

expansion and evaluated leading terms for the phonon frequency and damping which were not available before.

The rather sizable reduction in algebraic complexity using our method seems to indicate that the next order, i. e., the two-ring terms, is not out of reach. The study of two-ring diagrams will be much more than just a mathematical exercise. It will be a critical examination of the so-called "four-phonon process" and it will indicate the role of close-range interactions. The numerical results (5.38)–(5.40) are not expected to be too useful in fitting the pho-

non dispersion data of superfluid helium. Of course, useful numerical coefficients are not the objective of our calculation. We hope the above analysis has demonstrated a more novel method of calculation as well as given a clearer physical picture.

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Hydrodynamics and Collective Angular-Momentum Fluctuations in Molecular Fluids*

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Generalized hydrodynamics for classical fluids composed of structured molecules is discussed from a fundamental microscopic viewpoint. The analysis is concentrated on collective fluctuations of the intrinsic molecular angular momentum, and their coupling to the conserved densities of particle number, linear momentum, and energy. It is found from symmetry that the transverse components of linear and angular momentum are dynamically coupled, while the longitudinal angular momentum density moves independently of the other variables. By using the Zwanzig-Mori projection-operator technique, we derive closed and rigorous equations of motion for the set of fluctuations considered. For the case where the intrinsic angular momentum is not far from being separately conserved, approximations can be motivated which reduce these equations to simple relaxation equations, valid for small k and long times. General, Kubo-type expressions for the relaxation coefficients are given. Finally, sum-rule considerations are presented from which these coefficients can be approximately calculated.

I. INTRODUCTION

The dynamics of collective fluctuations in mon-

atomic classical gases and liquids has been studied extensively and is, in general terms, fairly well understood. Comparatively little is known about the

dynamical behavior of molecular fluids which are capable of translational as well as internal, e. g., rotational, motion. While there is an increasing number of experiments¹⁻⁴ and computer studies^{5,6} on polyatomic liquids, their interpretation is often uncertain. Typical of this are the studies of depolarized light scattering by Stegeman and Stoicheff,²⁻⁴ In several polyatomic liquids including quinoline, they have observed a depolarized doublet centered at the incoming laser frequency. It is not clear whether this splitting is caused by high-frequency shear waves⁷ as they suggested, by individual molecular orientational fluctuations,⁸ or by some other mechanism.⁹ The difficulty in molecular fluids is due to the fact that translational and internal modes of collective motion are generally mixed. In this paper we will restrict attention to a particularly interesting example of this, namely, the coupling between molecular rotations and mass flow.

Consider, for simplicity, a classical isotropic one-component fluid of rigid structured molecules. The rotation of the α th molecule around its center of mass can be described by its space-fixed angular momentum $\vec{S}^\alpha(t)$ which we shall call its "spin." We will be interested in the decay of fluctuations of the corresponding locally averaged spin density $\vec{S}(rt)$, and its dynamical coupling to fluctuations of the linear momentum density $\vec{g}(rt)$. Since local deviations from equilibrium are usually small, such fluctuations can be conveniently discussed in terms of equilibrium-averaged, space- and time-dependent correlation functions¹⁰ which contain all the information obtained from scattering experiments and some of the information obtained from computer studies. Using the projection-operator methods of Zwanzig¹¹ and Mori¹² we will derive and discuss generalized Langevin equations for the fluctuations of $\vec{g}(rt)$ and $\vec{S}(rt)$. These equations are rigorous and non-Markovian. In general, they are useful mainly in clarifying certain general properties of the fluctuation spectrum. However, in the important region of slow spatial variation (small wave number k) and long times (small frequency ω), they reduce to simple relaxation equations similar to those of phenomenological theory,¹³ provided that the spin density is "almost" conserved, in a manner described below. In this case, we obtain Kubo-like expressions for the relaxation coefficients in terms of well-defined correlation functions of microscopic fluxes. The description can be extended to shorter times if one is willing to approximate the memory functions involved by appropriate parametrized trial functions. Parameters can then be determined from equilibrium statistical mechanics through the use of high-frequency sum rules, and these can then be used to calculate the low-frequency relaxation coefficients. This procedure has been quite successful in simple liquids.¹⁴

Before embarking on a formal discussion, let us briefly recall the "hydrodynamical" theory of a viscous molecular fluid given by de Groot and Mazur.¹³ Strictly speaking, the hydrodynamical description (valid in the limit of small k and long times) is, of course, the same in polyatomic as in monatomic fluids and is given by the Navier-Stokes equations for the densities of mass, energy, and momentum.¹⁵ Because of the conservation laws, local fluctuations in any of these quantities decay extremely slowly since they cannot decay locally but must spread throughout the system. It is important to realize that there is no additional hydrodynamic mode (i. e., a mode whose lifetime increases to infinity as $k \rightarrow 0$) that would correspond to conservation of angular momentum, since the translational part of the angular momentum density $\vec{r} \times \vec{g}(rt)$ is not a local quantity. Indeed, a local fluctuation in the spin density $\vec{S}(rt)$, for example, can be locally and therefore rapidly transformed into translational vortex motion whose slow decay is then described by the usual equations of hydrodynamics.

The equations of de Groot and Mazur¹³ are supposed to be valid at shorter times when this process of the decay of spin-density fluctuations into vorticity takes place. From symmetry, $\vec{S}(rt)$ can only couple to the transverse part of $\vec{g}(rt)$. For spatial Fourier components, with \vec{k} chosen in the z direction, the phenomenological equations are of the form

$$\frac{\partial}{\partial t} g_x(k, t) = -\frac{\eta + \eta_r}{m\rho} k^2 g_x(k, t) + 2ik \frac{\eta_r}{I\rho} S_y(k, t), \quad (1.1a)$$

$$\frac{\partial}{\partial t} S_y(k, t) = -2ik \frac{\eta_r}{m\rho} g_x(k, t) - 4 \frac{\eta_r}{I\rho} S_y(k, t), \quad (1.1b)$$

where η and η_r are shear and rotational viscosity coefficients, respectively, ρ is the number density, m the molecular mass, and I the average moment of inertia of a molecule. The longitudinal spin density $S_z(k, t)$ does not couple to the hydrodynamical variables and relaxes according to the equation

$$\frac{\partial}{\partial t} S_z(k, t) = -4 \frac{\eta_r}{I\rho} S_z(k, t). \quad (1.2)$$

The interesting feature of these equations is that the same coefficient η_r describes both the decay of spin-density fluctuations and their coupling to mass flow. This is a consequence of angular momentum conservation. We will verify this behavior from the microscopic theory, and show that near $k=0$ it can be extended to arbitrary times or frequencies when η_r becomes a frequency-dependent memory function.

Equations (1.1) and (1.2) are essentially hydrodynamic and expected to hold only when $(ka)^2 \ll 1$, where $a = (I/m)^{1/2}$ characterizes the size of a molecule. If also $(ka)^2 \ll \eta_r/\eta$, the normal modes have a particularly simple physical meaning; they can be written in the form

$$(\vec{\nabla} \times \vec{v} - 2\vec{\omega})_y(\vec{k}, t) \sim e^{-i(\eta r/I\rho)t}, \quad (1.3a)$$

$$(\vec{g} + \frac{1}{2}\vec{\nabla} \times \vec{S})_x(\vec{k}, t) \sim e^{-i(\eta/m\rho)k^2 t}. \quad (1.3b)$$

$\vec{\nabla} \times \vec{v}(rt) \equiv \vec{\nabla} \times \vec{g}(rt)/m$ is the local angular velocity of vortex motion which first equalizes with the local angular velocity of molecular rotation $\vec{\omega}(rt) = \vec{S}(rt)/I$.¹⁶ The slower process (1.3b) is the truly hydrodynamic one of viscous flow; we show in Appendix A that $\vec{g} + \frac{1}{2}\vec{\nabla} \times \vec{S}$ is the total momentum density if the finite size of molecules is taken into account.

