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Density Fluctuations in Single-Component Fluids

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The memory-function formalism of Zwanzig and Mori is used to study the density-density correlation function $\langle \tilde{\rho}(S)\,\rho^*\rangle$ in a single-component fluid. Using the hydrodynamic variables suitable for longitudinal disturbances, $\langle \tilde{\rho}\,(S)\,\rho^*\rangle$ is expressed in terms of the appropriate memory functions. This formally exact relation is then shown to be equivalent to the result obtained by Kadanoff and Martin in terms of a dispersion function. By considering the approximations suitable for the analysis of Brillouin scattering experiments, it is also shown that the formal expression for $\langle \tilde{\rho}\,(S)\,\rho^*\rangle$ can be reduced to results previously derived by Mountain and by Bhatia and Tong on the basis of a macroscopic analysis using the linearized hydrodynamic equations coupled either with relaxing shear and bulk viscosities or with thermodynamic relaxation theory. Present analysis thereby provides a microscopic basis for these hydrodynamic theories, as well as revealing to some extent the nature of approximations involved. Our microscopic analysis also suggests a simple model to take into account the effects of coupling between heat flux and the viscosity stress tensor.

I. INTRODUCTION

It is known that a variety of radiation scattering experiments can be used to probe the density fluctuations and their correlations in a fluid. Among them, the spectra of inelastic-slow-neutron and light-scattering experiments have been analyzed quite extensively; for both these, one can relate[1-3] the scattered intensity to the dynamical structure factor $S(\vec{k}, \omega)$ which is the space-time Fourier transform of the density-density correlation function of Van Hove. Because the neutron directly couples to the nuclear motion in the fluid, such a relation is quite direct,[1] whereas for a light-scattering probe, one usually assumes that the fluctuations in the dielectric constant arise solely from the fluctuations in the local fluid density. Theoretical understanding of the density correlations in a fluid, and thereby the calculation of $S(\vec{k}, \omega)$, is one of the central problems in nonequilibrium statistical mechanics.

For dilute gases (both monatomic and polyatomic), $S(\vec{k}, \omega)$ has been calculated[4-6] by solving the linearized Boltzmann equation with appropriate initial conditions and for a variety of models of the collision integral. For higher-density fluids, light-scattering experiments probe, to a large extent, the hydrodynamic region where the fluctuations are relatively slowly varying in space and time. Thus, the usual approach in analyzing these experiments has been to use the linearized hydrodynamic equations of irreversible thermodynamics.[7-11] For fluids with internal degrees of freedom, such a macroscopic approach has to be supplemented[8-11] either with frequency-dependent transport coefficients or with some relaxing internal parameter which is treated via the thermodynamic theory of relaxation.[12] The use of frequency-dependent transport coefficients has been justified on a microscopic basis by Zwanzig[13,14] for those situations in which the coupling between the internal and translational motions is weak.

In recent years, however, two general formalisms have been developed to deal directly with space-time-dependent correlation functions for dense systems. The correlation-function formalism of Martin[15,16] utilizes the equivalence of the linear-response theory and the linearized hydrodynamic equations to describe the slowly varying response of a system to an external disturbance, as well as general analytic properties of the correlation functions, and thereby deduces the expressions for the various response functions which are correct for arbitrary frequency and wave number. The formalism leaves open the form of the unknown dispersion function in these expressions; this form has to be guessed on the basis of some physical model depending on the problem at hand. In the memory-function formalism developed by Zwanzig[17] and Mori,[18] one applies the projection-operator technique to the formally exact Liouville equation to derive the so-called generalized Langevin equation for an arbitrary set of dynamical variables. The memory-function matrix appearing in this formally exact equation is, in principle, known in terms of the detailed interactions in the system, but is quite complex even for the simplest systems. The arbitrariness in this formalism is in the choice of the set of dynamical variables which has to be guided by the pertinent macroscopic variables for a given system.

For the simple dense system of liquid argon, both these formalisms have been recently applied[19-21] to study the high-frequency–wave-number behavior of various correlation functions encountered in analyzing the molecular-dynamics (computer) experiments and the slow neutron-scattering experiments.

Our main objective in the present work is to extend the existing microscopic formulations for monatomic systems[20,21] to the study of density-density correlations in one-component molecular fluids with internal degrees of freedom, and thereby develop a microscopic basis for the thermodynamic relaxation theory (see Secs. IV and V). Depending on the particular physical situation, the internal degrees of freedom (used here in the same sense as in Ref. 13) could involve either the rotational modes of motion, the vibrational modes, or both; the generality of the memory-function formalism enables one to build a general framework in which different physical situations would give rise to different behavior for the appropriate memory functions.

In Sec. II, we explain the motivation in the choice of the pertinent set of dynamical variables and write down the formal result for the density-density correlation function. We follow the procedure (and as far as possible the notation as well) of Akcasu and Daniels[20]; in fact, we use a subset of the dynamical variables chosen by them. The choice of this subset is guided by our interest in the longitudinal disturbances, the remaining variables being pertinent to the transverse correlations. Thus, the results summarized in this section are not new, but form a convenient starting point for our purpose. Because of our special interest in the hydrodynamic behavior encountered in light-scattering experiments, we assume that the fluid is spatially isotropic; this assumption may not be rigorously valid at high frequencies for molecular fluids. In Sec. III, we show that the density-density correlation function given by the memory-function formalism is formally equivalent to that given[15] by the correlation-function formalism of Martin; in particular, we relate the dispersion function to the pertinent memory functions. On account of the general equivalence between the linearized version of the memory-function approach and the linear-response theory, it was expected that the formalisms would yield identical results.

In Sec. IV, we consider the special case of zero coupling between heat flux $\vec{q}$ and viscosity stress tensor $\overleftrightarrow{\sigma}$. We show that with the proper hydrodynamic identifications (where we neglect the frequency dependence of the memory functions) of various coefficients, the expression for the density-density correlation function derived in Sec. II reduces to the results previously derived from the macroscopic approach.[8,10] Neglect of the $\vec{q}, \overleftrightarrow{\sigma}$ coupling implies in the hydrodynamic limit

$$B_S^\infty - B_S = B_T^\infty - B_T, \tag{1}$$

where B_S^∞, B_T^∞ are, respectively, the instantaneous values of adiabatic and isothermal bulk moduli; B_S, B_T are the corresponding zero-frequency values. Equation (1) means that the relaxing part of the bulk modulus is the same isothermally or adiabatically; under this condition, it is also known[10] that the general result of the thermodynamic theory of relaxation[22] reduces to the result obtained[8] by considering an exponentially relaxing bulk viscosity.

In Sec. V, we consider a simple model in which the $\vec{q}, \overleftrightarrow{\sigma}$ coupling is treated via a single parameter. We show that the density-density correlation function obtained from this model reduces, in the hydrodynamic region, to the general result[22] obtained from the thermodynamic theory of relaxation. In the memory-function formalism, the coupling parameter has a definite expression, which can be evaluated in principle. The hydrodynamic identifications of the various coefficients which are made in Secs. IV and V are justified in the Appendix. We conclude the paper with a number of remarks in Sec. VI.

II. FORMULATION IN MEMORY-FUNCTION FORMALISM

According to Mori,[18] the equation of motion of a set of dynamical variables $\vec{A}(t)$ is the generalized Langevin equation

$$\frac{d\vec{A}(t)}{dt} - i\hat{\omega}\cdot\vec{A}(t) + \int_0^t \hat{\phi}\,(t-S)\cdot\vec{A}(S)\,dS = \vec{f}(t), \quad t>0 \tag{2}$$

where $\hat{\omega}$ (frequency matrix), $\hat{\phi}\,(t)$ (memory-function matrix), and $\vec{f}(t)$ (random force vector) are defined by

$$i\hat{\omega} = (\dot{\vec{A}}, \vec{A}^\dagger)\cdot(\vec{A}, \vec{A}^\dagger)^{-1}, \tag{3a}$$

$$\hat{\phi}(t) = (\vec{f}(t), \vec{f}^\dagger)\cdot(\vec{A}, \vec{A}^\dagger)^{-1}, \tag{3b}$$

$$\vec{f}(t) = e^{t(1-P)iL}(1-P)\dot{\vec{A}}\ . \tag{3c}$$

Also, we have

$$\vec{A}(t) = e^{iLt}\vec{A}, \tag{3d}$$

and we have denoted $\vec{A}(0)$ by $\vec{A}$, $iL\vec{A}$ by $\dot{\vec{A}}$. In Eq. (3), L is the Liouville operator and P is a projection operator defined by

$$P\vec{G}(t) = (\vec{G}(t), \vec{A}^\dagger)\cdot(\vec{A}, \vec{A}^\dagger)^{-1}\cdot\vec{A}\ , \tag{4a}$$

