)$. Using Eq. (3.5a), we can express this result in terms of $M_{a\rho}(\vec{R},\vec{q})$ and obtain

$$I(\vec{R}_0,\vec{k})=I^H(\vec{R}_0,\vec{k})+I^+(\vec{R}_0,\vec{k})+I^-(\vec{R}_0,\vec{k}) \tag{4.4}$$

with

$$\begin{aligned} I^H(\vec{R}_0,\vec{k}) &= \mathrm{Re}\left[\int d\vec{R}\,P^2(\vec{R})\right]^{-2} \\ &\quad\times\int d\vec{R}\int\frac{d\vec{q}}{(2\pi)^3}P^2(\vec{R}) \\ &\quad\times P^2_{\vec{k}-\vec{q}}M_{H\rho}(\vec{R},\vec{q}) \end{aligned} \tag{4.5a}$$

and

$$\begin{aligned} I^\sigma(\vec{R}_0,\vec{k}) &= \mathrm{Re}\left[\int d\vec{R}\,P^2(\vec{R})\right]^{-2} \\ &\quad\times\int d\vec{R}\int\frac{d\vec{q}}{(2\pi)^3}P^2(\vec{R}) \\ &\quad\times P^2_{\vec{k}-\vec{q}}M_{\sigma\rho}(\vec{R},\vec{q})\,. \end{aligned} \tag{4.5b}$$

If we now identify $I^H(\vec{R}_0,\vec{k})$ and $I^\sigma(\vec{R}_0,\vec{k})$ with the integrated intensities of the central and the σ-Brillouin line,[20] respectively, use Eqs. (2.10), (3.4), (3.7), (3.8), (3.15), and (3.21), and assume that $kL \gg 1$ and $L\,|X^T| \ll 1$, then we also obtain Eqs. (4.3). Therefore, for the line shape, Eq. (4.1) is valid if all conditions listed in Eq. (4.2) are satisfied, but for the integrated intensities we need only require that $kL \gg 1$ and $L\,|X^T| \ll 1$. In addition, one has used throughout the inequality $c\,|X^T|\,/\Gamma_s k^2 \ll 1$, since in a theory linear in the gradients we can only consistently discuss changes in the integrated intensities that are small compared to the equilibrium contributions [cf. Eqs. (4.3)]. Equations (4.1) and (4.3) are the results quoted in the Introduction.

V. DISCUSSION

We discuss the following points.

(a) We note that the central line is not affected by the temperature gradient to $O(X^T)$, but that the Brillouin lines, although their location is unchanged, are asymmetric and non-Lorentzian, with their asymmetry proportional to $cX^T/\Gamma_s k^2$. Furthermore, the difference between the integrated intensities of the Brillouin lines is proportional to the magnitude of the nonequilibrium part $D_{\sigma\rho,1}(\vec{R}_0,\vec{k})$ of the equal-time correlation functions, and is proportional to $cX^T/\Gamma_s k^2$. This k^{-2} dependence of the correlation function indicates the presence of long-range correlations in the fluid, proportional to $|\vec{R}_{12}|^{-1}$. Hence, the existence of long-range correlations in nonequilibrium fluids can be detected by experimentally verifying the difference in the integrated intensities of the two Brillouin lines.

(b) The corrections to the equilibrium result in I^σ arise from the coupling of the $(\sigma,\vec{k})$ sound modes in the fluid to the heat current S_{xT}, produced by the thermal gradient. Although to lowest order in $\vec{k}$, a single sound mode does not couple to the heat current since they are orthogonal, the product of two sound modes does. That is, while the expression $(\delta a_{\sigma,\hat{q}} S_{xT})=0$, $(\delta a_{\sigma,\hat{q}} \delta a_{-\sigma,-\hat{q}} S_{xT})$ in Eq. (3.18b) does *not* vanish, and the two relevant sound modes are described by the subscripts $(\sigma,\vec{k})$ and $(-\sigma,-\vec{k})$, since $\vec{q}\approx\vec{k}$. Owing to the coupling of these two sound modes to the heat current, the sound waves that travel in the same direction as the macroscopic heat flow will have a larger amplitude than the waves that move in the direction opposite to the heat flow.[21] For example, in the case where $\hat{k}_x(dT/dR_x)>0$, $I^-(\vec{R}_0,\vec{k})$, the integrated intensity of the Brillouin peak centered at $\omega=-ck$, is due to sound waves that propagate in the direction of the heat flow, while $I^+(\vec{R}_0,\vec{k})$ is due to sound waves propagating in a direction opposite to the heat flow. Consequently, $I^-(\vec{R}_0,\vec{k})>I^+(\vec{R}_0,\vec{k})$ for this case and while $I^-(\vec{R}_0,\vec{k})$ is larger than the equilibrium Landau-Placzek result, $I^+(\vec{R}_0,\vec{k})$ is smaller.

(c) A difficulty with the theory developed here for the shape of the Brillouin lines is that the various conditions in Eq. (4.2), especially the second and the fourth, are severely restrictive. One can easily see that when these conditions are satisfied, the $O(X^T)$ corrections to $S_{\text{eq}}(\vec{k},\omega)$ will be very small on the order of a few tenths of a percent at most.

However, as discussed in Sec. IV, the Eqs. (4.3) for the integrated intensities are valid under much less restrictive conditions. In fact, the major restriction is that the nonequilibrium contributions to the integrated intensities will be much smaller than the equilibrium contributions, i.e., $c\,|X^T|/\Gamma_s k^2 \ll 1$. Therefore, with the linear theory developed in this paper we can consistently predict changes in the integrated intensities of the Brillouin lines that are, say, on the order of 5%.

In the next paper we will develop the theory needed when the above condition is relaxed, i.e., when $c\,|X^T|/\Gamma_s k^2 \approx 1$.[22] In principle, we will then be able to predict changes from the equilibrium results that are large, i.e., on the order of 1. Further, the theory for $I^\sigma(\vec{k})$ can then be applied to the recent experiments of Beysens *et al.*,[23] who used temperature gradients and wave numbers such that $c\,|X^T|/\Gamma_s k^2 \approx 1$, provided our neglect of boundary effects can be justified. We also remark that in the next paper we will find large changes in the central line when terms of higher than linear order in X^T are taken into account.

(d) In the calculations presented here we have ignored effects due to the walls of the container of the fluid. While we have incorporated the finite size of the scattering volume through the use of the form factors $P(\vec{R})$, we have treated the entire fluid as if it were of infinite extent. This can be seen from the fact that we constructed and used the modes of the operator $\bar{H}_{\alpha\beta,0}(\vec{R},\vec{q})$ without imposing any boundary conditions on the hydrodynamic fields, i.e., we have considered an unbounded fluid. While this may be a valid approximation for sufficiently large systems, it certainly must fail to be valid for sufficiently small systems. For example, if the cell size is comparable to the mean-free path of a sound wave $l_s \approx c/\Gamma_s k^2$, then the effects of the cell boundaries on the hydrodynamic properties of the fluid could be important. Recently, Satten and Ronis[14] have reported a calculation of the effects of boundaries on the light-scattering spectrum for a system with a small temperature gradient and they found that for sufficiently small systems the asymmetry between the Brillouin line is much smaller than that for large systems. While their method is based on fluctuating hydrodynamics, and in particular, on some assumptions concerning the properties of fluctuations of the hydrodynamic variables at the walls of the container, one can arrive at similar conclusions in a more straightforward way. In Appendix C, we outline such a calculation of the integrated intensities of the Brillouin lines for a fluid with a small temperature gradient in the x direction, and in which the separation between the walls in the x direction, d, can be comparable to l_s. There we show that the dominant finite-size corrections are due mainly to modifications of the hydrodynamic sound-mode eigenfunctions. We remark that the formulas derived there for small gradients in small systems show that under realistic experimental conditions—as, for instance, in the experiments of Beysens *et al.*[23]—the intensities of the Brillouin lines are very considerably reduced by finite-size effects. A similar calculation shows that the Rayleigh line is unaffected by finite-size effects. Although these calculations as well as those by Satten and Ronis give results consistent with those of Beysens *et al.* for the intensities of the Brillouin lines, they do not have a direct bearing on the latter, since, as mentioned before, the experimental results were obtained for large thermal gradients in the fluid.