Much of this article is devoted to a derivation of phenomenological equations like (1.1) and (1.2) starting from the Liouville equation of motion. In Sec. II, we introduce the relevant dynamical variables $\{A_\mu\} = \{\rho, u, \vec{g}, \vec{S}\}$, namely, the densities of number, energy, momentum, and intrinsic angular momentum. We then use the symmetries of the system to show that S_y couples only to g_x , for example, while the longitudinal component S_x is uncoupled from the rest. In Sec. III we write down rigorous Langevin-type equations for the A_μ , and discuss their general properties. Sections IV and V are then devoted to the reduction of these rigorous and complicated equations to simple relaxation equations like those exhibited above. In Sec. VI we indicate how the relaxation coefficients could be approximately calculated from various sum rules.

II. DEFINITIONS AND SYMMETRIES

We begin with a definition of the microscopic densities with which we are concerned. These include the locally conserved densities $\rho(rt)$, $u(rt)$, and $\vec{g}(rt)$ of particle number, energy, and momentum which are needed if the hydrodynamic limit is to be rendered properly, and the spin density $\vec{S}(rt)$ in whose correlations we are particularly interested. They can be defined by

$$\rho(\vec{r}t) = \sum_{\alpha} \delta(\vec{r} - \vec{r}^{\alpha}(t)), \quad (2.1a)$$

$$u(\vec{r}t) = \sum_{\alpha} \epsilon^{\alpha}(t) \delta(\vec{r} - \vec{r}^{\alpha}(t)), \quad (2.1b)$$

$$\vec{g}(\vec{r}t) = \sum_{\alpha} \vec{p}^{\alpha}(t) \delta(\vec{r} - \vec{r}^{\alpha}(t)), \quad (2.1c)$$

$$\vec{S}(\vec{r}t) = \sum_{\alpha} \vec{S}^{\alpha}(t) \delta(\vec{r} - \vec{r}^{\alpha}(t)), \quad (2.1d)$$

where the sums extend over all molecules of the system. $\vec{r}^{\alpha}(t)$ and $\vec{p}^{\alpha}(t)$ are the center-of-mass position and momentum of the α th molecule at time t , $\vec{S}^{\alpha}(t)$ is its internal angular momentum about its center of mass, with respect to the laboratory frame of reference. Its energy $\epsilon^{\alpha}(t)$ includes translational and rotational kinetic energy as well as the potential energy in the generally noncentral field of its neighbors. These definitions treat the molecules as oriented and spinning particles but neglect their finite size otherwise. They are appropriate only if the fluctuations occur at wavelengths $\lambda \gg a$. (This point is dealt with in Appendix A.)

ρ , u , and \vec{g} obey differential conservation laws. In particular, momentum conservation can be written as (summation over repeated vector indices is implied)

$$\frac{\partial}{\partial t} g_i(\vec{r}t) + \nabla_j \tau_{ij}(\vec{r}t) = 0. \quad (2.2)$$

Here, τ_{ij} is the microscopic stress tensor which serves as a momentum current. In simple liquids, τ_{ij} is symmetric. In a system of molecules which interact through noncentral forces, τ_{ij} has an antisymmetric part $\tau_{ij}^a = \frac{1}{2}(\tau_{ij} - \tau_{ji})$ whose spatial integral is given by

$$\begin{aligned} \int d\vec{r} \tau_{ij}^a(\vec{r}) &\equiv \sqrt{N} \tau_{ij}^a(k=0) \\ &= -\frac{1}{4} \epsilon_{ijk} \sum_{\alpha \neq \beta} [(\vec{r}^{\alpha} - \vec{r}^{\beta}) \times \vec{F}^{\alpha\beta}]_k, \end{aligned} \quad (2.3)$$

where $F^{\alpha\beta}$ is the force between molecules α and β , N is the number of molecules, and ϵ_{ijk} is the Levi-Civita symbol. τ_{ij}^a is thus a torque density which couples rotational and translational motion. Because of this coupling, the spin density is not independently conserved but obeys the equation

$$\frac{\partial}{\partial t} S_i(\vec{r}t) + \nabla_j \sigma_{ij}(\vec{r}t) = \epsilon_{ijk} \tau_{jk}^a(\vec{r}t), \quad (2.4)$$

where σ_{ij} is the spin current.¹⁷ Combining Eqs. (2.2) and (2.4), one can readily see that the total angular momentum $\int d\vec{r} [\vec{r} \times \vec{g}(\vec{r}t) + \vec{S}(\vec{r}t)]$ is conserved. However, the spin density is independently conserved only if the intermolecular forces are purely central so that $\tau_{ij}^a = 0$.

The central objects of our discussion are the correlation functions

$$C_{\mu\nu}(\vec{r}t) = \langle A_{\mu}(00) A_{\nu}(\vec{r}t) \rangle - \langle A_{\mu}(00) \rangle \langle A_{\nu}(\vec{r}t) \rangle \quad (2.5)$$

and, more conveniently, their Fourier transforms ($k \neq 0$)

$$C_{\mu\nu}(\vec{k}t) = \langle A_{\mu}^*(\vec{k}, 0) A_{\nu}(\vec{k}t) \rangle. \quad (2.6)$$

Here, $\langle \rangle$ indicates an equilibrium average, and $\{A_{\mu}(rt)\}$ is the set of dynamical variables of Eqs. (2.1a)-(2.1d) whose Fourier components are given by, e. g.,

$$\vec{S}(\vec{k}, t) = N^{-1/2} \sum_{\alpha} \vec{S}^{\alpha}(t) e^{i\vec{k} \cdot \vec{r}^{\alpha}(t)}, \quad (2.7)$$

and similarly for the other variables. We shall always choose \vec{k} to point in the z direction.

Before discussing the equations of motion for the correlation matrix $C_{\mu\nu}(\vec{k}, t)$, let us exploit the symmetries of the system. In writing down Eqs. (2.5) and (2.6) we have tacitly assumed translational invariance in space and time. Since all of the variables $A_{\mu}(\vec{r}t)$ are real we get in addition

$$C_{\mu\nu}(\vec{k}, t) = C_{\mu\nu}^*(-\vec{k}, t) = C_{\nu\mu}(-\vec{k}, -t). \quad (2.8)$$

Invariance under time reversal results in

$$C_{\mu\nu}(\vec{k}, t) = \epsilon_\mu^T \epsilon_\nu^T C_{\mu\nu}(\vec{k}, -t), \quad (2.9)$$

where ϵ_μ^T is the signature of A_μ ; $\epsilon^T = 1$ for $\{\rho, u\}$ and $\epsilon^T = -1$ for $\{\vec{g}, S\}$. We further assume that both the Hamiltonian and the equilibrium ensemble are invariant under the parity operation, excluding from consideration such systems as nonracemic mixtures of optically active molecules. In this case we have

$$C_{\mu\nu}(\vec{k}, t) = \epsilon_\mu^P \epsilon_\nu^P C_{\mu\nu}(-\vec{k}, t), \quad (2.10)$$

where $\epsilon^P = 1$ for $\{\rho, u, \vec{S}\}$ and $\epsilon^P = -1$ for \vec{g} . The most important simplification results from rotational invariance in association with parity. For example, $\langle g_i^*(\vec{k}, 0) S_j(\vec{k}, t) \rangle$ transforms like a pseudotensor under improper rotations. However, the only function of \vec{k} with that property is $\epsilon_{ijl} k_l = \epsilon_{ij3} k$, so that we have

$$\langle g_i^*(\vec{k}, 0) S_j(\vec{k}, t) \rangle = i \epsilon_{ij3} k F_{gs}(k^2, t), \quad (2.11)$$

where $F_{gs}(k^2, t)$ is a scalar function of k^2 , and is real and even in t because of (2.8) and (2.9). Similar arguments show that $\{A_\mu\}$ separates into four sets, namely,

$$\{A_\mu\} = \{\rho, u, g_d\}, \{S_d\}, \{g_x, S_y\}, \{g_y, S_x\}, \quad (2.12)$$

such that members of any two sets are uncorrelated. The last two sets are, of course, equivalent. We note that these arguments hold only in the absence of long-range order, excluding liquid crystals in which three-dimensional rotational symmetry is broken.