$$(1-P)\vec{A} = 0\ . \tag{4b}$$

In the linear-response approximation, Mori has shown that a suitable definition of the scalar product used in Eqs. (3) is

$$(\vec{F}, \vec{G}^\dagger) = \langle\vec{F}\cdot\vec{G}^\dagger\rangle, \quad \text{classical} \tag{5a}$$

$$= (1/\beta)\int_0^\beta \langle e^{\lambda H}\vec{F}e^{-\lambda H}\cdot\vec{G}^\dagger\rangle\,d\lambda, \quad \text{quantal} \tag{5b}$$

where $\langle\cdots\rangle$ denotes canonical ensemble average, H is the Hamiltonian of the system, and β the equilibrium value of inverse temperature in energy units. $\vec{F}$ and $\vec{G}$ are defined such that $\langle\vec{F}\rangle = \langle\vec{G}\rangle = 0$. For the calculation of the density-density correlation function, we choose the relevant dynamical variables as follows:[20,23] We define the microscopic mass-density and energy-density variables as

$$\hat{\rho}(\vec{r}, t) = m \sum_{\alpha=1}^{N} \delta(\vec{r} - \vec{r}_\alpha(t)), \tag{6a}$$

$$\hat{E}(\vec{r}, t) = \tfrac{1}{2} \sum_{\alpha=1}^{N} \left(\frac{P_\alpha^2(t)}{m} + \sum_{\beta \neq \alpha} V(|\vec{r}_\alpha - \vec{r}_\beta|) \right) \delta(\vec{r} - \vec{r}_\alpha(t)). \tag{6b}$$

and the Fourier transform of their fluctuations as

$$\rho(\vec{k}, t) = (1/V_0) \int e^{i\vec{k}\cdot\vec{r}}\, \delta\rho\, d^3\vec{r}, \tag{7a}$$

with

$$\delta\rho = \hat{\rho}(\vec{r}, t) - \langle \hat{\rho}(\vec{r}, t) \rangle, \tag{7b}$$

and similarly for $E(\vec{k}, t)$. We have chosen to exclude the part of the energy density associated with internal motion of the molecules since in the present work we are interested in the correlated translational motion in a one-component fluid. For simplicity, we shall sometimes denote $\rho(\vec{k}, t)$ by ρ, etc. If the current density $\vec{J}(\vec{k}, t)$, stress tensor $\overleftrightarrow{\pi}(\vec{k}, t)$, and energy current density $\vec{Q}(\vec{k}, t)$ have the usual microscopic definitions,[24] then the following conservation laws can be proved:

$$\frac{\partial \rho}{\partial t} = i \vec{k} \cdot \vec{J}, \tag{8a}$$

$$\frac{\partial \vec{J}}{\partial t} = i \vec{k} \cdot \overleftrightarrow{\pi}, \tag{8b}$$

$$\frac{\partial E}{\partial t} = i \vec{k} \cdot \vec{Q}. \tag{8c}$$

It is now convenient to define a new variable $\theta(\vec{k}, t)$ as

$$\theta = E - \langle E\rho^* \rangle \langle \rho\rho^* \rangle^{-1} \rho. \tag{9a}$$

Fluctuations in $\hat{\rho}$ and $\hat{\theta}$ are thus uncoupled. The heat flux $\vec{q}(\vec{k}, t)$ and viscosity stress tensor $\overleftrightarrow{\sigma}(\vec{k}, t)$ can then be defined as

$$\vec{q} = \vec{Q} - \langle \vec{Q} \cdot \vec{J}^\dagger \rangle \cdot \langle \vec{J} \cdot \vec{J}^\dagger \rangle^{-1} \cdot \vec{J}, \tag{9b}$$

$$\overleftrightarrow{\sigma} = \overleftrightarrow{\pi} - \langle \overleftrightarrow{\pi} \rho^* \rangle \langle \rho\rho^* \rangle^{-1} \rho - \langle \overleftrightarrow{\pi} \theta^* \rangle \langle \theta\theta^* \rangle^{-1} \theta. \tag{9c}$$

For fluids, the spatial isotropy implies that

$$\langle \overleftrightarrow{\pi} \cdot \overleftrightarrow{\pi}^\dagger \rangle = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}, \tag{10a}$$

with

$$C_{44} = \tfrac{1}{2}(C_{11} - C_{12}). \tag{10b}$$

We assume that $\langle \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\sigma}^\dagger \rangle$ also has this symmetry. Since density fluctuations are longitudinal disturbances, we shall choose as our dynamical variables

$$\vec{A} = \mathrm{col}[\rho, \theta, \sigma_1, \sigma_2, \sigma_3, J, q], \tag{11}$$

where

$$\sigma_1 = \sigma_{xx}, \sigma_2 = \sigma_{YY}, \sigma_3 = \sigma_{zz}, J = J_z, q = q_z,$$

and the z axis is chosen along the direction of $\vec{k}$. This is a subset of the variables chosen by Akcasu and Daniels,[20] and is relevant for the study of longitudinal disturbances. The inclusion of the variables q and σ_i enables one to incorporate the important loss mechanisms which give rise to thermal conductivity, shear viscosity, and bulk viscosity in the dynamical description of the fluid system.

To calculate the frequency matrix and the memory-function matrix, we shall make use of the following results which can be shown from symmetry considerations:

$$\langle \rho\theta^* \rangle = 0, \tag{12a}$$

$$\langle \rho \vec{J}^\dagger \rangle = \langle \rho \vec{q}^\dagger \rangle = \langle \theta \vec{J}^\dagger \rangle = \langle \theta \vec{q}^\dagger \rangle = \langle \vec{J}^\dagger \cdot \overleftrightarrow{\sigma} \rangle = \langle \vec{q}^\dagger \cdot \overleftrightarrow{\sigma} \rangle = \vec{0}, \tag{12b}$$

$$\langle \rho \overleftrightarrow{\sigma}^\dagger \rangle = \langle \theta \overleftrightarrow{\sigma}^\dagger \rangle = \langle \vec{J} \cdot \vec{q}^\dagger \rangle = 0, \tag{12c}$$

and it follows from Eq. (10) that

$$[\langle \sigma_i \sigma_j^* \rangle] = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{12} \\ \sigma_{12} & \sigma_{11} & \sigma_{12} \\ \sigma_{12} & \sigma_{12} & \sigma_{11} \end{bmatrix}, \quad i, j = 1, 2, 3. \tag{12d}$$

Using Eqs. (8) and (12) and the stationarity property of the correlation functions, we obtain

$$i\overleftrightarrow{\omega} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & ik & 0 \\ 0 & 0 & 0 & 0 & 0 & \dfrac{\langle \dot{\theta} J^* \rangle}{\langle JJ^* \rangle} & ik \\ 0 & 0 & 0 & 0 & 0 & \dfrac{ik\sigma_{12}}{\langle JJ^* \rangle} & \dfrac{\langle \dot{\sigma}_1 q^* \rangle}{\langle qq^* \rangle} \\ 0 & 0 & 0 & 0 & 0 & \dfrac{ik\sigma_{12}}{\langle JJ^* \rangle} & \dfrac{\langle \mathring{\sigma}_2 q^* \rangle}{\langle qq^* \rangle} \\ 0 & 0 & 0 & 0 & 0 & \dfrac{ik\sigma_{11}}{\langle JJ^* \rangle} & \dfrac{\langle \dot{\sigma}_3 q^* \rangle}{\langle qq^* \rangle} \\ \dfrac{ik\langle JJ^* \rangle}{\langle \rho\rho^* \rangle} & \dfrac{\langle \dot{J}\theta^* \rangle}{\langle \theta\theta^* \rangle} & 0 & 0 & ik & 0 & 0 \\ 0 & \dfrac{ik\langle qq^* \rangle}{\langle \theta\,\theta^* \rangle} & a_1' & a_2' & a_3' & 0 & 0 \end{bmatrix}, \tag{13a}$$

where

$$a_i' = \frac{\langle \dot{q}\sigma_i^* \rangle (\sigma_{11} + 2\sigma_{12}) - \sigma_{12}(\langle \dot{q}\sigma_1^* \rangle + \langle \dot{q}\sigma_2^* \rangle + \langle \mathring{q}\sigma_3^* \rangle)}{(\sigma_{11} - \sigma_{12})(\sigma_{11} + 2\sigma_{12})}. \tag{13b}$$

Using Eqs. (8) and (3c), the random force is of the form

$$\vec{f}(t) = \mathrm{col}[0\ 0\ f_{\sigma_1}\ f_{\sigma_2}\ f_{\sigma_3}\ 0\ f_q]. \tag{14}$$

Hence, the memory-function matrix $\hat{\overleftrightarrow{\phi}}(t)$ is of the form

$$\hat{\overleftrightarrow{\phi}}(t) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \phi_{11} & \phi_{12} & \phi_{12} & 0 & \phi_{\sigma_1 q} \\ 0 & 0 & \phi_{12} & \phi_{11} & \phi_{12} & 0 & \phi_{\sigma_2 q} \\ 0 & 0 & \phi_{12} & \phi_{12} & \phi_{11} & 0 & \phi_{\sigma_3 q} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \phi_{q\sigma_1} & \phi_{q\sigma_2} & \phi_{q\sigma_3} & 0 & \phi_{qq} \end{bmatrix} , \qquad (15)$$

where we have assumed that $\hat{\overleftrightarrow{\phi}}_{\vec{\sigma}\vec{\sigma}}$ has the same symmetry as in Eqs. (10a) and (12d).