We will comment on this further in the next paper, where we will also discuss a number of experiments that should not be affected by boundary effects at all.

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APPENDIX A: HYDRODYNAMIC MODE EIGENFUNCTIONS AND EIGENVALUES

In this appendix we show how Eqs. (3.2a) and (3.2b) can be solved by constructing the approximate eigenfunctions and eigenvalues of the matrix $\overline{H}_0(\vec{R},\vec{q})$ defined by Eq. (2.12). We will then illustrate the relation between the hydrodynamic mode eigenfunctions derived here and the combinations $M_{\alpha\rho,i}$ defined by Eq. (3.4). Finally, we will use the hydrodynamic mode eigenfunctions and eigenvalues to solve Eq. (3.14) and obtain Eq. (3.17).

I. Eigenfunctions and eigenvalues of $\overline{H}_0(\vec{R},\vec{q})$

To determine the eigenfunctions and eigenvalues of the matrix $\overline{H}_0(\vec{R},\vec{q})$ and to solve Eq. (3.2a) and (3.2b), it is convenient to write

$$M_{\vec{g}\rho}(\vec{R},\vec{q},\omega)=\hat{q}[\hat{q}\cdot M_{\vec{g}\rho}(\vec{R},\vec{q},\omega)] + \sum_{i=1,2} \hat{q}_{\perp}^{(i)}[\hat{q}_{\perp}^{(i)}\cdot M_{\vec{g}\rho}(\vec{R},\vec{q},\omega)] \tag{A1}$$

and choose as our independent variables $M_{\rho\rho}$, $\hat{q}\cdot M_{\vec{g}\rho}$, $\hat{q}_{\perp}^{(1)}\cdot M_{\vec{g}\rho}$, $\hat{q}_{\perp}^{(2)}\cdot M_{\vec{g}\rho}$, and $M_{\epsilon\rho}$. Here $\hat{q}$, $\hat{q}_{\perp}^{(1)}$, and $\hat{q}_{\perp}^{(2)}$ form a set of three mutually orthogonal unit vectors. Denoting this choice of independent variables by $\gamma,\delta=(\rho,\hat{q}\cdot\vec{g},\hat{q}_{\perp}^{(1)}\cdot\vec{g}, \hat{q}_{\perp}^{(2)}\cdot\vec{g},\epsilon)$, Eq. (3.2a) for example, can be written in terms of this set as

$$-i\omega M_{\gamma\rho,0}(\vec{R},\vec{q},\omega)-M_{\gamma\rho,0}(\vec{R},\vec{q}) =\overline{H}'_{\gamma\delta,0}(\vec{R},\vec{q})M_{\delta\rho,0}(\vec{R},\vec{q},\omega) \tag{A2a}$$

with

$$\overline{H}'_0(q)=\begin{bmatrix} 0 & -iq & 0 & 0 & 0 \\ -iqA_1 & -D_l q^2 & 0 & 0 & -iqA_2 \\ 0 & 0 & -\nu q^2 & 0 & 0 \\ 0 & 0 & 0 & -\nu q^2 & 0 \\ -\lambda q^2 A_4 & -iqA_3 & 0 & 0 & -\lambda q^2 A_5 \end{bmatrix}, \tag{A2b}$$

where $D_l=4\nu/3+\zeta/\rho$ and the rows and columns are labeled ρ, $\hat{q}\cdot\vec{g}$, $\hat{q}_{\perp}^{(1)}\cdot\vec{g}$, $\hat{q}_{\perp}^{(2)}\cdot\vec{g}$, and ϵ, respectively. A similar transformation can be applied to Eq. (3.2b) for the $M_{\alpha\rho,1}$. The equations for $\hat{q}\cdot M_{\vec{g}\rho}$, $\hat{q}_{\perp}^{(1)}\cdot M_{\vec{g}\rho}$, and $\hat{q}_{\perp}^{(2)}\cdot M_{\vec{g}\rho}$ can be obtained by multiplying the equation for $M_{\vec{g}\rho}$ by $\hat{q}\cdot$, $\hat{q}_{\perp}^{(1)}\cdot$, and $\hat{q}_{\perp}^{(2)}\cdot$, respectively. To simplify the notation, we will not indicate explicitly in this subsection the $\vec{R}$ dependence of the thermodynamic and hydrodynamic quantities, and we will suppress the subscript i on the $M_{\alpha\rho,i}$, which indicates the order in the gradient expansion used in Eq. (3.1a).

The matrix defined by Eq. (A2) is a 5×5 matrix with five eigenvalues $-\omega_i(q)$ $(i=1-5)$. Furthermore, since this matrix is not self-adjoint it has five right eigenfunctions $\vec{\theta}_i^{R'}(\vec{q})$, as well as five left eigenfunctions $\vec{\theta}_i^{L'}(\vec{q})$, where $\vec{\theta}_i^{R'}(\vec{q})$ is a five-component column vector and $\vec{\theta}_i^{L'}(\vec{q})$ is a five-component row vector, and the index i denotes the ith eigenfunction. With these definitions our eigenvalue problem reads

$$\underline{\overline{H}}'_0(\vec{q})\cdot\vec{\theta}_i^{R'}(\vec{q})=-\omega_i(q)\vec{\theta}_i^{R'}(\vec{q}) \,, \tag{A3a}$$

$$\vec{\theta}_i^{L'}(\vec{q})\cdot\underline{\overline{H}}'_0(\vec{q})=-\omega_i(q)\vec{\theta}_i^{L'}(\vec{q}) \,, \tag{A3b}$$

and for normalization we require

$$\vec{\theta}_i^{L'}(\vec{q})\cdot\vec{\theta}_j^{R'}(\vec{q})=\delta_{ij} \,. \tag{A3c}$$

Examining Eq. (A2b), we see that $\underline{H}'_0(\vec{q})$ can be decomposed into a 3×3 matrix where ρ, $\hat{q}\cdot\vec{g}$, and ϵ are coupled together and into two simple matrices for $\hat{q}_{\perp}^{(1)}\cdot\vec{g}$ and $\hat{q}_{\perp}^{(2)}\cdot\vec{g}$. From Eqs. (A2b) and (A3) it follows immediately that the eigenfunctions and eigenvalues for $\hat{q}_{\perp}^{(1)}\cdot\vec{g}$ and $\hat{q}_{\perp}^{(2)}\cdot\vec{g}$, the transverse (or shear) components of $\vec{g}$, are

$$\vec{\theta}_{\eta_1}^{R'}(\vec{q})=\begin{bmatrix}0\\0\\1\\0\\0\end{bmatrix}, \quad \vec{\theta}_{\eta_2}^{R'}(\vec{q})=\begin{bmatrix}0\\0\\0\\1\\0\end{bmatrix}, \tag{A4a}$$

$$\vec{\theta}_{\eta_1}^{L'}(\vec{q})=(0,0,1,0,0), \quad \vec{\theta}_{\eta_2}^{L'}(\vec{q})=(0,0,0,1,0) \,,$$

with eigenvalue $-\omega_{\eta_i}(q)$, where

$$\omega_{\eta_i}(q)=\nu q^2 . \tag{A4b}$$

These eigenfunctions and eigenvalues are denoted by the symbol η_i ($i=1,2$) to indicate they are shear eigenfunctions and eigenvalues.