Finally, let us note an important positiveness property which is connected to the dynamical stability of the system. If we define Fourier transforms in time by

$$C_{\mu\nu}(\vec{k}, t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\omega t} \tilde{C}_{\mu\nu}(\vec{k}, \omega), \quad (2.13)$$

then $\tilde{C}_{\mu\nu}(\vec{k}, \omega)$ is a positive matrix in any stable system,

$$\sum_{\mu\nu} \alpha_\mu^* \tilde{C}_{\mu\nu}(\vec{k}, \omega) \alpha_\nu \geq 0 \quad (2.14)$$

for all \vec{k}, ω and arbitrary $\{\alpha_\mu\}$. Equation (2.14) is easily proved from the definition (2.5) with the aid of Bochner's theorem.¹⁸

III. EQUATION OF MOTION

We now turn to the equation of motion for the correlation matrix $C(\vec{k}, t) \equiv \{C_{\mu\nu}(\vec{k}, t)\}$. It is by now well known that it can always be written in the compact form

$$\left(\frac{\partial}{\partial t} - i\Omega(\vec{k}) \right) C(\vec{k}, t) + \int_0^t d\tau K(\vec{k}, t-\tau) C(\vec{k}, \tau) = 0, \quad (3.1)$$

where $\Omega(\vec{k})$ is the frequency matrix and $K(\vec{k}, t)$ the memory-function matrix. Its existence can be

proved without difficulty from the positiveness property Eq. (2.14) (see Appendix B). Using the projector method of Zwanzig¹¹ and Mori¹² we can write down "explicit" expressions for Ω and K .

If L is the Liouville operator, defined such that $A_\mu(\vec{k}, t) = e^{iL t} A_\mu(\vec{k})$, then Ω and K are given by

$$\hat{\Omega}_{\mu\nu}(\vec{k}) \equiv \Omega_{\mu\lambda}(\vec{k}) C_{\lambda\nu}(\vec{k}) = \langle A_\mu^*(\vec{k}) L A_\nu(\vec{k}) \rangle, \quad (3.2)$$

$$\hat{K}_{\mu\nu}(\vec{k}, t) \equiv K_{\mu\lambda}(\vec{k}, t) C_{\lambda\nu}(\vec{k}) \\ = \langle \dot{A}_\mu^*(\vec{k}) e^{t(1-P)L} (1-P) \dot{A}_\nu(\vec{k}) \rangle, \quad (3.3)$$

where $C_{\mu\nu}(\vec{k}) \equiv C_{\mu\nu}(\vec{k}, t=0)$. P is the projector onto the subspace of the variables $\{A_\mu(\vec{k})\}$ which we can define by

$$PG(\vec{k}) \equiv \sum_{\mu'} A_\mu(\vec{k}') C_{\mu\nu}^{-1}(\vec{k}') \langle A_\nu^*(\vec{k}') G(\vec{k}) \rangle \\ = A_\mu(\vec{k}) C_{\mu\nu}^{-1}(\vec{k}) \langle A_\nu^*(\vec{k}) G(\vec{k}) \rangle. \quad (3.4)$$

Because of translational invariance, only the k th component of P is effective in (3.3). We have included the $\sum_{\mu'}$ in (3.4) to demonstrate that P is invariant under rotations and parity, as well as time reversal. It is therefore clear that $\hat{K}_{\mu\nu}(\vec{k}, t)$ has precisely the same symmetry properties as $C_{\mu\nu}(\vec{k}, t)$; in particular,

$$\hat{K}_{\mu\nu}(\vec{k}, t) = \hat{K}_{\mu\nu}^*(-\vec{k}, t) = \hat{K}_{\nu\mu}(-\vec{k}, -t) \\ = \epsilon_\mu^T \epsilon_\nu^T \hat{K}_{\mu\nu}(\vec{k}, -t) = \epsilon_\mu^P \epsilon_\nu^P \hat{K}_{\mu\nu}(-\vec{k}, t), \quad (3.5)$$

where $K_{\mu\nu}(\vec{k}, t) \neq 0$ only if μ, ν represent variables of the same set in (2.12). It is also easy to see that $\hat{\Omega}_{\mu\nu}(\vec{k}) = -i \hat{C}_{\mu\nu}(\vec{k}, t=0)$ connects only variables $A_\mu(\vec{k})$ with opposite signatures under time reversal; it is therefore zero in all but the first set of variables of (2.12), $\{\rho, u, g_d\}$. Note that this implies that

$$P\hat{S}(\vec{k}) = P\hat{g}_x(\vec{k}) = P\hat{g}_y(\vec{k}) = 0. \quad (3.6)$$

Most importantly, the Fourier transform

$$\hat{K}_{\mu\nu}(\vec{k}, \omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \hat{K}_{\mu\nu}(\vec{k}, t) \quad (3.7)$$

is a positive definite matrix

$$\sum_{\mu\nu} \alpha_\mu^* \hat{K}_{\mu\nu}(\vec{k}, \omega) \alpha_\nu \geq 0 \quad (3.8)$$

for all \vec{k}, ω and arbitrary $\{\alpha_\mu\}$. This is easily proved from (2.14) and (3.1), or directly from (3.3) using Bochner's theorem. Equation (3.8) guarantees that the solutions of Eq. (3.1) decay, rather than grow, as $t \rightarrow \infty$.

Equation (3.1) poses an initial value problem; it is more convenient to analyze it in terms of Laplace transforms which we define by

$$C_{\mu\nu}(\vec{k}, z) = \int_0^\infty dt e^{-izt} C_{\mu\nu}(\vec{k}, t), \quad \text{Im } z < 0 \quad (3.9)$$

and similarly for $K_{\mu\nu}(\vec{k}, z)$. Both functions are then analytic in the lower half of the complex z plane; in the upper half-plane, they are defined by analytic

continuation. Equation (3.1) then takes the form

$$[z - \Omega(\vec{k}) - iK(\vec{k}, z)]C(\vec{k}, z) = (1/i)C(\vec{k}). \quad (3.10)$$

For a system which is invariant under rotations and reflections, Eq. (3.10) separates into four uncoupled matrix equations, one each for the sets of variables of (2.12). These equations will be analyzed in Secs. IV and V. Since we are mostly interested in the spin density $\vec{S}(\vec{k}, t)$, we will not discuss any further the set $\{\rho, u, g_z\}$ from which \vec{S} is completely decoupled. In the limit of small k and long times (small $|\text{Im}z|$), the equations for this set reduce in a familiar manner¹⁹ to the Navier-Stokes equations of hydrodynamics, and only the numerical values of the transport coefficients reflect the molecular structure of the fluid.

We already noted that for the remaining variables, $\Omega(\vec{k}) = 0$. As to the initial values $C_{\mu\nu}(\vec{k})$ we shall assume for simplicity that the static correlations between the vector variables \vec{g} and \vec{S} are of the simple form

$$\langle g_i^*(\vec{k})g_j(\vec{k}) \rangle = mk_B T \delta_{ij}, \quad (3.11a)$$

$$\langle S_i^*(\vec{k})S_j(\vec{k}) \rangle = Ik_B T \delta_{ij}, \quad (3.11b)$$

$$\langle g_i^*(\vec{k})S_j(\vec{k}) \rangle = 0, \quad (3.11c)$$

where m is the molecular mass, $I = \frac{1}{3}\text{tr}\bar{I}$ is the scalar part of the moment-of-inertia tensor of a molecule, and $k_B T$ is the temperature in energy units.