We now multiply Eq. (2) with $\vec{A}^\dagger$, take a canonical ensemble average, and then take the Laplace transform. Since $\langle \vec{f}(t)\cdot\vec{A}^\dagger\rangle = 0$, we get

$$\langle \tilde{\vec{A}}(S)\cdot\vec{A}^\dagger\rangle = [S\overleftrightarrow{I} - i\hat{\overleftrightarrow{\omega}} + \tilde{\overleftrightarrow{\phi}}(S)]^{-1}\cdot\langle\vec{A}\cdot\vec{A}^\dagger\rangle , \qquad (16)$$

where

$$\langle \tilde{A}_i(S)A_j^*\rangle = \int_0^\infty e^{-st}\langle A_1(t)A_j^*\rangle\,dt, \quad \mathrm{Re}S > 0 \qquad (17)$$

with a similar equation for $\hat{\overleftrightarrow{\phi}}(S)$; $\overleftrightarrow{I}$ is a unit matrix. Equation (16) is a matrix equation from which various correlation functions can be calculated. It is then important to calculate the inverse of the matrix $[S\overleftrightarrow{I} - i\overleftrightarrow{\omega} + \overleftrightarrow{\phi}(S)]$ if one wishes to evaluate all the correlation functions $\langle\tilde{A}_i(S)A_j^*\rangle$. Since our interest is only for $\langle\tilde{\rho}(S)\rho^*\rangle \equiv \langle\tilde{A}_1(S)A_1^*\rangle$, we can easily show from Eq. (16) that, on account of the simple form of $\langle\vec{A}\cdot\vec{A}^\dagger\rangle$, we obtain

$$\frac{\langle\tilde{\rho}(S)\rho^*\rangle}{\langle\rho\rho^*\rangle} = \frac{F_{\rho\rho}(S)}{|S\overleftrightarrow{I} - i\hat{\overleftrightarrow{\omega}} + \tilde{\overleftrightarrow{\phi}}(S)|} , \qquad (18a)$$

where

$F_{\rho\rho}(S)$

$$= \begin{vmatrix} S & 0 & 0 & 0 & -\dfrac{\langle\dot{\theta}J^*\rangle}{\langle JJ^*\rangle} & -ik \\ 0 & S+\tilde{\phi}_{11} & \tilde{\phi}_{12} & \tilde{\phi}_{12} & -\dfrac{ik\sigma_{12}}{\langle JJ^*\rangle} & b_1 \\ 0 & \tilde{\phi}_{12} & S+\tilde{\phi}_{11} & \tilde{\phi}_{12} & -\dfrac{ik\sigma_{12}}{\langle JJ^*\rangle} & b_2 \\ 0 & \tilde{\phi}_{12} & \tilde{\phi}_{12} & S+\tilde{\phi}_{11} & -\dfrac{ik\sigma_{11}}{\langle JJ^*\rangle} & b_3 \\ -\dfrac{\langle\dot{J}\theta^*\rangle}{\langle\theta\theta^*\rangle} & 0 & 0 & -ik & S & 0 \\ -ik\dfrac{\langle qq^*\rangle}{\langle\theta\theta^*\rangle} & a_1 & a_2 & a_3 & 0 & S+\tilde{\phi}_{qq} \end{vmatrix} , \qquad (18b)$$

and

$$a_i = -a_i' + \tilde{\phi}_{q\sigma_i}(S) , \qquad (18c)$$

$$b_i = -\langle\dot{\sigma}_i q^*\rangle\langle qq^*\rangle^{-1} + \tilde{\phi}_{\sigma_i q}(S) . \qquad (18d)$$

For the case of zero coupling between heat flux and the viscosity stress tensor, one simply sets $a_i = b_i = 0$. Results summarized in this section are not new,[20] but we have reexpressed them in a form that is convenient for our purposes. For any given system, knowing the explict form of the Liouville operator, the memory-function formalism, in principle gives the formal expressions for the nonzero coefficients in $\overleftrightarrow{\phi}(S)$. However, since these are quite complicated, most applications known to us have taken recourse to modelizing at this stage. For our present purposes, we do not need the explicit expressions for these memory functions.

III. RELATION WITH CORRELATION-FUNCTION FORMALISM OF MARTIN

Relation between the memory-function formalism and the correlation-function formalism can be deduced via the use of the fluctuation-dissipation theorem. A well-known and useful formula which relates the time-correlation function and the response function is[25]

$$(\dot{x}(t), y^*) = (1/\beta)\langle[x(t), y^*]\rangle , \qquad (19)$$

where the scalar product is defined in Eq. (5), and the square bracket is the commutator divided by $i\hbar$ (quantum mechanically), or the Poisson bracket (classically). In our notations, Martin's response function[15] is

$$\chi(k,S) = -(\beta/m^2)\int_0^\infty (\dot{\rho}(t), \rho^*)e^{-St}\,dt , \qquad (20)$$

$$m^{-2}\langle[\rho(t),\rho^*]\rangle = \int (d\omega/\pi)\,\chi''(k,\omega)e^{-i\omega t} . \qquad (21)$$

Using Eq. (19) and the stationarity property of the scalar product, one can show that

$$\chi(k,S) = \int \frac{d\omega}{\pi}\,\frac{\chi''(k,\omega)}{\omega - iS} , \qquad (22)$$

and derive the sum rules

$$\left(\frac{\beta}{m^2}\right)(\rho,\rho^*) = \int\frac{d\omega}{\pi}\,\frac{\chi''(k,\omega)}{\omega} = \chi(k, S=0) \equiv \chi(k) , \qquad (23)$$

$$\left(\frac{\beta}{m^2}\right)(\dot{\rho},\dot{\rho}^*) = \left(\frac{\beta k^2}{m^2}\right)(J, J^*) = \int\frac{d\omega}{\pi}\,\omega\chi''(k,\omega) . \qquad (24)$$

Equation (20), on integration by parts, yields

$$\chi(k,S) = -(\beta/m^2)\,S(\tilde{\rho}(S),\rho^*) + \chi(k) . \qquad (25)$$

From Eq. (18), one obtains

$$\frac{\beta}{m^2}\,\frac{S\langle\tilde{\rho}(S)\rho^*\rangle}{\chi(k)} = \frac{SF_{\rho\rho}(S)}{SF_{\rho\rho}(S) - (ik\beta/m^2)[\langle JJ^*\rangle/\chi(k)]F_{\rho J}(S)} , \qquad (26a)$$

where

$F_{\rho J}(S)$

$$
=-\begin{vmatrix}
0 & 0 & 0 & 0 & -ik & 0 \\
S & 0 & 0 & 0 & -\dfrac{\langle\dot{\theta}J^*\rangle}{\langle JJ^*\rangle} & -ik \\
0 & S+\tilde{\phi}_{11} & \tilde{\phi}_{12} & \tilde{\phi}_{12} & -ik\dfrac{\sigma_{12}}{\langle JJ^*\rangle} & b_1 \\
0 & \tilde{\phi}_{12} & S+\tilde{\phi}_{11} & \tilde{\phi}_{12} & -ik\dfrac{\sigma_{12}}{\langle JJ^*\rangle} & b_2 \\
0 & \tilde{\phi}_{12} & \tilde{\phi}_{12} & S+\phi_{11} & -ik\dfrac{\sigma_{11}}{\langle JJ^*\rangle} & b_3 \\
-\dfrac{ik\langle qq^*\rangle}{\langle\theta\theta^*\rangle} & a_1 & a_2 & a_3 & 0 & S+\tilde{\phi}_{qq}
\end{vmatrix}
\qquad (26b)
$$

Hence,

$$
\frac{1}{\chi(k,S)}-\frac{1}{\chi(k)}
=\frac{m^2}{\beta}\left(\frac{S^2}{k^2\langle JJ^*\rangle}-\frac{S[F_{\rho\rho}(S)-(S/ik)F_{\rho J}(S)]}{ik\langle JJ^*\rangle F_{\rho J}(S)}\right). \qquad (27)
$$