The remaining three eigenfunctions and eigenvalues can be determined from the eigenvalue problem

$$\begin{aligned}&\underline{\bar{h}}'(\vec{q})\cdot\vec{\theta}_i^{R''}(\vec{q})=-\omega_i(q)\vec{\theta}_i^{R''}(\vec{q}) ,\\ &\vec{\theta}_i^{L''}(\vec{q})\cdot\underline{\bar{h}}'(\vec{q})=-\omega_i(q)\vec{\theta}_i^{L''}(\vec{q}) ,\\ &\vec{\theta}_i^{L''}(\vec{q})\cdot\vec{\theta}_j^{R''}(\vec{q})=\delta_{ij} ,\end{aligned} \tag{A5a}$$

where

$$\underline{\bar{h}}'(\vec{q})=\begin{bmatrix}0 & -iq & 0\\ -iqA_1 & -D_l q^2 & -iqA_2\\ -\lambda q^2 A_4 & -iqA_3 & -\lambda q^2 A_5\end{bmatrix} \tag{A5b}$$

and $\vec{\theta}^{L''}$ and $\vec{\theta}^{R''}$ are three-component row and column vectors, respectively. Their three components will be the first, second, and fifth components of $\vec{\theta}^{L'}$ and $\vec{\theta}^{R'}$, with the third and fourth components being zero for these eigenfunctions since they are orthogonal to and independent of the shear eigenfunctions. In solving the eigenvalue problem defined by Eq. (A5), we shall use that only the small-$\vec{q}$ behavior of the eigenfunctions and eigenvalues is needed for the light scattering. That is, we make the expansions

$$\begin{aligned}&\underline{\bar{h}}'(\vec{q})=iq\underline{\bar{h}}^{(1)}+q^2\underline{\bar{h}}^{(2)} ,\\ &\omega_i(q)=iq\omega_i^{(1)}+q^2\omega_i^{(2)}+\cdots ,\\ &\vec{\theta}_i^{(R,L)''}(q)=\vec{\theta}_{i0}^{(R,L)''}+iq\vec{\theta}_{i1}^{(R,L)''}+\cdots ,\end{aligned} \tag{A6}$$

and determine $\omega_i(q)$ and $\vec{\theta}_i^{(R,L)''}(q)$ using perturbation theory.

The technique used to compute these eigenfunctions and eigenvalues is straightforward and can be found in the literature.[24] Here we only quote the final results for $\vec{\theta}_i^{(R,L)''}$ to $O(q^0)$ and for $\omega_i(q)$ to $O(q^2)$: There is one heat mode (H) with eigenvalue $-\omega_H(q)$, where

$$\omega_H(q)=D_T q^2 \tag{A7a}$$

and eigenfunctions

$$\vec{\theta}_{H,0}^{R'}=\frac{A_1}{A_2}\begin{bmatrix}A_2/A_1\\0\\0\\0\\-1\end{bmatrix} , \quad \vec{\theta}_{H,0}^{L'}=\frac{A_2}{c^2}(A_3,0,0,0,-1) . \tag{A7b}$$

There are two sound modes ($\sigma=\pm1$) with eigenvalues $-\omega_\sigma(q)$, where

$$\begin{aligned}\omega_\sigma(q)&=i\sigma cq+\frac{q^2}{2}[D_l+(\gamma-1)D_T]\\ &\equiv i\sigma cq+\frac{\Gamma_s}{2}q^2 \quad (\sigma=\pm1)\end{aligned} \tag{A8a}$$

and corresponding eigenfunctions

$$\vec{\theta}_{\sigma,0}^{R'}=\begin{bmatrix}1\\ \sigma c\\0\\0\\A_3\end{bmatrix} \quad (\sigma=\pm1) \tag{A8b}$$

$$\vec{\theta}_{\sigma,0}^{L'}=\frac{1}{2c^2}(A_1,\sigma c,0,0,A_2) \quad (\sigma=\pm1) \cdot$$

In order to derive these results and others quoted in the text of this paper, we have used the thermodynamic identities

$$A_1=\left(\frac{\partial p}{\partial\rho}\right)_\epsilon=c^2\left(1-\frac{\alpha_T h}{c_p}\right) , \tag{A9a}$$

$$A_2=\left(\frac{\partial p}{\partial\epsilon}\right)_\rho=\frac{c^2\alpha_T}{c_p} , \tag{A9b}$$

$$A_4=\left(\frac{\partial T}{\partial\rho}\right)_\epsilon=\frac{(\gamma-1)}{\rho\alpha_T}-\frac{h}{\rho^2 c_v} , \tag{A9c}$$

$$A_5=\left(\frac{\partial T}{\partial\epsilon}\right)_\rho=\frac{1}{\rho c_v} , \tag{A9d}$$

$$A_1+A_2A_3=c^2 , \tag{A9e}$$

$$\gamma-1=\frac{T\alpha_T^2 c^2}{c_p} , \tag{A9f}$$

and

$$\left(\frac{\partial\epsilon}{\partial\rho}\right)_T=\frac{h}{\rho}-\frac{c_p}{\alpha_T}+\frac{c_v}{\alpha_T} , \tag{A9g}$$

where the coefficient of thermal expansion $\alpha_T=-(\partial\rho/\partial T)_p/\rho$.

The eigenfunctions and eigenvalues given by Eqs. (A4), (A7), and (A8) are those for the hydrodynamic equations [cf. Eq. (A2)] expressed in terms of the variables $M_{\rho\rho}$, $\hat{q}\cdot M_{\vec{g}\rho}$, $\hat{q}_\perp^{(1)}\cdot M_{\vec{g}\rho}$, $\hat{q}_\perp^{(2)}\cdot M_{\vec{g}\rho}$, and $M_{\epsilon\rho}$. The five eigenfunctions and eigenvalues for the choice of variables $M_{\rho\rho}$, $M_{g_x\rho}$, $M_{g_y\rho}$, $M_{g_z\rho}$, and $M_{\epsilon\rho}$, i.e., the eigenfunctions of the matrix $\underline{\bar{H}}_0(q)$, follow directly from Eqs. (A1), (A4), (A7), and (A8) with the following results: two shear modes with eigenvalues given by Eq. (A4b) and eigenfunctions given by

$$\vec{\theta}^{R}_{\eta_i}(\vec{q})=\begin{bmatrix}0\\ \hat{q}^{(i)}_{1x}\\ \hat{q}^{(i)}_{\perp y}\\ \hat{q}^{(i)}_{\perp z}\\ 0\end{bmatrix}, \tag{A10a}$$

$$\vec{\theta}^{L}_{\eta_i}(q)=(0,\hat{q}^{(i)}_{\perp x},\ \hat{q}^{(i)}_{\perp y},\ \hat{q}^{(i)}_{\perp z},\ 0)\quad (i=1,2)$$

and a heat mode with eigenvalue and eigenfunctions given by Eq. (A7a) and (A7b); two sound modes with eigenvalues given by Eq. (A8a) and eigenfunctions by

$$\vec{\theta}^{R}_{\sigma,0}(\vec{q})=1\begin{bmatrix}1\\ \sigma c\hat{q}_x\\ \sigma c\hat{q}_y\\ \sigma c\hat{q}_z\\ A_3\end{bmatrix}\quad(\sigma=\pm 1) \tag{A10b}$$

$$\vec{\theta}^{L}_{\sigma,0}(\vec{q})=\frac{1}{2c^2}(A_1,\sigma c\hat{q}_x,\sigma c\hat{q}_y,\sigma c\hat{q}_z,A_2)\quad(\sigma=\pm 1)\ .$$