Equations (3.11a)-(3.11c) are exact classically if, as is usually the case, the molecules interact via velocity and spin-independent forces. Otherwise, they hold at least in the limit as $k \rightarrow 0$; they are not crucial to our discussion, and could easily be dropped.

IV. LONGITUDINAL SPIN FLUCTUATIONS

We first consider the longitudinal spin density $S_z(k, t)$ since it is fully decoupled from the other variables under consideration. Its correlation function is given from Eq. (3.10) by

$$C_{S_z S_z}(k, z) \equiv C_S^1(k, z) = \frac{(1/i)Ik_B T}{z - iK_S^1(k, z)} \quad (4.1)$$

in terms of the memory function

$$K_S^1(k, z) = (Ik_B T)^{-1} \int_0^\infty dt e^{-i\epsilon t} \times \langle \dot{S}_z^*(k) e^{i(1-P)Lt} (1-P) \dot{S}_z(k) \rangle. \quad (4.2)$$

From Eq. (2.4) we have

$$\dot{S}_z(k) = ik\sigma_{zz}(k) + 2\lambda\hat{\tau}_{xy}^a(k), \quad (4.3)$$

where we have written $\tau_{ij}^a = \lambda\hat{\tau}_{ij}^a$ for the antisymmetric part of the microscopic stress tensor to display the strength λ of the interparticle torque.

A. Infinitesimal Torque

Let us consider infinitesimally small k and λ ,

the case where S_z is almost conserved. Since all of the conserved variables have been projected out, $K_S^1(k, t)$ presumably decays as $e^{-\gamma t}$ where $1/\gamma$ is a microscopic relaxation time and finite even as $k \rightarrow 0$ and $\lambda \rightarrow 0$; this means that $K_S^1(k, z)$ is analytic in z for $\text{Im}z < \gamma$. However, $K_S^1(k, z)$ vanishes as $k \rightarrow 0$ and $\lambda \rightarrow 0$, so that in this limit $C_S^1(k, z)$ has a single pole at the origin which reflects Eq. (4.3). Assuming that $K_S^1(k, z)$ is a well-behaved function of both k and λ , this single pole moves upward on the imaginary z axis. To lowest order in k and λ , it is given by

$$z = iK_S^1(k, z=0) = i(4\lambda^2\nu_r + k^2D), \quad (4.4)$$

where the rotational viscosity coefficient ν_r is given by

$$\nu_r = (Ik_B T)^{-1} \lim_{\epsilon \rightarrow 0} \lim_{\substack{k \rightarrow 0 \\ \lambda \rightarrow 0}} \int_0^\infty dt e^{-\epsilon t} \times \langle \hat{\tau}_{xy}^{a*}(k) e^{i(1-P)Lt} (1-P) \hat{\tau}_{xy}^a(k) \rangle, \quad (4.5)$$

and the spin diffusion coefficient D by

$$D = (Ik_B T)^{-1} \lim_{\epsilon \rightarrow 0} \lim_{\substack{k \rightarrow 0 \\ \lambda \rightarrow 0}} \int_0^\infty dt e^{-\epsilon t} \times \langle \sigma_{zz}^*(k) e^{i(1-P)Lt} (1-P) \sigma_{zz}(k) \rangle. \quad (4.6)$$

In the limit of small k and λ , the behavior of $C_S^1(k, z)$ is dominated by the "hydrodynamic" pole (4.4). Instead of (4.1), we can write the correlation function as

$$C_S^1(k, z) = \frac{(1/i)Ik_B T}{z - i(4\lambda^2\nu_r + k^2D)}, \quad (4.7)$$

which corresponds to the equation of motion

$$\frac{\partial}{\partial t} S_z(k, t) = -(4\lambda^2\nu_r + k^2D)S_z(k, t) \quad (4.8)$$

for the longitudinal spin density. This is the equation (1.2) of de Groot and Mazur, with $\eta_r/I\rho = \lambda^2\nu_r$. However, Eq. (4.8) contains the additional relaxation term k^2D to account for spin diffusion.

Both transport coefficients ν_r and D are real and positive as is clear from Eq. (4.4): They are real because from Eqs. (3.5) the imaginary part of $K_S^1(k, \omega - i0)$ is odd in ω and vanishes at $\omega = 0$; they are positive because the real part of $K_S^1(k, \omega - i0)$ is positive [see Eq. (3.8)]. Both coefficients can also be expressed by Kubo relations which are obtained from Eqs. (4.5) and (4.6) by omitting the projector P everywhere. This is accomplished with the help of the relation²⁰

$$K_S^1(k, z) = \Phi_S^1(k, z)[1 + (i/z)\Phi_S^1(k, z)]^{-1}, \quad (4.9)$$

where $\Phi_S^1(k, z)$ is given by Eq. (4.2), but without the projector. To order k^2 and λ^2 , therefore, we have $K = \Phi$ and the projector P can be omitted from Eqs. (4.5) and (4.6).

ν_r can then be calculated from the autocorrelation

function of the total torque $\vec{N} = \lambda \vec{\hat{N}}$ which is given by [cf. Eqs. (2.3) and (2.4)]

$$\frac{\partial}{\partial t} \int d\vec{r} \vec{S}(\vec{r}, t) = \lambda \vec{\hat{N}}(t) = -\frac{1}{2} \sum_{\alpha \neq \beta} \vec{r}^{\alpha\beta}(t) \times \vec{F}^{\alpha\beta}(t), \quad (4.10)$$

and to which, obviously, only the noncentral interparticle forces contribute. With this definition of $\vec{\hat{N}}$, we get

$$\nu_r = (Ik_B T)^{-1} \lim_{\epsilon \rightarrow 0} \left(\frac{1}{3} N \right) \int_0^\infty dt e^{-\epsilon t} \langle \vec{\hat{N}}(0) \cdot \vec{\hat{N}}(t) \rangle, \quad (4.11)$$

where $\vec{\hat{N}}(t) = e^{iL_0 t} \cdot \vec{\hat{N}}(0)$ is calculated in the absence of noncentral forces.

Let us note here that the limit $\lambda \rightarrow 0$ does not necessarily imply that interparticle torques disappear completely. In this limit the Hamiltonian is separately invariant under rotations in coordinate space and in "spin space" so that the total spin $\vec{S} = \sum_\alpha \vec{S}^\alpha(t)$ is conserved even though the individual $\vec{S}^\alpha(t)$ might continue to depend on time. This would be the case, for example, if the potential energy between two particles contained terms of the type $V(|\vec{r}^{\alpha\beta}|) \times B(\theta^{\alpha\beta})$ where the function B depends only on the relative orientation of the particles, not on their position.

However, if there are no such terms left at $\lambda = 0$, we have $\vec{S}^\alpha(t) = \text{const}$ at $\lambda = 0$ for each particle. In this case, \vec{S}^α is just a tag attached to the molecule. D is then simply the self-diffusion coefficient. Indeed, noticing that $\sigma_{\alpha\alpha}(k=0) = N^{-1/2} \sum_\alpha S_\alpha^\alpha D_\alpha^\alpha / m$ we can, at $\lambda = 0$, take the spin average independently: $\langle S_\alpha^\alpha S_\alpha^\beta \rangle = \delta_{\alpha\beta} (Ik_B T)$. Then Eq. (4.6) reduces to the familiar form

$$D = \lim_{\epsilon \rightarrow 0} \frac{1}{3} \int_0^\infty dt e^{-\epsilon t} \langle \vec{v}(0) \cdot \vec{v}(t) \rangle_{\lambda=0} \quad (4.12)$$

in terms of the one-particle velocity autocorrelation function. Of course, in the absence of interparticle torques, the spin-density correlation function is simply proportional to the self- (or test-particle) correlation function, $C_{S_i S_j}(k, t) = \delta_{ij} (Ik_B T) F_S(k, t)$.