If one puts $S=-iZ=-i\omega+\epsilon$ in Eq. (27) and identifies $\Gamma(k,\omega)$ as

$$
\frac{F_{\rho\rho}(-iZ)+(Z/k)F_{\rho J}(-iZ)}{kF_{\rho J}(-iZ)}=-\int\frac{d\omega'}{\pi}\,\frac{\Gamma(k,\omega')}{\omega'-Z}\,, \qquad (28)
$$

then Eq. (27) becomes identical to Eq. (85) of Ref. 15. From Eqs. (22) and (27), one can also evaluate $\chi''(k,\omega)=\mathrm{Im}\chi(k,S)$. We observe that Eq. (28) implies

$$
\Gamma(k,\omega)=-\lim_{\epsilon\to 0}\,\mathrm{Im}\left(\frac{F_{\rho\rho}(-iZ)+(Z/k)F_{\rho J}(-iZ)}{kF_{\rho J}(-iZ)}\right)_{Z=\omega+i\epsilon} \qquad (29)
$$

In those physical situations where we can ignore the coupling between $\vec{\mathrm{q}}$ and $\overleftrightarrow{\sigma}$, i.e., when $a_i=b_i=0$, Eqs. (18b), (26b), and (29) give

$$
\Gamma(k,\omega)=\mathrm{Re}\left(\frac{\omega^2[A-(\sigma_{11}/\langle JJ^*\rangle)k^2]+i\omega[A\Phi_1-ck^2-(\sigma_{11}/\langle JJ^*\rangle)D_Tk^4]+(D_Tk^4c-A\Phi_2)}{k^2[i\omega^3-\omega^2(\Phi_1+D_Tk^2)-i\omega(\Phi_2+\Phi_1D_Tk^2)+\Phi_2D_Tk^2]}\right), \qquad (30)
$$

where

$$D_T(k,\omega)=\langle qq^*\rangle\langle\theta\theta^*\rangle^{-1}(\tilde{\phi}_{qq}-i\omega)^{-1}\,, \qquad (31a)$$

$$\Phi_1(k,\omega)=2\tilde{\phi}_{11}+\tilde{\phi}_{12}\,, \qquad (31b)$$

$$\Phi_2(k,\omega)=(\tilde{\phi}_{11}+2\tilde{\phi}_{12})(\tilde{\phi}_{11}-\tilde{\phi}_{12})\,, \qquad (31c)$$

$$A(k)=\langle\dot{J}\theta^*\rangle\langle\dot{\theta}J^*\rangle\langle\theta\theta^*\rangle^{-1}\langle JJ^*\rangle^{-1}\,, \qquad (31d)$$

$$c(k,\omega)=[\sigma_{11}(\tilde{\phi}_{11}+\tilde{\phi}_{12})-2\sigma_{12}\tilde{\phi}_{12}]\langle JJ^*\rangle^{-1}\,. \qquad (31e)$$

For the situations when the coupling cannot be ignored, the expression for $\Gamma(k,\omega)$ is considerably more complex. It can be seen from Eq. (30) that $\Gamma(k,\omega)$ is an even function of ω, and it has different limits depending on the order in which ω and k approach zero. In Sec. IV, we shall see that for small k and ω, $k^2\Gamma(k,\omega)$ reduces to the familiar expressions for sound absorption per cycle under appropriate approximations.

The equivalence between the two formalisms has also been previously shown in a similar manner for the simpler case of spin diffusion.[26]

IV. REDUCTION TO INTEGRAL-REPRESENTATION METHOD

As discussed in the Introduction, for systems with internal degrees of freedom, the analysis of Rayleigh and Brillouin spectra can be carried out[8-11] using frequency-dependent or relaxing bulk and shear viscosities. Since shear processes do not involve changes in volume or temperature of the fluid, such an integral representation for shear viscosity can be justified. However, for bulk processes, justification can be made only in the limit of very weak coupling between internal and translational motions. In this section, we attempt such a justification from the microscopic formulation of Sec. II. In this section, we consider the special case of zero coupling between $\vec{\mathrm{q}}$ and $\overleftrightarrow{\sigma}$, i.e., we set $a_i=b_i=0$. In terms of the memory functions $\tilde{\phi}_{11}(S)$ and $\tilde{\phi}_{12}(S)$, we also define

$$\tau_S^{-1}=\tilde{\phi}_{11}-\tilde{\phi}_{12}\,, \qquad (32a)$$

$$\tau_d^{-1}=\tilde{\phi}_{11}+2\tilde{\phi}_{12}\,. \qquad (32b)$$

Then we have

$$\Phi_1=\tau_d^{-1}+\tau_S^{-1}\,, \qquad (33a)$$

$$\Phi_2=\tau_d^{-1}\tau_S^{-1}\,, \qquad (33b)$$

$$c=\{\tfrac{1}{3}[(\sigma_{11}+2\sigma_{12})\tau_S^{-1}]+\tfrac{1}{3}[2(\sigma_{11}-\sigma_{12})\tau_d^{-1}]\}\langle JJ^*\rangle^{-1}\,. \qquad (33c)$$

The density-density correlation function, given in Eq. (18), then reduces to

$$\langle\tilde{\rho}(S)\rho^*\rangle/\langle\rho\rho^*\rangle=\mathfrak{F}(S)/\mathfrak{G}(S)\,, \qquad (34a)$$

where

$$
\begin{aligned}
\mathfrak{F}(S)={}&S^4+S^3(\tau_d^{-1}+\tau_S^{-1}+D_Tk^2)+S^2[\tau_d^{-1}\tau_S^{-1}+\sigma_{11}k^2/\langle JJ^*\rangle\\
&-A+(\tau_d^{-1}+\tau_S^{-1})D_Tk^2]+S\{D_Tk^2(\tau_d^{-1}\tau_S^{-1}+\sigma_{11}k^2/\langle JJ^*\rangle)\\
&+[ck^2-A(\tau_d^{-1}+\tau_S^{-1})]\}+(cD_Tk^4-A\tau_d^{-1}\tau_S^{-1})\,, \qquad (34b)
\end{aligned}
$$

$$\mathfrak{G}(S)=S\mathfrak{F}(S)+k^2\langle JJ^*\rangle\langle\rho\rho^*\rangle^{-1}(S+D_Tk^2)(S+\tau_d^{-1})(S+\tau_S^{-1})\,. \qquad (34c)$$

Equations (34) contains, in general, three relaxation mechanisms: (i) a frequency-dependent thermal diffusivity $D_T(k, S)$, (ii) a relaxing bulk viscosity related to $\tau_d(k, S)$, and (iii) a relaxing shear viscosity related to $\tau_S(k, S)$. For analyzing light-scattering experiments in dense fluids, it is proper to consider the hydrodynamic limit of various coefficients in Eqs. (34b) and (34c). Then it is reasonable to *assume* that in the frequency and wave-number range of interest, the memory functions $\tilde{\phi}_{11}$, and $\tilde{\phi}_{12}$, and $\tilde{\phi}_{qq}$ are (k, S)-independent constants. This assumption gives constant values for τ_d and τ_S and is equivalent to the single-relaxation approximation for bulk and shear viscosities. Expressions given in Eq. (34) are, however, capable of dealing with those situations where single-relaxation approximations fail. If analysis of a certain experiment requires frequency dependence in either τ_d or τ_S, it would imply a distribution of relaxation times. It has been observed[27] that in viscous liquids, both the *mean* relaxation times $\bar{\tau}_d$ and $\bar{\tau}_S$ are of the same order and have the same temperature dependence. If $\tilde{\phi}_{11} \gg \tilde{\phi}_{12}$, then the definitions of τ_d and τ_S given in Eq. (32) would also yield such a conclusion for the *mean* relaxation times $\bar{\tau}_d$ and $\bar{\tau}_S$. We further assume that, in the frequency range of interest, thermal diffusivity D_T can be replaced by its zero-frequency (static) value, thus ignoring the explicit frequency dependence in Eq. (31a). Then for hydrodynamic k and S values (appropriate to Rayleigh and Brillouin spectra), the following identifications result:

$$D_T(k, S) \to \lambda/(\rho_0 c_v)\,, \tag{35a}$$

$$\langle JJ^*\rangle\langle \rho\rho^*\rangle^{-1} \to B_T/\rho_0\,, \tag{35b}$$

$$A(k) \to (B_T - B_S)k^2/\rho_0\,, \tag{35c}$$

$$\tfrac{1}{3}[(\sigma_{11} + 2\sigma_{12})\langle JJ^*\rangle^{-1}] \to (B_S^\infty - B_S)/\rho_0\,, \tag{35d}$$

$$(\sigma_{11} - \sigma_{12})\langle JJ^*\rangle^{-1} \to 2G^\infty/\rho_0\,, \tag{35e}$$

where G^∞ is the adiabatic (instantaneous) shear modulus, c_v the specific heat per unit mass at constant volume, λ the thermal conductivity, and ρ_0 the equilibrium density. Justification of the identifications in (35) is made in the Appendix. Using Eqs. (35), Eqs. (34) reduce to the earlier results derived from macroscopic considerations in Refs. 10 and 8. Equations (30)–(33) of Ref. 10 contain the $\vec{q}$, $\overleftrightarrow{\sigma}$ coupling; it is easy to verify that Eq. (34) with identifications in Eq. (35) is equivalent to Eqs. (30)–(33) of Ref. 10 provided one sets $B_S^\infty - B_S = B_T^\infty - B_T$ (or equivalently $c_v = c_v^\infty$), i.e., provided one neglects the coupling. Also, Eqs. (28) and (29) of Ref. 8 become a special case of our Eqs. (34) and (35) with nonrelaxing shear viscosity.