II. Relations between hydrodynamic mode eigenfunctions and Eq. (3.4)

In order to understand the relation between the hydrodynamic mode eigenfunctions given above and the combinations of the $M_{\alpha\beta}$ denoted by $M_{H\rho}$, $M_{+\rho}$, $M_{-\rho}$, $M_{\eta_1\rho}$, and $M_{\eta_2\rho}$ given in Eq. (3.4), we consider as an example the sum $\overline{H}_{\alpha\gamma,0}(\vec{q})M_{\gamma\rho,0}(\vec{R},\vec{q},\omega)$, appearing on the right-hand side of Eq. (3.2a). We represent the matrix $\overline{H}_{\alpha\beta,0}(\vec{q})$ in terms of its exact eigenfunctions and eigenvalues by

$$\overline{H}_{\alpha\beta,0}(\vec{q})=-\sum_{a'}\omega_{a'}(q)\theta^{R,\alpha}_{a'}(\vec{q})\theta^{L,\beta}_{a'}(\vec{q})\ , \tag{A11a}$$

where $\theta^{R,\alpha}_{a'}$ is the α component of the right eigenfunction $\vec{\theta}^{R}_{a'}$ with $\alpha=(\rho,g_x,g_y,g_z,\epsilon)$ and $\theta^{L,\beta}_{a'}(\vec{q})$ is defined in a similar way. If we now multiply Eq. (A11a) by $\theta^{L,\alpha}_{a}(\vec{q})$ and sum over the index α, we obtain

$$\theta^{L,\alpha}_{a}(\vec{q})\overline{H}_{\alpha\beta,0}(\vec{q})=-\omega_a(q)\theta^{L,\beta}_{a}(\vec{q})\ , \tag{A11b}$$

where we have used the orthonormality relation

$$\theta^{L,\alpha}_{a}(\vec{q})\theta^{R,\alpha}_{a'}(\vec{q})=\delta_{aa'}\ . \tag{A11c}$$

Consequently, if we multiply Eq. (3.2a) by $\theta^{L,\alpha}_{a}(q)$ and sum over α, we immediately obtain

$$[-i\omega+\omega_a(q)]M_{a\rho,0}(\vec{R},\vec{q},\omega)=M_{a\rho,0}(\vec{R},\vec{q})\ , \tag{A11d}$$

where for a general $M_{\alpha\rho,i}$ we define $M_{a\rho,i}$ by

$$M_{a\rho,i}(\vec{R},\vec{q},\omega)=\theta^{L,\alpha}_{a}(q)M_{\alpha\rho,i}(\vec{R},\vec{q},\omega)\ . \tag{A11e}$$

Strictly speaking, we should use the exact hydrodynamic eigenfunctions $\vec{\theta}^{L,R}$ in Eqs. (A11a)–(A11e). Since the construction of these functions requires a computation of the higher-order terms in their q expansion, which is very cumbersome, we have replaced the $\vec{\theta}^{L}_{a}$ in Eq. (A11e) by the lowest-order term in their q expansion $\vec{\theta}^{L}_{a,0}$ as given by Eqs. (A7b), (A8b), and (A10). These lowest-order eigenfunctions also satisfy the orthonormality relation (A11c). The difference between the $M_{a\rho}$ defined by (A11e) with $\vec{\theta}^{L}_{a}$ replaced by $\vec{\theta}^{L}_{a,0}$, and the exact expression for the $M_{a\rho}$, is of order $qM_{a\rho}$ and accounts for the off-diagonal terms that appear in Eqs. (3.6). Although these off-diagonal terms ultimately do not contribute to the $M_{a\rho}$, as they do not contribute to the D_{ab}, they have to be retained for consistency at this stage of the calculation of the $M_{a\rho,0}$, since they appear in the Eq. (3.2b) for the $M_{a\rho,1}$. With the use of the explicit form of $\theta^{L,\beta}_{a,0}$ given above, one can show that the $M_{a\rho,0}$ defined here correspond to those given by Eq. (3.4). We note that the coefficients A_2/c^2, $1/2c^2$, and $1/c$ multiplying the linear combinations appearing in Eq. (3.4) have been chosen so that $M_{\rho\rho}=M_{+\rho}+M_{-\rho}+M_{H\rho}$.

III. Derivation of Eq. (3.17)

Equation (3.17) for $D_{ab}(\vec{R},\vec{q})$ $(a,b)=(H,\sigma=\pm 1,\eta_i(i=1,2))$ can be derived from Eq. (3.14) by using the eigenfunctions and eigenvalues of $\underline{H}_0$ given in part I of this appendix. Inserting [cf. Eq. (3.14)] both

$$\overline{H}_{\alpha\gamma,0}(\vec{q})D_{\gamma\beta,1}(\vec{R},\vec{q})=-\omega_{a'}(q)\theta^{R,\alpha}_{a',0}(\vec{q})[\theta^{L,\delta}_{a',0}(\vec{q})D_{\delta\beta}(\vec{R},\vec{q})]$$

and

$$\overline{H}_{\beta\gamma,0}(-\vec{q})D_{\alpha\gamma,1}(\vec{R},\vec{q})=-\omega_{b'}(q)\theta^{R,\beta}_{b',0}(-\vec{q})[\theta^{L,\delta}_{b',0}(-\vec{q})D_{\alpha\delta}(\vec{R},\vec{q})]$$

into Eq. (3.14), multiplying the resulting expression by

$$\sum_{\alpha,\beta=\rho,\vec{g},\epsilon} \theta_{a,0}^{L,\alpha}(\vec{q})\theta_{b,0}^{L,\beta}(-\vec{q})$$

using Eq. (A11c), and knowing that only zeroth-order hydrodynamic eigenfunctions are needed to determine $D_{\alpha\beta,1}$ to $O(X^T/q^2)$, yields Eq. (3.17) with

$$\delta a_{\sigma\hat{q}} = \frac{1}{2c^2}(A_1\delta\rho_T + A_2\delta\epsilon_T + \sigma c\hat{q}_i\delta g_{iT}) , \tag{A12a}$$

$$\delta a_{H\hat{q}} = \frac{1}{c^2}A_2(A_3\delta\rho_T - \delta\epsilon_T) , \tag{A12b}$$

$$\delta a_{\eta_i\hat{q}} = \frac{1}{c}\hat{q}_j^{(i)}\delta g_{jT} . \tag{A12c}$$

APPENDIX B: ORDERING OF TERMS IN THE HYDRODYNAMIC EQUATIONS

In this appendix we first outline the method used to order and select the contributions to the quantities $M_{\alpha\beta,1}(\vec{R},\vec{q},\omega)$ that were needed in the calculations presented in Secs. II and III. We then use this same method to justify the neglect of a number of terms in the derivation of the hydrodynamiclike equations for the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ and the $D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ in paper I.

I. Equations for $M_{\alpha\rho}(\vec{R},\vec{q},\omega)$

As described in Sec. II, we wish to consistently retain terms in $M_{\alpha\rho,1}(\vec{R},\vec{q},\omega)$ which are at least of order $cX^T/\Gamma_s q^2$ compared to $M_{\alpha\beta,0}$. To do this, we consider the hydrodynamic equations (2.9) for $M_{\alpha\rho}$ and solve them by first expanding the $\overline{H}_{\alpha\beta}$ about their values at the center-of-mass point $\vec{R}=(\vec{R}_1+\vec{R}_2)/2$ in powers of X^T. For the case of small gradients, we need to retain only the first-order term in X^T and consider the q dependence of the terms that contribute to the zeroth- and first-order terms in X^T. In the discussion below, we will also see that the $M_{H\rho,0}$ is sharply peaked about $\omega=0$, while the $M_{\sigma\rho,0}$ are sharply peaked about $\omega=\sigma kc$.