Finally, note that the Kubo relations (4.11) and (4.12) [or (4.6) without the P 's] can also be expressed in terms of the Fourier transform $\vec{C}(\omega) = 2 \text{Re} C(\omega - i0)$ by

$$\nu_r = (8Ik_B T)^{-1} \lim_{\omega \rightarrow 0} \lim_{\lambda \rightarrow 0} \lim_{k \rightarrow 0} (\omega^2 / \lambda^2) \vec{C}_S^i(k, \omega), \quad (4.13)$$

$$D = (2Ik_B T)^{-1} \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \lim_{\lambda \rightarrow 0} (\omega^2 / k^2) \vec{C}_S^i(k, \omega). \quad (4.14)$$

In these formulas, it is crucial that the limits be taken in the order indicated. This is apparent from the hydrodynamic form

$$\vec{C}_S^i(k, \omega) = 2Ik_B T \frac{4\lambda^2 \nu_r + k^2 D}{\omega^2 + (4\lambda^2 \nu_r + k^2 D)^2}. \quad (4.15)$$

B. Finite Small Torque

The assumption of an infinitesimally small non-

central force is, of course, quite restrictive. In this section we will relax this restriction somewhat, assuming that λ is finite but still small enough for the spin density to relax more slowly than other non-conserved microscopic variables. As λ increases, the hydrodynamic pole (4.4) of $C_S^i(k, z)$ solution of the equation

$$z - iK_S^i(k, z) = 0 \quad (4.16)$$

moves farther away from the real axis into the upper half z plane. From Eqs. (3.5) it is easy to see that $K_S^i(k, z) = [K_S^i(k, -z^*)]^*$, so that solutions to (4.16) come in conjugate pairs. Therefore, as long as the pole (4.4) remains single, it is forced to stay on the imaginary z axis. Let us first neglect terms of order k^2 . Then Eq. (4.16) reads

$$z = 4i\eta_r(z)/I\rho \equiv 4i\eta_r/I\rho, \quad (4.17)$$

where

$$\begin{aligned} \frac{1}{4} I\rho K_S^i(0, z) &\equiv \eta_r(z) \\ &= (12k_B T V)^{-1} \int_0^\infty dt e^{-izt} \langle \vec{N} \cdot e^{i(1-P)Lt} \vec{N} \rangle. \end{aligned} \quad (4.18)$$

We have inserted (4.10) into (4.2), and used rotational invariance. $4i\eta_r/I\rho$ is that value of z which solves Eq. (4.17). More to the point, it is the solution which moves to the origin as $\lambda \rightarrow 0$. For small λ , then, $4\eta_r/I\rho$ will still be considerably smaller than the imaginary parts of all other singularities of $C_S^i(k, z)$, and therefore will dominate the long-time behavior of $C_S^i(k, t)$. Only for such values of λ will the solution to (4.17) be useful. Note that η_r can no longer be written as a Kubo relation.

The correlation function can then be written in the form

$$C_S^i(k, z) \approx \frac{1}{i} Ik_B T \frac{Z_r}{z - 4i\eta_r/I\rho}. \quad (4.19)$$

The renormalized pole strength Z_r is the residue at the pole position, and is given by

$$Z_r^{-1} = 1 - \frac{4i}{I\rho} \left. \frac{d\eta_r(z)}{dz} \right|_{z=4i\eta_r/I\rho}. \quad (4.20)$$

It is not difficult to see that Z_r is real and positive; otherwise, Eq. (4.17) would have another solution closer to the real axis.

Equation (4.19) is valid near $k=0$, and for λ still so small that

$$4\eta_r/(I\rho) \ll \gamma. \quad (4.21)$$

Under this condition, the phenomenological equation (1.2) is therefore expected to hold for long times, i. e., times $t \gg 1/\gamma$. In calculating the correlation function from Eq. (1.2), its failure at short times has to be corrected by the renormalized pole strength Z_r . It measures the portion of the integrated power spectrum $\vec{C}_S^i(k, \omega)$ which is contained in the central peak

$$\frac{1}{2Ik_B T} \tilde{C}_S^t(k, \omega) = Z_r \frac{4\eta_r/I\rho}{\omega^2 + (4\eta_r/I\rho)^2} . \quad (4.22)$$

The rest of the integrated strength is given by $(1 - Z_r)$ and is distributed over a broad background with little structure, at least at small frequencies ω .

It may be worth pointing out that while Z_r is always positive, there is no general reason for it to be smaller than 1. Indeed, if $\eta_r(t) \sim e^{-\gamma t}$ for example, we have $Z_r > 1$, and the broad background in $\tilde{C}_S^t(k, \omega)$ is negative. It is only the total power spectrum, central peak plus background, which must be positive for all ω .

It is straightforward to include in the above equations terms of order k^2 which have been omitted here. In this case, a diffusion term is added in the denominator of Eq. (4.19).

C. Finite Torque

As the strength λ of the interparticle torques increases further, the decay times which are contained in $K_S^t(k, t)$ and $C_S^{(1)}(k, t)$ will be of the same order of magnitude. For small k , we can still write a spectral representation

$$C_S^{(1)}(k, z) = \frac{(1/i)Ik_B T}{z - 4i\eta_r(z)/I\rho} , \quad (4.23)$$

but it is hardly useful. In this case, the phenomenological equation (1.2) loses its validity, even for long times, and the spectrum can no longer be approximately represented by a Lorentzian.

V. TRANSVERSE FLUCTUATIONS

Let us now consider the transverse 2×2 correlation matrix

$$C_{\alpha\beta}^t(\vec{k}, t) = \langle A_\alpha^*(\vec{k}, 0) A_\beta(\vec{k}, t) \rangle , \quad (5.1)$$

with $A_1 = g_x$ and $A_2 = S_y$. The second set $\{g_y, S_x\}$ of transverse variables is, of course, equivalent. The general memory function [Eq. (3.10)] for the Laplace transform is now a 2×2 matrix equation

$$[z - iK^t(k, z)]C^t(k, z) = (1/i)C^t(k) , \quad (5.2)$$

with the initial values $C^t(k) = mk_B T$, $C_{22}^t(k) = Ik_B T$, and $C_{12}^t(k) = C_{21}^t(k) = 0$ as given by (3.11). The memory functions $K_{\alpha\beta}^t(k, z)$ can be read off from Eq. (3.3); e. g., we have

$$K_{11}^t(k, z) = (mk_B T)^{-1} \int_0^\infty dt e^{-izt} \langle \dot{g}_x^*(k) e^{i(1-P)Lt} \dot{g}_x(k) \rangle . \quad (5.3)$$

Let us now assume as before that k is small. We insert

$$\dot{g}_x = ik\tau_{xx} = ik(\tau_{xx}^s + \tau_{xx}^a) , \quad (5.4a)$$

$$\dot{S}_y = ik\sigma_{yx} - 2\tau_{xx}^a \quad (5.4b)$$

from Eqs. (2.2) and (2.4). Omitting only terms of order k^3 , $K^t(k, z)$ then takes the form

$$K^t(k, z) = \begin{pmatrix} k^2[\eta(z) + \eta_r(z)]/m\rho & -2ik\eta_r(z)/I\rho \\ 2ik\eta_r(z)/m\rho & 4\eta_r(z)/I\rho + k^2 D_t \end{pmatrix} , \quad (5.5)$$

where

$$\eta(z) = \rho/(k_B T) \int_0^\infty dt e^{-izt} \langle \tau_{xx}^{s*}(0) e^{i(1-P)Lt} \tau_{xx}^s(0) \rangle , \quad (5.6a)$$

$$D_t(z) = (Ik_B T)^{-1} \int_0^\infty dt e^{-izt} \langle \sigma_{xx}^*(0) e^{i(1-P)Lt} \sigma_{xx}(0) \rangle , \quad (5.6b)$$

$$\eta_r(z) = \rho/(k_B T) \int_0^\infty dt e^{-izt} \langle \tau_{xx}^{a*}(0) e^{i(1-P)Lt} \tau_{xx}^a(0) \rangle . \quad (5.6c)$$