With the identifications of Eqs. (35), we can also consider the behavior of $\Gamma(k, \omega)$ given in Eq. (30). Two different limits are of interest. If $\omega\tau_d \ll 1$, $\omega\tau_S \ll 1$, we get

$$k^2\Gamma(k, \omega) \to k^2\left[\frac{B_S^\infty - B_S}{\rho_0}\,\tau_d + \frac{4}{3}\,\frac{G^\infty}{\rho_0}\,\tau_S + \frac{\lambda}{\rho_0 c_P}\left(\frac{c_P}{c_v} - 1\right)\right], \tag{36}$$

whereas in the other extreme when $\omega\tau_d \gg 1$, $\omega\tau_S \gg 1$,

$$k^2\Gamma(k, \omega) \to \frac{B_S^\infty - B_S}{\rho_0 v_\infty^2}\,\frac{1}{\tau_d} + \frac{4}{3}\,\frac{G^\infty}{\rho_0 v_\infty^2}\,\frac{1}{\tau_S} + \frac{B_S}{\rho_0 v_\infty^2}\,\frac{\lambda k^2}{\rho_0 c_P}\left(\frac{c_P}{c_v} - 1\right). \tag{37}$$

In Eqs. (36) and (37), c_P is the specific heat per unit mass at constant pressure and $v_\infty^2 = (B_S^\infty + \frac{4}{3}G^\infty)/\rho_0$. These are the well-known expressions for sound absorption [see, for example, Eqs. (69) and (72) in Ref. 10]. From the results obtained in Eqs. (36) and (37), one sees that when shear and bulk viscosities are very rapidly relaxing $\Gamma(k, \omega)$ reduces to a constant, whereas when the bulk and shear relaxations are very slow the sound absorption per cycle, $k^2\Gamma(k, \omega)$, becomes constant.

V. CORRECTION FOR COUPLING BETWEEN HEAT FLUX AND VISCOSITY STRESS TENSOR

In this section, we consider a simple model to take into account the coupling between the heat flux $\vec{q}$ and the viscosity stress tensor $\overleftrightarrow{\sigma}$. In view of the isotropy of a fluid, we assume that in Eqs. (18)

$$a_1 = a_2 = a_3 = a\,, \tag{38a}$$

$$b_1 = b_2 = b_3 = b\,. \tag{38b}$$

Then using the definitions in Eqs. (31) and (33), Eq. (18a) reduces to

$$\langle \tilde{\rho}(S)\,\rho^*\rangle/\langle \rho\rho^*\rangle = \mathfrak{F}(S)/\mathfrak{G}(S)\,, \tag{39a}$$

where

$$\begin{aligned}\mathfrak{F}(S) = {}& S^4 + S^3(\tau_d^{-1} + \tau_S^{-1} + D_T'k^2) + S^2(\tau_d^{-1}\tau_S^{-1} + \sigma_{11}k^2/\langle JJ^*\rangle \\ & - A + D_T'k^2\tau_S^{-1} + D_Tk^2\tau_d^{-1}) + S\{D_Tk^2\tau_d^{-1}\,\tau_S^{-1} + D_T'k^4 \\ & \times[\mathfrak{B} + \tfrac{2}{3}(\sigma_{11} - \sigma_{12})/\langle JJ^*\rangle\,] + ck^2 - A(\tau_d^{-1} + \tau_S^{-1})\} \\ & + \{D_Tk^4\,\tfrac{2}{3}[(\sigma_{11} - \sigma_{12})/\langle JJ^*\rangle\,]\tau_d^{-1} + D_T'k^4\mathfrak{B}\,\tau_S^{-1} - A\tau_d^{-1}\,\tau_S^{-1}\}.\end{aligned} \tag{39b}$$

$$\begin{aligned}(S) = {}& S\mathfrak{F}(S) + k^2\langle JJ^*\rangle\langle \rho\rho^*\rangle^{-1}[S^3 + S^2(D_T'k^2 + \tau_S^{-1} + \tau_d^{-1}) \\ & + S(D_T'k^2\tau_S^{-1} + D_Tk^2\tau_d^{-1} + \tau_d^{-1}\,\tau_S^{-1}) + D_Tk^2\,\tau_d^{-1}\,\tau_S^{-1}]\,.\end{aligned} \tag{39c}$$

In Eqs. (39), we obtain

$$D_T'(k, S) = \frac{\langle qq^*\rangle\langle \theta\theta^*\rangle^{-1} - 3ab/k^2}{S + \tilde{\phi}_{qq}}\,, \tag{40a}$$

$$\mathfrak{B}(k, S) = \frac{D_T}{D_T'}\;\frac{\sigma_{11} + 2\sigma_{12}}{3\langle JJ^*\rangle} - \frac{A(k)}{k^2}\left(1 - \frac{D_T}{D_T'}\right) - \frac{b}{k^2}\,\frac{D_T}{D_T'}\,\frac{\langle \dot{\theta}J^*\rangle}{\langle JJ^*\rangle}$$

$$-\frac{a}{k^2}\frac{D_T}{D_T'}\frac{\langle\dot{J}\theta^*\rangle}{\langle qq^*\rangle}\frac{(\sigma_{11}+2\sigma_{12})}{\langle JJ^*\rangle}\ . \tag{40b}$$

It is easy to verify that Eqs. (39) reduce to (34) if $a=b=0$. In general, the coupling constants a and b are not independent. The dependence is clearly seen in a special case when we *assume* that

$$\tilde{\phi}_{\sigma_i q}=\tilde{\phi}_{q\sigma_i}=0, \quad i=1,2,3.$$

For this case, Eqs. (13b), (18c), and (18d) imply

$$b^*=-\frac{a(\sigma_{11}+2\sigma_{12})}{\langle qq^*\rangle}=-\frac{\langle\dot{\sigma}_i q^*\rangle^*}{\langle qq^*\rangle}\ . \tag{41}$$

Thus, if we ignore the memory functions $\tilde{\phi}_{q\sigma_i}$ and $\tilde{\phi}_{\sigma_i q}$, the density-density correlation function is given by Eqs. (39) with a single coupling parameters $b(k)$ in terms of which $D_T'(k, S)$ and $\mathcal{B}(k, S)$ are given as

$$D_T'(k,S)=D_T(k,S)\left(1+\frac{3|b|^2\langle\theta\theta^*\rangle}{k^2(\sigma_{11}+2\sigma_{12})}\right)\ , \tag{42a}$$

$$\mathcal{B}(k,S)=\frac{D_T}{D_T'}\frac{\sigma_{11}+2\sigma_{12}}{3\langle JJ^*\rangle}-\frac{A(k)}{k^2}\left(1-\frac{D_T}{D_T'}\right)-\frac{D_T}{D_T'}\frac{2}{k^2}$$

$$\times\mathrm{Re}\left(\frac{b\langle\dot{\theta}J^*\rangle}{\langle JJ^*\rangle}\right)\ . \tag{42b}$$

Again, the reduction of (39) in the hydrodynamic region is of interest. For such k and S values, the identifications given in Eqs. (35) remain valid in the presence of the $\vec{q}-\overleftrightarrow{\sigma}$ coupling; also, (42) reduces to

$$D_T'(k,S)\to\lambda/\rho_0 C_v^\infty\ , \tag{43a}$$

$$\mathcal{B}(k,S)\to(B_T^\infty-B_T)/\rho_0\ . \tag{43b}$$

The justification for Eqs. (35) and (43) is given in the Appendix. Using these identifications, we can show that Eqs. (39) reduce to the result previously obtained from the thermodynamic theory of relaxation and given in Eqs. (30)–(33) of Ref. 10. [In showing the equivalence, one has to use the definitions given in Eqs. (34), (35), and (44) of Ref. 10.] We also note in passing that in absence of $\vec{q}\,\overleftrightarrow{\sigma}$ coupling, Eq. (43a) becomes

$$D_T=D_T'\to\lambda/\rho_0 C_v\ , \tag{44a}$$

so that

$$C_v=C_v^\infty\ , \tag{44b}$$

$$\mathcal{B}\to(B_S^\infty-B_s)/\rho_0=(B_T^\infty-B_T)/\rho_0\ . \tag{44c}$$

It is also of interest to see the effect of the coupling on the bulk relaxation processes. To that end, we consider the (k, S)-dependent bulk viscosity:[28]

$$\zeta(k,S)=\frac{\rho_0}{3ik}\frac{\langle\tilde{\sigma}_3(S)J^*\rangle+2\langle\tilde{\sigma}_1(S)J^*\rangle}{\langle\tilde{J}(S)J^*\rangle}\ . \tag{45}$$