In Sec. II, we expanded the spatial dependence of $M_{\alpha\rho}(\vec{R}_1,\vec{R}_2,\omega)$ about its value at point $\vec{R}$ and then considered the Fourier transform of $M_{\alpha\rho}(\vec{R},\vec{R}_{12},\omega)$ with respect to $\vec{R}_{12}$, where $\vec{R}_{12}=\vec{R}_1-\vec{R}_2$. Denoting the Fourier-transform variable by $\vec{q}$, we obtained equations for the linear combinations of the $M_{\alpha\rho}$, $M_{H\rho,1}$, and $M_{\sigma\rho,1}$ that have the formal structure given by Eqs. (3.10a) and (3.10b), respectively. We also neglected the terms proportional to $M_{\eta_i\rho}$. Formally solving Eqs. (3.10a) and (3.10b) by iteration, we obtain

$$\begin{aligned}
M_{H\rho,1}(R_x,\vec{q},\omega) = &-(-i\omega+D_Tq^2)^{-1}\left[X^TR_{HH}^{(1)}+X^TR_{HH}^{(2)}q\frac{\partial}{\partial q_x}+R_{HH}^{(3)}\frac{\partial}{\partial R_x}\right]M_{H\rho,0}\\
&+\sum_{\sigma=\pm1}(-i\omega+P_Tq^2)^{-1}\bigg[\bigg[X^TR_{H\sigma}^{(1)}+X^TR_{H\sigma}^{(2)}q\frac{\partial}{\partial q_x}\\
&\qquad+R_{H\sigma}^{(3)}\frac{\partial}{\partial R_x}\bigg]M_{\sigma\rho,0}+q^2D_T(\gamma-1)M_{\sigma\rho,1}\bigg]\\
&+(-i\omega+D_Tq^2)^{-1}(A_{H\rho,1}+D_{H\rho,1})+O((X^T)^2)
\end{aligned} \tag{B1a}$$

and

$$\begin{aligned}
M_{\sigma\rho,1}(R_x,\vec{q},\omega) = &-(-i\omega+\omega_\sigma)^{-1}\left[X^TR_{\sigma,\sigma}^{(1)}+X^TR_{\sigma,\sigma}^{(2)}q\frac{\partial}{\partial q_x}+R_{\sigma,\sigma}^{(3)}\frac{\partial}{\partial R_x}\right]M_{\sigma\rho,0}\\
&+(-i\omega+\omega_\sigma)^{-1}\bigg[\left[X^TR_{\sigma,-\sigma}^{(1)}+X^TR_{\sigma,-\sigma}^{(2)}q\frac{\partial}{\partial q_x}+R_{\sigma,-\sigma}^{(2)}\frac{\partial}{\partial R_x}\right]M_{-\sigma\rho,0}\\
&\qquad+\frac{q^2}{2}(D_l-D_T(\gamma-1))M_{-\sigma\rho,1}\bigg]\\
&+(-i\omega+\omega_\sigma)^{-1}\left[\left[X^TR_{\sigma H}^{(1)}+X^TR_{\sigma H}^{(2)}q\frac{\partial}{\partial q_x}+R_{\sigma H}^{(3)}\frac{\partial}{\partial R_x}\right]M_{H\rho,0}+\frac{D_Tq^2}{2}M_{H\rho,1}\right]\\
&+(-i\omega+\omega_\sigma)^{-1}(A_{\sigma\rho,1}+D_{\sigma\rho,1})+O((X^T)^2) .
\end{aligned} \tag{B1b}$$

Here $M_{H\rho,0}$ and $M_{\sigma\rho,0}$ are given by Eqs. (3.9).

If we examine the expressions given by Eqs. (B1a) and (B1b), we see that they contain denominators which are combinations of powers of the quantities $(-i\omega+D_Tq^2)$ and $(-i\omega+\omega_\sigma)^{-1}$. Each of these terms becomes large in a different range of frequencies, that is, $(-i\omega+D_Tq^2)^{-1}$ is of order q^{-2} for $\omega\cong q^2$, while in this region $(-i\omega+\omega_\sigma)^{-1}$ is of order q^{-1}. Similarly, $(-i\omega+\omega_\sigma)^{-1}$ is of order q^{-2} for $\omega=\sigma qc+O(q^2)$, while in this region $(-i\omega+D_Tq^2)^{-1}$ is of order q^{-1}. As long as $cq \gg D_Tq^2$ or $cq \gg \Gamma_s q^2$ these frequency ranges are well separated. Therefore, the quantities $M_{H\rho,1}$ and $M_{\sigma\rho,1}$ have qualitatively the same features as their equilibrium values, in that they are sharply peaked either at $\omega=O(q^2)$ or at $\omega=\sigma qc+O(q^2)$, but there are important corrections of order X^Tq^{-2} to the equilibrium values in these frequency ranges.

To see this, we first consider $M_{H\rho,1}$ and $M_{\sigma\rho,1}$ in the range $\omega=\sigma qc+O(q^2)$. We need the following estimates, all valid for ω in this range:

$$(-i\omega+D_Tq^2)^{-1}=O(q^{-1}) ,$$
$$\frac{\partial}{\partial R_x}(-i\omega+D_Tq^2)^{-1}=O(X^T) , \tag{B2a}$$
$$q\frac{\partial}{\partial q_x}(-i\omega+D_Tq^2)^{-1}=O(1) .$$

Furthermore,

$$(-i\omega+\omega_\sigma)^{-1}=O(q^{-2}) ,$$
$$\frac{\partial}{\partial R_x}(-i\omega+\omega_\sigma)^{-1}= O(X^Tq^{-3}) + O(X^Tq^{-2}) , \tag{B2b}$$
$$q\frac{\partial}{\partial q_x}(-i\omega+\omega_\sigma)^{-1}=O(q^{-3})+O(q^{-2}) ,$$

while

$$(-i\omega+\omega_{-\sigma})^{-1}=O(q^{-1}) ,$$
$$\frac{\partial}{\partial R_x}(-i\omega+\omega_{-\sigma})^{-1}=O(X^Tq^{-1}) , \tag{B2c}$$
$$q\frac{\partial}{\partial q_x}(-i\omega+\omega_{-\sigma})^{-1}=O(q^{-1}) .$$

We now use that the $R_{\alpha\beta}^{(i)}$ appearing in Eqs. (B1a) and (B1b) can be expanded in powers of q according to Eq. (3.11). By combining Eqs. (3.11), (B1), and (B2), we can see that to obtain corrections of order (cX^T/Γ_sq^2) or $c^2X^T/\Gamma_s^2q^3$, compared to $M_{\sigma\rho,0}$ in the range $\omega=\sigma qc+O(q^2)$, we need to retain $R_{H\sigma}^{(2)}$ and $R_{H\sigma}^{(3)}$ to $O(q^0)$ and $R_{\sigma\sigma}^{(1)}$ to $O(q^0)$. All other $R_{ab}^{(i)}$ can be neglected in this range. When these various terms are retained and explicitly computed, Eqs. (3.12a) and (3.12b) are obtained. It is worth mentioning that the corrections of order $c^2X^T/\Gamma_s^2q^3$ eventually cancel when the explicit calculations are done. Therefore, the leading corrections are of order cX^T/Γ_sq^2.