To derive (5.5), note that $\tau_{xx}^{s*}(0) \cdots \tau_{xx}^a(0) = 0$ from rotational invariance. We have assumed that there are no correlations between $\tau^a(0)$ and $\sigma(0)$; this can always be arranged.¹⁷ Equation (5.2), with $K^t(k, z)$ as given in (5.5), is valid for small k but arbitrary frequency z (and torque strength λ). The interesting feature of the matrix K^t of (5.5) is the multiple occurrence of the function $\eta_r(z)$. Note that because of rotational invariance, $\eta_r(z)$ is the same function which we defined in (4.18), and which thus also determines the motion of the longitudinal spin component. It is an expression of angular momentum conservation that this one function $\eta_r(z)$ describes, for small k , the decay of longitudinal and transverse spin motion, as well as the coupling of spin and linear momentum.

As it stands $K^t(kz)$ of (5.5) is not very useful, however, since the functional form of $\eta_r(z)$, etc., is difficult to determine. However, if the torque strength λ is small (but finite) we can effectively replace $K^t(k, z)$ by a z -independent matrix of the same structure to obtain an equation for $C^t(kz)$ which holds for small k and long times. The argument is very similar to that presented in Sec. IV, and we will therefore be brief. The dominant poles of $C^t(k, z)$ are obtained by solving

$$\det[z - iK^t(k, z)] = 0 . \quad (5.7)$$

Using (5.5) it is easy to see that one of these poles is given to order k^2 by

$$z = ik^2 \eta/m\rho , \quad (5.8)$$

so that $\eta \equiv \eta(z=0)$ is the shear viscosity. Indeed, an argument similar to that following Eq. (4.9) can be used to show that at $z=0$, the projector can be omitted from Eq. (5.6a) and we obtain the familiar Kubo relation²¹

$$\eta = \lim_{\epsilon \rightarrow 0} \lim_{k \rightarrow 0} \rho/(k_B T) \int_0^\infty dt e^{-\epsilon t} \langle \tau_{xx}^{s*}(k, 0) \tau_{xx}^s(k, t) \rangle . \quad (5.9)$$

Note that it is only the symmetric part of the microscopic stress tensor which determines the shear viscosity.

To order k^2 , Eq. (5.9) has a second solution where we have

$$z = 4i\eta_r(z)/(I\rho) + ik^2[\eta_r(z)/(m\rho) + D_t(z)] \quad (5.10a)$$

$$\equiv 4i\eta_r/(I\rho) + ik^2[\eta_r/(m\rho) + D_t], \quad (5.10b)$$

where (5.10b) defines that solution of (5.10a) which vanishes as $k \rightarrow 0$ and $\lambda \rightarrow 0$. η_r is therefore the same constant rotational viscosity which was given in Eq. (4.17); the transverse-spin-diffusion constant D_t is equal to the corresponding longitudinal D [which we omitted from (4.17) and (4.19)] only in the conserving limit $\lambda \rightarrow 0$; in this case, both reduce to D of Eq. (4.12).

For infinitesimal k and small λ , the two poles (5.8) and (5.10b) are closer to the real axis than all other singularities of $C^t(k, z)$, and dominate the long-time behavior of $C^t(k, t)$. For long times, we can therefore replace Eq. (5.2) by

$$[z - iR^t(k)] C^t(k, z) = (1/i)[C^t(k) - Z^t(k)], \quad (5.11)$$

with the relaxation matrix

$$R^t(k) = \begin{pmatrix} k^2(\eta + \eta_r)/(m\rho) & -2ik\eta_r/(I\rho) \\ 2ik\eta_r/(m\rho) & 4\eta_r/(I\rho) + k^2D_t \end{pmatrix} \quad (5.12)$$

to order k^2 . $R^t(k)$ is thus of the same form $K^t(k, z)$ in (5.5) but with constant coefficients so that Eq. (5.11) yields only the dominant poles (5.8) and (5.10b). Since (5.11) is a long-time equation, the initial value matrix on the right-hand side is changed from $C^t(k)$ by

$$Z^t(k) = Ik_B T(1 - Z_r) \begin{pmatrix} 0 & -(i/2)k \\ (i/2)k & 1 \end{pmatrix} \quad (5.13)$$

to order k^2 , where Z_r is the normalized pole strength defined in (4.20). Equation (5.13) is simply obtained by the same procedure that led to (4.19).

According to Eq. (5.11) then, the correlation functions can be obtained from the equations of motion for the local variables

$$\frac{\partial}{\partial t} g_x = -\frac{\eta + \eta_r}{m\rho} k^2 g_x + 2ik \frac{\eta_r}{I\rho} S_y, \quad (5.14)$$

$$\frac{\partial}{\partial t} S_y = -2ik \frac{\eta_r}{m\rho} g_x - \left(4 \frac{\eta_r}{I\rho} + k^2 D_t\right) S_y,$$

which are the phenomenological equations (1.1a), and (1.1b) modified to account for spin diffusion. From our discussion it is now clear that these equations can be used for infinitesimal k and small λ , i. e., if we have

$$k^2 \eta / m\rho \ll 4\eta_r / I\rho \ll \gamma, \quad (5.15)$$

where $1/\gamma$ is a microscopic relaxation time. They describe the dynamics only for long times, $t \gg 1/\gamma$. Their failure at shorter times is compensated in Eq. (5.11) by the pole strength matrix Z^t .

VI. SUM-RULE CALCULATIONS

The considerations that lead to Eqs. (5.12) or (5.14) do not, of course, constitute a calculation of the transport coefficients. In a sense, Eqs. (5.2) and (5.5) merely shift the problem from the calculation of the correlation functions $C^t(k, z)$ to that of calculating the "frequency-dependent transport coefficients" $\eta(z)$, $\eta_r(z)$, and $D_t(z)$, which is almost as forbidding. However, for small frequencies these functions are presumably smoother than $C^t(kz)$ itself, and we expect that a simple parametrized ansatz for their frequency (or time) dependence will be successful.

Consider the three functions of time $\eta(t)$, $\eta_r(t)$, and $D_t(t)$ whose Laplace transforms are given by Eqs. (5.6a)–(5.6c). We write these memory functions in terms of their initial value, and their time dependence:

$$\eta(t) = \eta_\infty \phi_1(t), \quad (6.1a)$$

$$\eta_r(t) = \eta_{r,\infty} \phi_2(t), \quad (6.1b)$$

$$D_t(t) = D_{t,\infty} \phi_3(t), \quad (6.1c)$$

where $\phi_i(t=0) = 1$, $i = 1, 2, 3$. The initial values are then given by

$$\eta_\infty = \rho(k_B T)^{-1} \langle \tau_{xx}^{s*}(0) \tau_{xx}^s(0) \rangle, \quad (6.2a)$$

$$\eta_{r,\infty} = \rho(k_B T)^{-1} \langle \tau_{xx}^{a*}(0) \tau_{xx}^a(0) \rangle, \quad (6.2b)$$

$$D_{t,\infty} = (Ik_B T)^{-1} \langle \sigma_{xx}^*(0) \sigma_{xx}(0) \rangle. \quad (6.2c)$$