This definition can be understood from the static case in coordinate space, where ζ is defined as

$$\tfrac{1}{3}\mathrm{Tr}[\sigma_{ij}]=\zeta\,\mathrm{div}u=\zeta\,\mathrm{div}(\vec{J}/\rho_0)\ . \tag{45$'$}$$

Using Eq. (16), we can show that for the model considered in this section, Eq. (45) reduces to

$$\zeta(k,S)=\rho_0\frac{[(\sigma_{11}+2\sigma_{12})/3\langle JJ^*\rangle](S+D_Tk^2)-b(\langle\dot{\theta}J^*\rangle/\langle JJ^*\rangle)D_T}{(S+\tau_d^{-1})(S+D_Tk^2)+k^2(D_T'-D_T)S}\ . \tag{46}$$

In this expression, if one neglects the coupling or lets $k\to 0$ and uses the hydrodynamic identification of Eq. (35d), then one gets

$$\zeta(k,i\omega)\to\frac{(B_S^\infty-B_S)\tau_d}{1+i\omega\tau_d}\ , \tag{47}$$

which is the familiar result corresponding to the single-relaxation approximation. As has been previously observed,[13] it is important to realize that the result in Eq. (47) is valid for arbitrary k only when the $\vec{q}$, $\overleftrightarrow{\sigma}$ coupling can be legitimately ignored.

Similarly, by using the definition

$$\eta(k,S)=\frac{\rho_0}{2ik}\frac{\langle\tilde{\sigma}_3(S)J^*\rangle-\langle\tilde{\sigma}_1(S)J^*\rangle}{\langle\tilde{J}(S)J^*\rangle} \tag{48}$$

and Eq. (16), we can show that for the model considered in this section $\eta(k, S)$ becomes

$$\eta(k,S)=\frac{\rho_0}{2}\frac{(\sigma_{11}-\sigma_{12})\langle JJ^*\rangle^{-1}}{S+\tilde{\phi}_{11}-\tilde{\phi}_{12}} \tag{49}$$

and is independent of the coupling constant b, as expected. If one uses the hydrodynamic identification of Eq. (35e), then one obtaind

$$\eta(k,i\omega)\to G_\infty\tau_S/(1+i\omega\tau_S)\ , \tag{50}$$

which is the single-relaxation form usually assumed.

VI. CONCLUDING REMARKS

In this paper, we have applied the memory-function formalism of Zwanzig and Mori to elucidate the general form of the density-density correlation function $\langle\tilde{\rho}(S)\rho^*\rangle$ in one-component fluids. By assuming isotropy in the fluid system, we arrive at a general (but quite complex) form for $\langle\tilde{\rho}(S)\rho^*\rangle$ given in Eqs. (18). We show that it is equivalent to the result previously obtained by Kadanoff and Martin[15]; in particular, we relate their dispersion function to the appropriate memory functions through Eqs. (29)–(31). By specializing the general form of Eqs. (18) to specific hydrodynamic situations, we rederive in Secs. IV and V results previously obtained[8–11] from macroscopic points of view.

In particular, when the coupling between heat flux $\tilde{q}$ and the viscosity stress tensor $\overleftrightarrow{\sigma}$ is negligible, we isolate the three relaxation functions $\tilde{\phi}_{qq}^{-1}(S)$, $\tau_d(S)$, and $\tau_S(S)$, defined in Eqs. (31a) and (32), which represent the relaxing behavior of thermal diffusivity, bulk viscosity, and shear viscosity, respectively. If one replaces the thermal diffusivity $D_T(k, S)$ by its static local value, then one is led to two distribution functions of relaxation times: one for bulk and another for shear processes.[29,30] If, instead, one chooses to ignore the frequency dependence of the memory functions $\tilde{\phi}_{qq}$, $\tilde{\phi}_{11}$, and $\tilde{\phi}_{12}$, then one arrives at the single-relaxation models for the relaxing transport behavior for thermal conductivity,[31] bulk viscosity,[8] and shear viscosity.[10]

We further show that the model discussed in Sec. V, which takes into account the $\vec{q}$, $\overleftrightarrow{\sigma}$ coupling in terms of a single parameter [defined in Eq. (41)], is equivalent to the general result obtained[22] from the thermodynamic theory of relaxation. The model implies the use of a static local thermal diffusivity, and exponentially relaxing shear and bulk viscosities. In general, the presence of $\vec{q}$, $\overleftrightarrow{\sigma}$ coupling implies an extra relaxation function $\phi_{q\sigma i}(S)$. [Isotropy in the fluid system would imply that $\tilde{\phi}_{\sigma i q}(S)$ and $\tilde{\phi}_{q\sigma i}(S)$ are not independent.] It is found that the single-relaxation-time model of Bhatia and Tong[10] implies the neglect of this relaxation (memory) function [see Eq. (A39) in the Appendix]. The presence of this extra relaxation function is consistent with the more recent finding[30] that for highly viscous liquids one does need two relaxation functions associated with bulk processes.

We would expect that in Eqs. (18c) and (18d), $\tilde{\phi}_{q\sigma_i}$ and $\tilde{\phi}_{\sigma i q}$ can be neglected for molecular gases, thus, the model described in Sec. V would provide a unified prescription to analyze the Rayleigh-Brillouin scattering experiments on molecular gases, thereby predicting the extent of $\vec{q}$, $\overleftrightarrow{\sigma}$ coupling. Recently, such experiments have been performed on gaseous H_2, D_2, and HD, and in analyzing them it has been found[32] that the theories[5,8,9] which do not take this coupling into account properly show some definite areas of disagreement with experiment.

In this paper, we have chosen to concentrate only on the correlated translational motion in molecular fluids. Memory-function formalism can also be applied to study the collective modes arising from internal motions. The set of dynamical variables appropriate for such a study should include the internal degrees of freedom explicitly. Such a study can provide a microscopic basis for the shear waves[33] which have been observed experimentally in a variety of liquids and for which the existing theories are either phenomenological or of macroscopic thermodynamic type. Also, in this paper we have not expressed the various memory functions in terms of molecular interactions, even though the formalism provides such a connection via the Liouville operator for the system. Understanding the dynamical role that the molecular interactions play in the detailed behavior of the memory functions is difficult even for the monatomic systems and has to be gained for such simpler systems first; however, by using some physical models for the memory functions, one can now proceed to study the detailed role that memory functions play in the experimentally observable behavior of the different space-time-dependent correlation functions in molecular fluids.

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APPENDIX

We attempt the justification of Eqs. (35) and (43) here. Using Eq. (16) and ignoring a_i and b_i, it can be shown that

$$D_T(k, S) = \frac{1}{ik} \frac{\langle \tilde{q}(S) J^* \rangle}{\langle \tilde{\theta}(S) J^* \rangle} = \frac{\langle qq^* \rangle \langle \theta\theta^* \rangle^{-1}}{S + \tilde{\phi}_{qq}} \ . \qquad \text{(A1)}$$

Now, one can use Eq. (9a) to write the small-frequency limit of Eq. (A1) as

$$D_T = V_0 \tilde{\phi}_{qq}^{-1} \langle qq^* \rangle / (k_B T_0^2 \rho_0 c_v) \ , \qquad \text{(A2)}$$

where we have used the relation [Eq. (49) of Ref. 23]

$$\langle \theta\theta^* \rangle = \rho_0 k_B T_0^2 c_v / V_0 \ . \qquad \text{(A3)}$$

Here c_v is, in general, a function of k; we expect this dependence to be slowly varying in the hydrodynamic region. Quantities which are labeled with a zero subscript refer to equilibrium values.