We can apply similar arguments to determine $M_{H\rho,1}$ and $M_{\sigma\rho,1}$ near $\omega=0$. For this we need the following estimates, all valid for $\omega=O(q^2)$:

$$(-i\omega+D_Tq^2)^{-1}=O(q^{-2}) ,$$
$$\frac{\partial}{\partial R_x}(-i\omega+D_Tq^2)=O(X^Tq^{-2}) , \tag{B3a}$$
$$q\frac{\partial}{\partial q_x}(-i\omega+D_Tq^2)^{-1}=O(q^{-2}) ,$$

while

$$(-i\omega+\omega_\sigma)^{-1}=O(q^{-1}) ,$$
$$\frac{\partial}{\partial R_x}(-i\omega+\omega_\sigma)^{-1}=O(X^Tq^{-1}) , \tag{B3b}$$
$$q\frac{\partial}{\partial q_x}(-i\omega+\omega_\sigma)^{-1}=O(q^{-1}) .$$

Combining these estimates with Eqs. (3.11) and (B1), we find that to determine corrections to $M_{H\rho,0}$ and $M_{\sigma\rho,0}$ of order (X^Tq^{-2}) in the range $\omega=O(q^2)$, we need to retain $R_{HH}^{(1)}$, $R_{HH}^{(2)}$, and $R_{HH}^{(3)}$ all to order $O(q^0)$, while all other $R_{ab}^{(i)}$ can be neglected. However, as $R_{HH}^{(i)}=0$ for $i=1,2,3$, and as $D_{H\rho,1}=0$ [Eq. (3.21a)], one can easily check that for $\omega=O(q^2)$,

$$M_{\sigma\rho}(\vec{R},\vec{q},\omega)=M_{\sigma\rho,0}(\vec{R},\vec{q},\omega)+O(X^Tq^{-3}) \tag{B4a}$$

and

$$M_{H\rho}(\vec{R},\vec{q},\omega)= M_{H\rho,0}(\vec{R},\vec{q},\omega)+O(X^Tq^{-3}) +O((X^T)^2) \tag{B4b}$$

so that there is no change in the Rayleigh line of order X^T/q^2 relative to the equilibrium result.

II. Discussion of neglected terms

We now discuss the terms that were neglected in paper I in the derivation of the hydrodynamiclike equations for $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ and $D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$. The introduction of the Fourier transform-variable $\vec{q}$ and the temperature gradient $X^T=(1/T)(\partial T/\partial R_x)$ in this paper greatly simplifies the discussion of the terms neglected in I. That is, we will show below that the neglected terms are all smaller than the terms retained above for the calculation of the $M_{\alpha p}$, the structure factor $S(\vec{k},\omega)$, and the integrated intensities.

We begin by considering the kinetic-theory derivation of the hydrodynamic equations for the $M_{\alpha\beta}(\vec{R}_1,\vec{R}_2,t)$ in Sec. II of paper I. To derive the set of hydrodynamic equations (I.2.42a) – (I.2.42c), we first derived a kinetic equation for the quantity $P\hat{C}(1,2,z)$, which was given by Eq. (I.2.40). In the derivation of Eq. (I.2.40) we neglected two types of terms: (a) terms of order $(cL_{\nabla}^{-1})(lL_{\nabla}^{-1})^2$ and higher, compared to terms of the order cL_{∇}^{-1} and $(cL_{\nabla}^{-1})(lL_{\nabla}^{-1})$ that were retained, and (b) an initial condition term of relative order (lL_{∇}^{-1}) compared to the initial condition term $PC(1,2,t=0)$ that is retained. When we consider those terms in the Fourier representation and see that each power of L_{∇}^{-1} is replaced by either a factor q or X^T, it becomes clear that the terms neglected in (a) above are of order cl^2q^3, $cl^2q^2X^T$, $cl^2q(X^T)^2$, or $cl^2(X^T)^3$ compared to the terms of order cq, clq^2, and cX^T that we retain. Now the terms in (a) can be neglected provided that the conditions

$$lq=\Gamma_s q^2/cq \ll 1$$

and

$$l\,|X^T|=(lq)^2(c\,|X^T|/\Gamma_s q^2) \ll 1$$

are satisfied. The initial condition terms (b) are of order lq and lX^T compared to the initial condition terms of order unity and $cX^T/\Gamma_s q^2$, respectively, that are retained in the $A_{\alpha\beta}$ and $D_{\alpha\beta}$. Here, too, the neglect of the terms in (b) is consistent provided $lq \ll 1$.

Similar considerations apply to the terms that are neglected in Eq. (I.3.13) when the hydrodynamic equations for the $D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ are derived. Furthermore, the argument given above for the kinetic-theory calculations in paper I, Secs. II and III may be immediately extended to the more general fluid theory described in paper I, Secs. IV and V. The arguments are identical to those given above, and one needs only note that for a liquid the microscopic length l is the range of the intermolecular potential, while for a gas l is the mean-free path.

APPENDIX C: INTEGRATED INTENSITIES OF BRILLOUIN LINES IN THE PRESENCE OF WALLS

In this appendix we briefly sketch how the integrated intensities of the Brillouin lines may be calculated to linear order in the temperature gradient when effects due to the finite size of the container are taken into account. To simplify the calculation, we take the fluid to be finite in the x direction with parallel plates at $x=0$ and d but infinite in the y and z direction. Further, we assume that slip boundary conditions[25,26,27] are satisfied at $x=0$ and d. As in the text, the temperature gradient is in the x direction.

To calculate the integrated intensities of the Brillouin lines to linear order in X^T, we need to determine the equal-time correlation functions given by Eq. (2.4) to linear order. The local equilibrium contribution $A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ is not sensitive to the boundaries because it has a correlation length on the order of a molecular diameter. The long-range contribution $D_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$, on the other hand, is sensitive to the boundaries. To linear order in X^T, $D_{\alpha\beta}$ satisfies the equation

$$H_{\alpha\gamma,\mathrm{eq}}(\vec{R}_1)D_{\gamma\beta,1}(\vec{R}_1,\vec{R}_2)+H_{\beta\gamma,\mathrm{eq}}(\vec{R}_2)D_{\alpha\gamma,1}(\vec{R}_1,\vec{R}_2)=\delta(\vec{R}_{12})(\delta a_{\alpha T}\delta a_{\beta T}S_{xT})_{\mathrm{eq}}\beta X^T \tag{C1}$$

with $(\;)_{\mathrm{eq}}$ an equilibrium ensemble average and $\underline{H}_{\mathrm{eq}}(\vec{R}_i)$ the equilibrium hydrodynamic matrix.[28] $\underline{H}_{\mathrm{eq}}(\vec{R}_1)$ equals the $\underline{H}(\vec{R}_1)$ in paper I [cf. Eqs. (I.4.21) and (I.4.25)], with constant (i.e., space-independent) thermodynamic and hydrodynamic quantities. To solve Eq. (C1), we use the method of Appendix A, and Sec. III, but we replace the infinite-space hydrodynamic modes of Appendix A by a set of finite-space hydrodynamic modes for slip boundary conditions and for the geometry given above. Since only the integrated intensities of the Brillouin lines are needed, we quote only the results for the sound modes which have eigenvalues given by $\omega_\sigma(q)=\sigma icq+\Gamma_s q^2/2$ $(\sigma=\pm 1)$ and right and left eigenfunctions given by[27]