It is not difficult to calculate these values from equilibrium statistical mechanics, and we shall consider them known. Note that Eqs. (6.2a)–(6.2c) express the frequency sum rules

$$\rho(k_B T)^{-1} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 C_{11}^t(k, \omega) = k^2(\eta_\infty + \eta_{r,\infty}) + O(k^4), \quad (6.3a)$$

$$\rho(k_B T)^{-1} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega^2 C_{12}^t(k, \omega) = 2ik \eta_{r,\infty} + O(k^3), \quad (6.3b)$$

$$\rho(k_B T)^{-1} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^2 C_{22}^t(k, \omega) = 4\eta_{r,\infty} + k^2 I\rho D_{t,\infty} + O(k^4). \quad (6.3c)$$

The real dynamical problem is contained in the functions $\phi_i(t)$. Their time dependence stems from the numerous microscopic processes which are not connected to a conservation law but which can take place at short times. While the $\phi_i(t)$ can in general be of quite forbidding complexity, they all presumably decay within times of the order of a collision time $\tau = \gamma^{-1}$. For an order-of-magnitude calculation, it is probably sufficient to lump all these rapid processes together in one relaxation function

$$\phi_i(t) = \phi(t) = e^{-\gamma t} \quad (6.4a)$$

or

$$\phi_i(z) = \phi(z) = (iz + \gamma)^{-1}. \quad (6.4b)$$

If this is accepted, we can use (6.1a) and (5.8) to express the shear viscosity η in terms of the relaxation frequency γ , or vice versa:

$$\eta = \eta_\infty / \gamma \equiv \eta_\infty \tau. \quad (6.5)$$

Furthermore, Eqs. (6.1b), (6.1c), (5.10), and (4.20) give the rotational viscosity η_r , the renormalized pole strength Z_r , and the spin diffusion coefficient D_i as

$$\frac{4\eta_r}{I\rho} = \frac{1}{2} \gamma \left[1 - \left(1 - \frac{16\eta_{r,\infty}}{I\rho\gamma^2} \right)^{1/2} \right], \quad (6.6)$$

$$Z_r = \left(1 - \frac{4\eta_r}{I\rho} \frac{\eta_r}{\eta_{r,\infty}} \right)^{-1}, \quad (6.7)$$

$$D_i = \frac{D_{i,\infty} \eta_r}{\eta_{r,\infty}} + \frac{(Z_r - 1) \eta_r}{m\rho}. \quad (6.8)$$

These equations allow us to calculate η_r , Z_r , and D_i in terms of η if the initial values of (6.2) are known. (Note that $Z_r > 1$ here.) Whereas the ansatz (6.4) is crude, it should give results of the right order of magnitude, a welcome feature at this point since we know of no measurements of η_r .²²

Equations (6.1a)–(6.4b) constitute the simplest in a series of approximations that can be used to calculate transport coefficients from sum rules, and to extend the theory to shorter times and possibly larger values of k . All of these approximations consist in parametrizing the time dependence of the memory functions $K_{\mu\nu}(k, t)$, and determining parameters from sum rules like (6.3). In simple liquids, this procedure has been very successful.¹⁴ We refrain here from writing down the relevant expressions for a molecular fluid since too little is known at present about sum rules of higher order.

APPENDIX A: ROTATIONAL CONTRIBUTION TO $\vec{g}^{\text{tot}}(r, t)$

In this appendix, we show that there is a rotational contribution $\frac{1}{2} \vec{\nabla} \times \vec{S}(r, t)$ to the momentum density if the finite size of molecules is accounted for. The argument is very similar to that familiar one which shows that a magnetization $\vec{M}(r, t)$ contributes to the electromagnetic current an amount $c \vec{\nabla} \times \vec{M}(r, t)$.

If we resolve each molecule into the atoms of which it consists, the total momentum density, which includes internal motion, should be written as (time dependence is omitted)

$$\vec{g}^{\text{tot}}(\vec{r}) = \sum_{\alpha} \sum_{\nu_{\alpha}} \vec{p}^{\alpha, \nu} \delta(\vec{r} - \vec{r}^{\alpha, \nu}), \quad (A1)$$

where $\vec{r}^{\alpha, \nu}$ and $\vec{p}^{\alpha, \nu}$ are position and momentum of the ν th atom within the α th molecule. Center-of-

mass position \vec{r}^{α} and momentum \vec{p}^{α} are defined by

$$\vec{r}^{\alpha, \nu} = \vec{r}^{\alpha} + \vec{\xi}^{\alpha, \nu} \quad \text{with} \quad \sum_{\nu_{\alpha}} m^{\alpha, \nu} \vec{\xi}^{\alpha, \nu} = 0, \quad (A2a)$$

$$\vec{p}^{\alpha, \nu} = (m^{\alpha, \nu} / m^{\alpha}) \vec{p}^{\alpha} + \vec{\pi}^{\alpha, \nu} \quad \text{with} \quad \sum_{\nu_{\alpha}} \vec{\pi}^{\alpha, \nu} = 0, \quad (A2b)$$

where $m^{\alpha, \nu}$ is the mass of the ν_{α} th atom and m^{α} is the molecular mass. If Eqs. (A2a) and (A2b) are inserted in (A1) we obtain, after some simple manipulations,

$$g_i^{\text{tot}}(\vec{r}) = g_i(\vec{r}) + \nabla_j \Gamma_{ij}(\vec{r}), \quad (A3a)$$

where

$$g_i(\vec{r}) = \sum_{\alpha} \vec{p}^{\alpha} \delta(\vec{r} - \vec{r}^{\alpha}) \quad (A3b)$$

is the center-of-mass momentum density which we introduced in Eq. (2.1c). The correction term Γ can be written as

$$\begin{aligned} \Gamma_{ij}(\vec{r}) = & - \sum_{\alpha} \sum_{\nu_{\alpha}} \left(\pi^{\alpha, \nu} + \frac{m^{\alpha, \nu}}{m^{\alpha}} p^{\alpha} \right) \\ & \times \xi_j^{\alpha, \nu} \int_0^1 ds \delta(\vec{r} - \vec{r}^{\alpha} - s \vec{\xi}^{\alpha, \nu}). \end{aligned} \quad (A3c)$$

In situations where variations in space are slow (i.e., k small so that $ka \ll 1$) we can expand the integrand of (A3c) in s retaining only the lowest-order term. We obtain

$$\begin{aligned} \Gamma_{ij}(\vec{r}) = & - \sum_{\alpha} \left(\sum_{\nu_{\alpha}} \pi_i^{\alpha, \nu} \xi_j^{\alpha, \nu} \right) \delta(\vec{r} - \vec{r}^{\alpha}) \\ \equiv & \Gamma_{ij}^a(\vec{r}) + \Gamma_{ij}^s(\vec{r}). \end{aligned} \quad (A4)$$

The antisymmetric part is

$$\begin{aligned} \Gamma_{ij}^s(\vec{r}) = & \frac{1}{2} \epsilon_{ijk} \sum_{\alpha} \left[\sum_{\nu_{\alpha}} (\xi_i^{\alpha, \nu} \pi_j^{\alpha, \nu} - \xi_j^{\alpha, \nu} \pi_i^{\alpha, \nu}) \right] \delta(\vec{r} - \vec{r}^{\alpha}) \\ = & \frac{1}{2} \epsilon_{ijk} S_k(\vec{r}), \end{aligned} \quad (A5)$$

since the term in square brackets is just the intrinsic angular momentum of the α th molecule. Combining (A3a) and (A5) and omitting Γ_{ij}^s , we therefore obtain

$$\vec{g}^{\text{tot}}(\vec{r}) = \vec{g}(\vec{r}) + \frac{1}{2} \vec{\nabla} \times \vec{S}(\vec{r}) \quad (A6)$$

for slow spatial variations.