Now, the general expression for thermal conductivity[34] is

$$\lambda = \lim_{S \to 0} \lim_{k \to 0} V_0 T_0^{-1} \int_0^\infty dt\, e^{-St}$$

$$\times \int_0^{(k_B T_0)^{-1}} d\lambda \, \langle q(-t - i\lambda) q^* \rangle \ , \qquad \text{(A4)}$$

which reduces to

$$\lambda = \lim_{S \to 0} \lim_{k \to 0} \frac{V_0}{k_B T_0^2} \langle \tilde{q}(S) q^* \rangle \qquad \text{(A5)}$$

in the classical limit. Using Eq. (16), this is

$$\lambda = \lim_{S \to 0} \frac{V_0}{k_B T_0^2} \frac{\langle qq^* \rangle}{S + \tilde{\phi}_{qq}} = \frac{V_0 \langle qq^* \rangle}{\tilde{\phi}_{qq}(0) k_B T_0^2} \ . \qquad \text{(A6)}$$

Equations (A2) and (A6) imply $D_T \to \lambda / \rho_0 c_v$, which is Eq. (36a). Now let us define the temperature fluctuations $T(k,t)$ as

$$\theta(k,t)=\rho_0 c_v(k) T(k,t) \ . \tag{A7}$$

Then, Eq. (9c) becomes

$$\pi_{ij}=\langle\pi_{ij}\rho^*\rangle\langle\rho\rho^*\rangle^{-1}\rho+\langle\pi_{ij}T^*\rangle\langle TT^*\rangle^{-1}T+\sigma_{ij} \ . \tag{A8}$$

Hence, we obtain

$$\tfrac{1}{3}\langle\textstyle\sum_i\pi_{ii}\rho^*\rangle\langle\rho\rho^*\rangle^{-1}=\langle JJ^*\rangle\langle\rho\rho^*\rangle^{-1} \ ,$$

which reduces to the thermodynamic relation

$$\left(\frac{\partial P}{\partial\rho}\right)_T=\frac{B_T}{\rho_0} \ .$$

This justifies Eq. (35b). Equation (A8) also gives

$$\tfrac{1}{3}\langle\textstyle\sum_i\pi_{ii}T^*\rangle\langle TT^*\rangle^{-1}=(1/ik)\langle\dot{J}\,T^*\rangle\langle TT^*\rangle^{-1} \ , \tag{A9}$$

which reduces to the thermodynamic relation

$$\left(\frac{\partial P}{\partial T}\right)_\rho=\beta_T B_T \ , \tag{A10}$$

where β_T is the coefficient of thermal expansion. From fluctuation theory,[35] one has the sum-rule results:

$$\langle\rho\rho^*\rangle=\rho_0^2 k_B T_0/(V_0 B_T) \ , \tag{A11}$$

$$\langle JJ^*\rangle=\rho_0 k_B T_0/V_0 \ , \tag{A12}$$

$$\langle TT^*\rangle=k_B T_0^2/(V_0\rho_0 c_v) \ . \tag{A13}$$

Hence, using Eqs. (A7), (A9), (A10), (A12), and (A13), we get

$$A(k)=\frac{\langle\dot{J}\theta^*\rangle\langle\dot{\theta}J^*\rangle}{\langle\theta\theta^*\rangle\langle JJ^*\rangle}\rightarrow\frac{(ik\beta_T B_T)^2 T_0}{(\rho_0^2 c_v)}=\frac{(B_T-B_S)k^2}{\rho_0} \ . \tag{A14}$$

This justifies Eq. (35c). Finally, we note that Eqs. (35d) and (35e) are consistent with the isotropic property of fluids and Eq. (10).

In order to justify Eq. (43), it is necessary to briefly discuss the pertinent aspects of the thermodynamic theory of relaxation.[12] We recall that the usual linearized macroscopic equations relevant for the study of longitudinal disturbances are

$$\frac{\partial\rho}{\partial t}+\rho_0\sum_i\frac{\partial u_i}{\partial x_i}=0 \ \text{(continuity)} \ , \tag{A15}$$

$$\rho_0\frac{\partial u_i}{\partial t}=-\frac{\partial P}{\partial x_i}+\sum_i\frac{\partial\sigma_{ji}}{\partial x_j} \quad \text{(Navier-Stokes)} \ , \tag{A16}$$

$$q_i=-\lambda\frac{\partial T}{\partial x_i} \ \text{(heat flow)} \ . \tag{A17}$$

When the transport coefficients become frequency dependent, the above equations are not appropriate. For the case of relaxing bulk viscosity, it has been shown[8] that a convolution time-integral-type modification of the last term in Eq. (A16) is a good model provided the internal and external degrees of freedom are weakly coupled. In general, the presence of such a coupling will modify both Eqs. (A16) and (A17). The microscopic approach described in this article contains, in principle, all such couplings in its formalism. Macroscopically, however, the thermodynamic theory of relaxation also attempts to describe relaxing bulk processes by the fewest possible macroscopic parameters. In its simplest form, the theory supplements the usual thermodynamic description (in terms of two variables) by introducing a third variable ξ, or its conjugate force Z, which would relax with time, say with relaxation time τ_d. Any quantity measured at constant ξ is labeled with a superscript ∞, corresponding to the limit $\omega\tau_d\rightarrow\infty$, e.g., c_v^∞; unlabeled quantities correspond to $\omega\tau_d\rightarrow 0$, i.e., measured at constant Z. The first law of thermodynamics then gives

$$\delta\epsilon=\hat{T}\delta S+(\hat{P}/\rho_0^2)\,\delta\rho+Z\delta\xi \ , \tag{A18}$$

where the thermodynamic quantities are defined per unit mass. $\hat{T}$ and $\hat{P}$ in Eq. (A18) will, in general, be different from the usual thermodynamic variables T, P. In calculating the density-density correlation function, one needs to transform Eqs. (A15)–(A17) to the variables $\hat{T}$, $\hat{P}$ and needs in addition the relaxation equation for ξ,[10]

$$\frac{\partial\xi}{\partial t}=-L\,\delta Z \ , \tag{A19}$$

which can also be written as

$$\left(\frac{\partial Z}{\partial\xi}\right)_{S,\rho}\left[\left(\frac{\partial\xi}{\partial\rho}\right)_{\hat{T},Z}\frac{\partial\rho}{\partial t}+\left(\frac{\partial\xi}{\partial\hat{T}}\right)_{\rho,Z}\frac{\partial\hat{T}}{\partial t}+\left(\frac{\partial\xi}{\partial Z}\right)_{\hat{T},\rho}\frac{\partial Z}{\partial t}\right]$$

$$=-\frac{1}{\tau_d}\,\delta Z \ , \tag{A20}$$

where

$$L\left(\frac{\partial Z}{\partial\xi}\right)_{S,\rho}=\frac{1}{\tau_d} \ .$$

The fluctuation in pressure is

$$\delta\hat{P}=\frac{B_T}{\rho_0}\,\delta\rho+\beta_T B_T\,\delta\hat{T}+\left(\frac{\partial\hat{P}}{\partial Z}\right)_{\hat{T},\rho}\delta Z \ . \tag{A21}$$

Comparing the Fourier transform of Eq. (A21) with Eq. (A8), one sees that the pressure fluctuations are not the usual thermodynamic pressure fluctuations δP, but are $\frac{1}{3}\sum_i\pi_{ii}$. Similarly, the temperature fluctuations $\delta\hat{T}$ in Eq. (A21) are not the usual temperature fluctuations δT, but also include the contribution due to the irreversible bulk processes. This is made more evident by noting that fluctuation analysis[35] gives

$$\langle\rho(k)\rho^*(k)\rangle=\rho_0^2 k_B T_0/(V_0 B_T) \ , \tag{A11$'$}$$

$$\langle T(k)\,T^*(k)\rangle=k_B T_0^2/(V_0\rho_0 c_v) \ , \tag{A13$'$}$$

$$\langle S(k)S^*(k)\rangle=k_B c_P/(V_0\rho_0) \ , \tag{A22}$$

$$\langle P(k)\,P^*(k)\rangle = k_B T_0 B_S / V_0\ , \tag{A23}$$

whereas the thermodynamic theory of relaxation gives the same relations as in Eqs. (A11) and (A22), but Eqs. (A13) and (A23) are replaced by

$$\langle \hat{T}(k)\,\hat{T}^*(k)\rangle = k_B T_0^2/(V_0\rho_0 c_v^\infty)\ , \tag{A24}$$

$$\langle \hat{P}(k)\,\hat{P}^*(k)\rangle = k_B T_0 B_S^\infty / V_0\ . \tag{A25}$$

Furthermore, we find

$$\langle Z(k)\,\hat{T}^*(k)\rangle = -\frac{k_B T_0^2}{\rho_0 V_0 c_v^\infty}\left(\frac{\partial S}{\partial \xi}\right)_{\hat{T},\rho}\ , \tag{A26}$$

$$\langle Z(k)\,Z^*(k)\rangle = \frac{k_B T_0}{\rho_0 V_0}\left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho}\ , \tag{A27}$$

$$\langle Z(k)\,S^*(k)\rangle = \langle Z(k)\,\rho^*(k)\rangle = 0\ . \tag{A28}$$