$$\vec{\theta}^{R}_{\sigma,0}(\vec{q},\vec{R}_1)=\frac{e^{i\vec{q}_{\parallel}\cdot\vec{R}_{1_{\parallel}}}}{2\pi}\sqrt{2/d}\begin{pmatrix}\cos q_x x_1\\ \sigma c\hat{q}_x i\sin q_x x_1\\ \sigma c\hat{q}_y\cos q_x x_1\\ \sigma c\hat{q}_z\cos q_x x_1\\ A_3\cos q_x x_1\end{pmatrix}, \tag{C2a}$$

$$\vec{\theta}^{L}_{\sigma,0}(\vec{q},\vec{R}_1)=\frac{e^{-i\vec{q}_{\|}\cdot\vec{R}_{1_{\|}}}}{2\pi}\sqrt{2/d}\,\frac{1}{2c^2}$$

$$\times(A_1\cos q_x x_1,-\sigma c\hat{q}_x i\sin q_x x_1,\sigma c\hat{q}_y\cos q_x x_1,\sigma c\hat{q}_z\cos q_x x_1,A_2\cos q_x x_1)\tag{C2b}$$

with the rows and columns labeled as in Appendix A. In Eq. (C2), $\vec{q}_{\|}=(q_y,q_z)$ is a continuous eigenfunction index, $q_x=n\pi/d$ ($n=0,1,2,\ldots$) is a discrete eigenfunction index, $\vec{q}=(q_x,q_y,q_z)$, $\hat{q}_i=q_i/q$, $q=(q_x^2+q_{\|}^2)^{1/2}$, and $\vec{R}_{1_{\|}}=(y_1,z_1)$. It should be remarked that Eqs. (C2) are the analog of Eq. (A10b) for fluid cells of finite extent. The set of hydrodynamic heat (H), sound (σ), and shear (η_i) modes satisfy the completeness and orthogonality relations

$$\underline{1}=\sum_{q_x}\sum_{a=H,\sigma,\eta_i}\int d\vec{q}_{\|}\,|\,\vec{\theta}^{R}_{a}(\vec{q},\vec{R}_1)\rangle\langle\vec{\theta}^{L}_{a}(\vec{q},\vec{R}_1)\,|\ ,\tag{C3a}$$

$$\sum_{\alpha}\langle\theta^{L,\alpha}_{a}(\vec{q},\vec{R}_1)\,|\,\theta^{R,\alpha}_{b}(\vec{q}\,',\vec{R}_1)\rangle=\delta_{ab}\delta_{q_xq_x'}\delta(\vec{q}_{\|}-\vec{q}\,'_{\|})\ ,\tag{C3b}$$

where in obvious Dirac notation $\langle f(\vec{R}_1)\,|\,g(\vec{R}_1)\rangle=\int_0^d dx_1\int d\vec{R}_{1_{\|}}f(\vec{R}_1)g(\vec{R}_1)$ for any two functions $f(\vec{R}_1)$ and $g(\vec{R}_1)$.

The completeness and orthogonality relations given by Eqs. (C3) can be used to express $D_{\alpha\beta,1}(\vec{R}_1,\vec{R}_2)$ in terms of hydrodynamic modes with the result

$$D_{\alpha\beta,1}(\vec{R}_1,\vec{R}_2)=-\sum_{q_x,q_x'}\sum_{a,b=\sigma,\eta_i,H}\int d\vec{q}_{\|}\int d\vec{q}\,'_{\|}\frac{||\theta^{R,\alpha}_{a}(\vec{q},\vec{R}_1)\theta^{R,\beta}_{b}(\vec{q}\,',\vec{R}_2)\rangle\rangle}{[\omega_a(q)+\omega_b(q')]}$$

$$\times\sum_{\gamma,\delta}\langle\langle\theta^{L,\gamma}_{a}(\vec{q},\vec{R}_1)\theta^{L,\delta}_{b}(\vec{q}\,',\vec{R}_2)||\delta(\vec{R}_{12})\rangle\rangle$$

$$\times\beta X^{T}(\delta a_{\gamma T}\delta a_{\delta T}S_{xT})_{\rm eq}\ .\tag{C4}$$

The integrated intensity of the σ-Brillouin line is then given by an expression similar to Eq. (4.5b):

$$I^{\sigma}(\vec{R}_0,\vec{k})$$

$$=\mathrm{Re}\left[\int_V d\vec{R}\,P^2(\vec{R})\right]^{-1}\int_V d\vec{R}_1\int_V d\vec{R}_2P(\vec{R}_1)P(\vec{R}_2)e^{-i\vec{k}\cdot\vec{R}_{12}}\ ,$$

$$\times\left[\rho^2(\vec{R}_1)\frac{k_BT(\vec{R}_1)}{2\gamma(\vec{R}_1)}\chi_T(\vec{R}_1)\delta(\vec{R}_{12})\right.$$

$$\left.+\sum_{q_x}\int d\vec{q}_{\|}\,|\,\theta^{R,\rho}_{\sigma}(\vec{q},\vec{R}_1)\rangle\sum_{\beta}\langle\theta^{L,\beta}_{\sigma}(\vec{q},\vec{R}_1)\,|\,D_{\beta\rho,1}(\vec{R}_1,\vec{R}_2)\rangle\right]$$

$$=I^{\sigma}_{\rm LE}(\vec{R}_0,\vec{k})+I^{\sigma}_{\nabla}(\vec{R}_0,\vec{k})\ ,\tag{C5}$$

with $I^{\sigma}_{\rm LE}(\vec{k})$ the local equilibrium contribution due to $A_{\alpha\beta}(\vec{R}_1,\vec{R}_2)$ and $I^{\sigma}_{\nabla}(\vec{R}_0,\vec{k})$ the contribution due to $D_{\beta\rho,1}(\vec{R}_1,\vec{R}_2)$ to $I^{\sigma}(\vec{R}_0,\vec{k})$. Inserting Eq. (C4) into (C5) and keeping only the dominant (for small q, q') contributions yields

$$I_{\nabla}^{\sigma}(\vec{R}_0,\vec{k})=-\mathrm{Re}\left[\int_V d\vec{R}\,P^2(\vec{R})\right]^{-1}\int_V d\vec{R}_1\int_V d\vec{R}_2 P(\vec{R}_1)P(\vec{R}_2)e^{-i\vec{k}\cdot\vec{R}_{12}}$$
$$\times\sum_{q_x q_x'}\int d\vec{q}_{||}\int d\vec{q}\,'_{||}\frac{||\theta_{\sigma}^{R,\rho}(\vec{q},\vec{R}_1)\theta_{-\sigma}^{R,\rho}(\vec{q}\,',\vec{R}_2)\rangle\rangle}{[\omega_{\sigma}(q)+\omega_{-\sigma}(q')]}$$
$$\times\sum_{\alpha,\beta}\langle\langle\theta_{\sigma}^{L,\alpha}(\vec{q},\vec{R}_1)\theta_{-\sigma}^{L,\beta}(\vec{q}\,',\vec{R}_2)||\delta(\vec{R}_{12})\rangle\rangle$$
$$\times\beta X^T(\delta a_{\alpha T}\delta a_{\beta T}S_{xT})_{\mathrm{eq}}\ . \tag{C6}$$

Inserting the explicit expressions for the hydrodynamic mode eigenfunctions in Eq. (C6), carrying out the summations and integrations and neglecting terms of order $(kL)^{-1}$, $(kd)^{-1}$, L/d, and $e^{-k_x^2L^2}$, all of which are taken to be much less than unity,[29] one obtains

$$I_{\nabla}^{\sigma}(x_0=d/2,\vec{k})\cong-\rho^2\frac{k_BT}{2\gamma}\chi_T\frac{\sigma c\hat{k}_xX^T}{\Gamma_sk^2}$$
$$\times\left[1-\tfrac{3}{2}\exp(-d\Gamma_sk^2/2\,|\hat{k}_x|\,c)+\tfrac{1}{2}\exp(-3d\Gamma_sk^2/2\,|\hat{k}_x|\,c)\right.$$
$$\left.-\frac{\sigma}{2}\frac{k_x}{|k_x|}\exp(-d\Gamma_sk^2/2\,|\hat{k}_x|\,c)+\frac{\sigma}{2}\frac{k_x}{|k_x|}\exp(-3d\Gamma_sk^2/2\,|\hat{k}_x|\,c)\right]\ , \tag{C7}$$

where we have taken the x coordinate of the point of observation $\vec{R}_0=(x_0,y_0,z_0)$ to be $x_0=d/2$.