Noting that $\pi_i^{\alpha, \nu} = m^{\alpha, \nu} \xi_i^{\alpha, \nu}$, the symmetric part is

$$\Gamma_{ij}^a(\vec{r}) = -\frac{1}{2} \sum_{\alpha} \left[\frac{\partial}{\partial t} \sum_{\nu_{\alpha}} m^{\alpha, \nu} \xi_i^{\alpha, \nu} \xi_j^{\alpha, \nu} \right] \delta(\vec{r} - \vec{r}^{\alpha}). \quad (A7)$$

Neglecting a gradient, Γ_{ij}^a is therefore the time derivative of a nonconserved quantity and can be omitted at long times.

In a sense, Eqs. (A3b) and (A3c) can be connected to Eq. (2.4). Let us assume that the intermolecular potential arises from central forces acting between any two atoms in the system. Then the total stress tensor, defined such that

$$\frac{\partial}{\partial t} g_i^{\text{tot}}(\vec{r}, t) + \nabla_j \tau_{ij}^{\text{tot}}(\vec{r}, t) = 0, \quad (\text{A8})$$

is symmetric. If we now use Eq. (2.2) and the rigorous equation

$$\int d\vec{r} \Gamma_{ij}^a(\vec{r}, t) = \frac{1}{2} \epsilon_{ijk} \int d\vec{r} S_k(\vec{r}, t), \quad (\text{A9})$$

we find

$$\frac{\partial}{\partial t} \int d\vec{r} S_i(\vec{r}, t) = \epsilon_{ijk} \int d\vec{r} \tau_{ij}^a(\vec{r}, t), \quad (\text{A10})$$

which is the content of Eq. (2.4).

APPENDIX B: EXISTENCE OF THE MEMORY FUNCTION

The positiveness property (2.14) of the correlation function implies the existence of a memory function such that Eq. (3.1) holds. In somewhat different language, this has been demonstrated before but the connection does not seem to be generally appreciated. The following quick proof is an adaptation of arguments given in the fundamental paper by Kadanoff and Martin.²³

For simplicity, we consider the case of one dynamical variable $A(\vec{k}, t)$ and its correlation function $C(\vec{k}, t)$, and suppress the argument \vec{k} ; the generalization to many variables is immediate. The Laplace transform $C(z)$ and Fourier transform $C(\omega)$, defined as in (2.13) and (3.9), are related by

$$C(z) = \int \frac{d\omega}{2\pi i} \frac{\tilde{C}(\omega)}{z - \omega}, \quad \text{Im} z < 0. \quad (\text{B1})$$

Now the positiveness of $\tilde{C}(\omega)$,

$$\tilde{C}(\omega) \geq 0, \quad (\text{B2})$$

implies that ($y > 0$)

$$\text{Re} C(x - iy) = y \int \frac{d\omega}{2\pi} \frac{\tilde{C}(\omega)}{(x - \omega)^2 + y^2} > 0. \quad (\text{B3})$$

Therefore, $C(z)$ vanishes nowhere in the lower-half z plane, and since it is analytic there, its inverse $C^{-1}(z)$ exists, and is analytic, too.

Now from (B1) we see that for large z , to order z^{-2} , we have

$$C(z) = \frac{1}{iz} \int \frac{d\omega}{2\pi} \tilde{C}(\omega) = \frac{1}{iz} C^0, \quad (\text{B4})$$

where $C^0 = C(t=0)$. Therefore, we can write

$$C^{-1}(z) = iz C^{0-1} + R(z), \quad (\text{B5})$$

where $R(z)$ is analytic, and at most constant as $z \rightarrow \infty$ in the lower half-plane. Or, multiplying by C^0 and defining

$$-i\Omega = \lim_{z \rightarrow \infty} C^0 R(z), \quad (\text{B6})$$

we obtain

$$C^0 C^{-1}(z) = i(z - \Omega) + K(z), \quad (\text{B7})$$

where $K(z)$ is analytic for $\text{Im} z < 0$, and vanishes as $z \rightarrow \infty$. It is therefore the Laplace transform of a function $K(t)$, and Eq. (B7) is equivalent to Eq. (3.1). Equation (B7) follows by the same line of arguments for the case of a correlation matrix $C_{\mu\nu}(\vec{k}, z)$. It can be used to directly obtain the symmetry and positiveness properties of $K(z)$ from those of $C(z)$.

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PHYSICAL REVIEW A

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Light Scattering from Shear Waves: The Role of Angular Momentum Fluctuations in Light Scattering*

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Recent light-scattering experiments which have investigated the splittings in the depolarized Rayleigh spectrum of certain nonassociated liquids are discussed in the context of generalized hydrodynamics. It is shown that a purely hydrodynamic or viscoelastic theory does not account for important features of the observed spectrum. However, if angular momentum fluctuations are considered, many of the features of the observed spectra can be accounted for. Moreover, a theory due to Rytov is discussed and studied in the context of generalized hydrodynamics.

I. INTRODUCTION

Recently, laser-light-scattering experiments¹⁻⁶ have been performed on a number of nonassociated liquids of relatively high viscosity (2 cP). In these liquids the depolarized spectrum contains, besides a broad background (of width 10 cm^{-1}), a sharp central peak (of width $\sim 0.1 \text{ cm}^{-1}$) that accounts for as much as 80% of the total depolarized spectrum. This narrow component sometimes shows a splitting into two components which are symmetrically displaced with respect to the incident light frequency. As in Brillouin scattering, this splitting varies directly as $\sin^2 \theta$, where θ is the scattering angle (i. e., the angle between the propagation directions of the incident and scattered light). The observed splitting occurs at frequencies which are roughly 20% of the Brillouin splittings, and therefore cannot be attributed to ordinary longitudinal sound as can the Brillouin splitting. It is the purpose of this article to review some of the explanations that have been offered for this phenomenon, and to offer yet another explanation.

Any theory of light scattering must proceed in two steps: (a) First it must be decided which fluctuations can couple to the radiation field; (b) second, a dynamical theory of the mechanism by which these fluctuations arise and regress must be developed.

Generally speaking, an isotropic fluid can support both longitudinal and transverse modes. These modes are specified by their frequency Ω and wave vectors \vec{q} . For small wave numbers q , the longitudinal modes are long-lived propagating modes (longitudinal sound) and the transverse modes are purely diffusive modes (shear modes). As the wave number q is increased, the lifetime of the

longitudinal modes decreases, whereas the transverse modes may change from purely diffusive to propagating modes with short lifetimes. In this limit the transverse modes may be regarded as "shear waves." They then correspond to transverse phonons (transverse sound) in glasses. The small- q modes in a fluid are adequately described by hydrodynamics, whereas the larger- q modes must be treated by other methods such as the theory of generalized hydrodynamics.

In Sec. II we discuss which modes in a liquid can couple to the radiation field. Let us assume here for the sake of argument that both longitudinal and transverse modes can couple to the light. Since light scattering probes modes of intermediate wave number ($q \sim 10^5 \text{ cm}^{-1}$), it is impossible to say whether or not the transverse modes corresponding to this value of q are propagating modes, without a detailed analysis.

If a fluid can support propagating transverse modes at the q of a light-scattering experiment, and if these transverse fluctuations couple to the radiation field, then it is expected that the depolarized spectrum will split. In this case the depolarized scattering can be regarded as a "Raman scattering" process in which a photon suffers an energy change Ω and a momentum change q , and thus "creates" or "annihilates" a transverse "phonon," thereby suffering a negative (Stokes) or positive (anti-Stokes) frequency shift as the case may be. The widths of these lines are determined by the lifetimes of the propagating transverse modes. If the only transverse modes occurring at q are purely diffusive modes, no splitting will be observed.

A split depolarized line has been observed in some molecular liquids. This has led some inves-