For the justification of Eqs. (43), we also need the following easily provable results:

$$c_v - c_v^\infty = T_0\left(\frac{\partial S}{\partial Z}\right)^2_{\hat{T},\rho}\left(\frac{\partial Z}{\partial \xi}\right)_{\hat{T},\rho}\ , \tag{A29}$$

$$B_S^\infty - B_S = \rho_0^{-1}\left(\frac{\partial \hat{P}}{\partial Z}\right)^2_{S,\rho}\left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho}\ , \tag{A30}$$

$$B_{\hat{T}}^\infty - B_{\hat{T}} = \rho_0^{-1}\left(\frac{\partial \hat{P}}{\partial Z}\right)^2_{\hat{T},\rho}\left(\frac{\partial Z}{\partial \xi}\right)_{\hat{T},\rho}\ , \tag{A31}$$

$$c_v/c_v^\infty = \left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho}\Big/\left(\frac{\partial Z}{\partial \xi}\right)_{\hat{T},\rho}\ , \tag{A32}$$

$$\left(\frac{\partial \xi}{\partial \hat{T}}\right)_{\rho,Z} = \left(\frac{\partial S}{\partial Z}\right)_{\hat{T},\rho}\ . \tag{A33}$$

We can now proceed to justify Eqs. (35) and (43) in presence of $\vec{q}, \overleftrightarrow{\sigma}$ coupling. Towards this end, we need to rewrite the Fourier transforms of Eqs. (A20) and (A21) in terms of the ordinary thermodynamic variables $\rho(k)$, $T(k)$, and $\sigma_{ij}(k)$. Because of the properties of $\rho(k)$ and $S(k)$ [as distinct from those of $\hat{T}(k)$ and $\hat{P}(k)$], it is desirable to write the fluctuation $\delta\hat{T}$ in Eq. (A21) in the form

$$\delta\hat{T} = \left(\frac{\partial \hat{T}}{\partial S}\right)_{\rho,Z}\delta S + \left(\frac{\partial \hat{T}}{\partial \rho}\right)_{S,Z}\delta\rho + \left(\frac{\partial \hat{T}}{\partial Z}\right)_{S,\rho}\delta Z\ .$$

Here, the last term arises from the bulk processes and is orthogonal to the other two terms. Also, the first two terms together represent the ordinary temperature fluctuation, so that

$$\delta\hat{T} = \delta T + \left(\frac{\partial \hat{T}}{\partial Z}\right)_{S,\rho}\delta Z\ , \tag{A34}$$

$$\langle Z(k) T^*(k)\rangle = \langle Z(k)\,\rho^*(k)\rangle = \langle \rho(k) T^*(k)\rangle = 0\ , \tag{A35}$$

in accordance with Eq. (12), but in contrast to Eq. (A26). The Fourier transform of Eq. (A21) can now be written, using Eq. (A34), as

$$\hat{P}(k) = \frac{B_T}{\rho_0}\,\rho(k) + \beta_T B_T\,T(k) + \left[\beta_T B_T\left(\frac{\partial \hat{T}}{\partial Z}\right)_{S,\rho} + \left(\frac{\partial \hat{P}}{\partial Z}\right)_{\hat{T},\rho}\right] Z(k)\ . \tag{A36}$$

Equation (A36) can be directly compared with Eq. (9c). For simplicity, we neglect shear viscosity in what follows, i.e., we set $\sigma_1 = \sigma_2 = \sigma_3 = \sigma$ and $\sigma_{11} = \sigma_{12}$ so that one can identify

$$\sigma \to \left[\beta_T B_T\left(\frac{\partial \hat{T}}{\partial Z}\right)_{S,\rho} + \left(\frac{\partial \hat{P}}{\partial Z}\right)_{\hat{T},\rho}\right] Z(k) \equiv \left(\frac{\partial \hat{P}}{\partial Z}\right)_{S,\rho} Z(k)\ . \tag{A37}$$

It is then straightforward to verify that Eq. (35d) remains valid even in presence of coupling. Justification for other identifications in Eqs. (35) remains unaffected. To justify (43), we note that the rate of change of entropy fluctation, $\dot{S}(k)$, is related to the heat flux $q(k)$ by[36]

$$\rho_0 T_0 \dot{S} = ikq\ . \tag{A38}$$

Hence, using (A37) and neglecting the memory functions $\phi_{\sigma_i q}$, $\phi_{q\sigma_i}$, as is done in the model of Sec. V, one has

$$b = -\frac{\langle \dot{\sigma} q^*\rangle}{\langle q q^*\rangle} \to -\left(\frac{\partial \hat{P}}{\partial Z}\right)_{S,\rho}\frac{\langle \dot{Z}\dot{S}^*\rangle}{\langle \dot{S}\dot{S}^*\rangle}\,\frac{ik}{\rho_0 T_0}\ .$$

Writing

$$\dot{Z} = \left(\frac{\partial Z}{\partial \rho}\right)_{S,\xi}\dot{\rho} + \left(\frac{\partial Z}{\partial S}\right)_{\rho,\xi}\dot{S} + \left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho}\dot{\xi}\ ,$$

and using Eq. (A19) and the orthogonality relations in Eqs. (12), one gets

$$b \to -\frac{ik}{\rho_0 T_0}\left(\frac{\partial \hat{P}}{\partial Z}\right)_{S,\rho}\left(\frac{\partial Z}{\partial S}\right)_{\rho,\xi} = \frac{ik}{\rho_0 T_0}\left(\frac{\partial \hat{P}}{\partial Z}\right)_{S,\rho}\left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho}\left(\frac{\partial \xi}{\partial S}\right)_{\rho,Z}\ ;$$

but

$$\left(\frac{\partial \xi}{\partial S}\right)_{\rho,Z} = -\left(\frac{\partial \hat{T}}{\partial Z}\right)_{S,\rho} = \left(\frac{\partial S}{\partial Z}\right)_{\hat{T},\rho}\left(\frac{\partial \hat{T}}{\partial S}\right)_{\rho,Z} = \frac{T_0}{c_v}\left(\frac{\partial S}{\partial Z}\right)_{T,\rho}\ .$$

Therefore, we obtain

$$b \to \frac{ik}{\rho_0 c_v}\left(\frac{\partial \hat{P}}{\partial Z}\right)_{S,\rho}\left(\frac{\partial S}{\partial Z}\right)_{\hat{T},\rho}\left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho}\ . \tag{A39}$$

From Eq. (42a), using Eqs. (A3), (A7), (A29), (A30), and (A39), one immediately obtains the following result:

$$\frac{D_T'}{D_T} \to \frac{c_v}{c_v^\infty}\ , \tag{A40}$$

which, together with Eq. (35a), implies Eq. (43a).

Now, since

$$\langle \theta \dot{J}^* \rangle \langle JJ^* \rangle^{-1} = \langle \dot{J} T^* \rangle^* \langle JJ^* \rangle^{-1} \rho_0 c_v \tag{A41}$$

by Eq. (A7), we can show using Eqs. (A9), (A10), and (A13) that

$$\langle \theta \dot{J}^* \rangle \langle JJ^* \rangle^{-1} \rightarrow -ik\beta_T B_T T_0 / \rho_0 \,. \tag{A42}$$

Hence, Eq. (42b) can be reduced, using Eqs. (A39), (A40), (A42), (35c), and (35d), to

$$\mathcal{B}(k,S) \rightarrow \frac{c_v^\infty}{c_v} \, \frac{B_S^\infty - B_S}{\rho_0} + \left(1 - \frac{c_v^\infty}{c_v}\right) \frac{B_S - B_T}{\rho_0} - 2\, \frac{\beta_T B_T T_0 c_v^\infty}{\rho_0^2 c_v^2}$$

$$\times \left(\frac{\partial \hat{P}}{\partial Z}\right)_{S,\rho} \left(\frac{\partial S}{\partial Z}\right)_{\hat{T},\rho} \left(\frac{\partial Z}{\partial \xi}\right)_{S,\rho} \,. \tag{A43}$$

Now we use Eqs. (A10) and (A29)–(A33) and the relation

$$\left(\frac{\partial \hat{P}}{\partial Z}\right)_{\hat{T},\rho} = \left(\frac{\partial \hat{P}}{\partial Z}\right)_{S,\rho} + \left(\frac{\partial S}{\partial Z}\right)_{\hat{T},\rho} \left(\frac{\partial \hat{P}}{\partial S}\right)_{\rho,Z}$$

to yield the result

$$\mathcal{B}(k,S) \rightarrow \rho_0^{-2} \left(\frac{\partial \hat{P}}{\partial Z}\right)^2_{\hat{T},\rho} \left(\frac{\partial Z}{\partial \xi}\right)_{\hat{T},\rho} = \frac{B_{\hat{T}}^\infty - B_{\hat{T}}}{\rho_0} \,. \tag{43'}$$

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