It should be said that in going from Eq. (C6) to (C7) the only place where finite-size effects are important under realistic experimental conditions is in the denominator of (C6). This follows from the fact that in an infinite fluid the isotropy in space leads to a factor $\delta(\vec{q}+\vec{q}\,')$, so that the denominator in (C6) reduces to $(\Gamma_sq^2)^{-1}$, since the $\pm iqc$ contributions to the two sound-mode eigenvalues exactly cancel. This leaves then a denominator that is much smaller than when the propagating parts would not have canceled. In finite space, however, $q_x\cong q_x'+O(1/d)$. This uncertainty in wave numbers leads to a denominator that schematically has the form $(i\sigma c/d+\Gamma_sq^2)^{-1}$ which implies that we can expect finite-size corrections of $O(c/d\Gamma_sq^2)$. This parameter can be on the order of unity in realistic experiments, i.e., finite-size corrections to the propagating part of the sound eigenvalues can be of the same order of magnitude as the damping part.

If $L\,|X^T|\ll1$, the local equilibrium contribution $I_{\mathrm{LE}}^{\sigma}(\vec{R}_0,\vec{k})$ [cf. Eq. (C5)] is

$$I_{\mathrm{LE}}^{\sigma}(\vec{R}_0,\vec{k})=\rho^2\frac{k_BT}{2\gamma}\chi_T \tag{C8}$$

with the thermodynamic parameters in Eq. (C8) evaluated at the point of observation $\vec{R}_0$. From Eqs. (C5), (C7), and (C8) the integrated intensity of the σ-Brillouin line, $I^{\sigma}(\vec{R}_0,\vec{k})$, follows.

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*Present address: Institute for Physical Science and Technology, The University of Maryland, College Park, Maryland 20742.

[1] T. R. Kirkpatrick, E. G. D. Cohen, and J. R. Dorfman, Phys. Rev. A 26, 950 (1982), preceding paper.

[2] R. Edwards, J. Angus, M. French, and J. Dunning, J. Appl. Phys. 42, 837 (1971).

[3] We will take $P(\vec{R})$ to be a Gaussian of the form $P(\vec{R})=A\exp[-(\vec{R}-\vec{R}_0)^2/L^2]$ since this is a convenient approximation that adequately describes the scattering volume. Here L is the characteristic dimension of the scattering volume and $\vec{R}_0$ locates the center of the scattering volume.

[4] L. Landau and E. M. Lifshitz, *Electrodynamics of Con-*

tinuous Media (Pergamon, New York, 1960), p. 391; see also, B. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), p. 243.

[5] 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).

[6] 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); E. G. D. Cohen, Kinam 3A, 39 (1981).

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

[8] D. Ronis and S. Putterman, Phys. Rev. A 22, 733 (1980); see also H. Grabert, J. Stat. Phys. 26, 113 (1981).

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

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

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

[12] These authors also made some simplifying assumptions, e.g., they set the coefficient of thermal expansion $\alpha_T=(-1/\rho)(\partial\rho/\partial T)_p$ equal to zero, and neglect the spatial variation of the thermodynamic quantities and the transport coefficients. While not entirely consistent, these assumptions result in a considerable simplication of the calculations and yield the correct answer.

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

[14] G. Satten and D. Ronis (unpublished).

[15] Since we consider a temperature gradient that is in the x direction, these quantities will only depend on the x component of the center-of-mass position R_x.

[16] In terms of quantities that appear in the hydrodynamic equations, $l\approx\Gamma_s/c$.

[17] One can easily check, using Eq. (A2b), that the shear modes given by Eq. (3.4c) are exact eigenfunctions of $\bar{H}_{\alpha\beta,0}$.

[18] See, for example, M. H. Ernst, E. Hauge, and J. M. J. van Leeuwen, J. Stat. Phys. 15, 7 (1976).

[19] One can see from Eqs. (3.6a) and (3.6b) that $M_{H\rho,0}$ and $M_{\sigma\rho,0}$ are not exact eigenfunctions of $H_{\alpha\beta,0}$, but only eigenfunctions to lowest order in q. This accounts for the extra off-diagonal terms in (3.6a) and (3.6b) and (3.9a) and (3.9b).

[20] It should be remarked that one cannot identify directly the shapes of the central and the Brillouin lines with $M_{H\rho}(\omega)$ and $M_{\sigma\rho}(\omega)$, respectively, since, for example, $M_{-\sigma\rho,1}(\omega)$ and $M_{H\rho,1}(\omega)$ contribute to the squared denominator in Eq. (4.1). However, the contributions of $M_{-\sigma\rho,1}$ and $M_{H\rho,1}$ to the integrated intensity of the σ-Brillouin line vanish. This can be seen by noting that in time language the second term in the large parentheses of Eq. (4.1) is proportional to $te^{-\omega_\sigma(q)t}$ and vanishes, for $t=t_1-t_2=0$, i.e., it gives no contribution to the integrated intensity. Because of this, the identification of the right-hand side of Eqs. (4.5a) and (4.5b) with $I^H(\vec{R}_0,\vec{k})$ and $I^\sigma(\vec{R}_0,\vec{k})$ can be justified.

[21] This also implies an extra contribution of the sound modes to the thermal conductivity of the fluid. See paper III, Appendix C.

[22] For example, for H_2O at 313 K, $c\,|X^T|\,/\Gamma_s k^2\approx 1$, if $k\approx 2000\ \text{cm}^{-1}$ and $|\vec{\nabla}T|\approx 75\ \text{K}\,\text{cm}^{-1}$.

[23] D. Beysens, Y. Garrabos, and G. Zalczer, Phys. Rev. Lett. 45, 403 (1980).

[24] See, for example, P. Résibois and M. DeLeener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977), p. 124.

[25] The hydrodynamic sound modes for slip (Ref. 26) and the more realistic stick (Ref. 26) boundary conditions are identical outside a thin hydrodynamic boundary layer (Ref. 27). This boundary layer is on the order of 10^{-5} cm. Here we use the slip hydrodynamic modes since the algebra is then greatly simplified. However, we expect qualitatively the same results when stick boundary conditions are used.

[26] Slip and stick boundary conditions are discussed by 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.

[27] J. Niewoudt, Ph.D. thesis, University of Maryland, 1982 (unpublished). In this reference, also Eq. (C1) for $D_{\alpha\beta}$ is justified, for dilute gases in the presence of walls, on the basis of kinetic theory. See also, T. R. Kirkpatrick and E. G. D. Cohen (unpublished).

[28] See, for example, L. Landau and E. M. Lifshitz, *Fluid Dynamics* (Addison-Wesley, Reading, Mass., 1959), Chaps. II and V.

[29] Note that L is the characteristic size of the scattering volume, while d is the separation of the walls of the container in the x direction.