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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 experiments[1-6] 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 ~ 0.1 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 $\sin\frac{1}{2}\theta$, 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 ($q \sim 10^5$ 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-

tigators to conclude that these liquids can support shear waves at even the low wave numbers probed by light scattering.[4,7] This interpretation is supposedly supported by the fact that the splitting is observed in nonassociated liquids of high viscosity since the higher the viscosity, the more "glasslike" the liquid will be. Moreover, these investigators claim that ordinary viscoelastic theory[8-10] predicts the precise line shape and geometrical characteristics observed in the experiments. In Secs. V and VI we comment on certain weaknesses in this approach.

In Sec. III we consider an alternative explanation of these observations which, as far as we know, is entirely new. We investigate the effect of angular-momentum fluctuations on light-scattering spectroscopy.

In ordinary hydrodynamics a central role is played by the constants of the motion: mass, linear momentum, and energy. As we have shown elsewhere,[11] when a fluid contains structured molecules (polyatomic molecules), the angular momentum can be considered in addition to the above constants of the motion. When this is done it is found that the transverse velocity field in the fluid couples to the angular momentum of the individual molecules.[12] In fact, if a molecule is set in rotational motion in an otherwise stationary fluid it will slow down by creating a vortex (transverse) field around itself. This vortex field will then diffuse away on a very long time scale. This introduces a very long time tail in the decay of a molecule's angular momentum.[13] Although at exceedingly long times the effects of angular momentum disappear and ordinary hydrodynamics pertain, at short times the angular momentum must be considered. In this article we consider the consequences of this modified hydrodynamics on light scattering. This theory accounts for the major characteristics of the experiments.

II. LIGHT SCATTERING AND DIELECTRIC FLUCTUATIONS IN FLUIDS

It is well known[14] that when light with a wave vector $\vec{k}$ passes through an isotropic fluid, the component scattered with wave vector $\vec{k}'$ is due to a fluctuation of the dielectric tensor $\delta\overleftrightarrow{\epsilon}$, which has a Fourier component $\delta\overleftrightarrow{\epsilon}(q, t)$, where $\vec{q} = \vec{k}' - \vec{k}$. Since Rayleigh scattering produces an almost negligible change in the wavelength of the light $|\vec{k}| = |\vec{k}'|$, $\vec{q}$ bisects the angle $(\vec{k}, \vec{k}')$ and moreover has a magnitude $|\vec{q}| = 2k \sin\frac{1}{2}\theta$, where θ is the scattering angle. In what follows we consider the geometry shown in Fig. 1. Given this geometry and the subsequent remarks, we are only interested in dielectric fluctuations that have a spatial dependence e^{iqz}.

If $\hat{i}$ and $\hat{f}$ are unit vectors specifying the direction of polarization of the incident and scattered light $(\vec{E}_i, \vec{E}_f)$ (or more precisely specifying the orienta-

tions of the polarizer and the analyzer in the experiment), and ω_0 is the frequency of the (monochromatic) incident light, then $I_{if}(q, \Omega)$, the suitably normalized intensity of the scattered light of frequency $\omega_0 + \Omega$, is proportional to the power spectrum of the dielectric fluctuations $\delta\epsilon_{if}(q, t)$ at the frequency Ω so that

$$I_{if}(q, \Omega) = \frac{1}{2} \int_{-\infty}^{+\infty} dt\, e^{-i\Omega t} \langle \delta\epsilon_{if}^*(q, 0)\delta\epsilon_{if}(q, t)\rangle \ , \quad (1)$$

where $\langle\ \rangle$ indicates an equilibrium ensemble average, and

$$\delta\epsilon_{if}(q, t) = \hat{i} \cdot \delta\overleftrightarrow{\epsilon}(q, t) \cdot \hat{f} = \sum_{\alpha,\beta=1}^{3} i_\alpha \delta\epsilon_{\alpha\beta}(q, t)f_\beta \ . \quad (2)$$

Three different polarization directions are considered. These are defined in Fig. 2.

The specific components of the dielectric fluctuations that are responsible for each of these spectral components are from Eq. (2) and the geometry given in Fig. 1:

$$\delta\epsilon_{VV}(q, t) = \delta\epsilon_{yy}(q, t) \ , \quad (3a)$$

$$\delta\epsilon_{VH}(q, t) = \delta\epsilon_{yx}(q, t)\sin\tfrac{1}{2}\theta - \delta\epsilon_{yz}(q, t)\cos\tfrac{1}{2}\theta \ , \quad (3b)$$

$$\delta\epsilon_{HH}(q, t) = \delta\epsilon_{xx}(q, t)\sin^2\tfrac{1}{2}\theta - \delta\epsilon_{zz}(q, t)\cos^2\tfrac{1}{2}\theta$$
$$+ [\delta\epsilon_{zx}(q, t) - \delta\epsilon_{xz}(q, t)]\sin\tfrac{1}{2}\theta\,\cos\tfrac{1}{2}\theta \ . \quad (3c)$$

For 90° and 180° scattering these formulas reduce considerably:

$$\theta = \tfrac{1}{2}\pi:$$

$$\delta\epsilon_{VV}(q, t) = \delta\epsilon_{yy}(q, t) \ , \quad (4a)$$

$$\delta\epsilon_{VH}(q, t) = 2^{-1/2}[\delta\epsilon_{yx}(q, t) - \delta\epsilon_{yz}(q, t)] \ , \quad (4b)$$

$$\delta\epsilon_{HH}(q, t) = \tfrac{1}{2}[\delta\epsilon_{xx}(q, t) - \delta\epsilon_{zz}(q, t)$$
$$+ \delta\epsilon_{zx}(q, t) - \delta\epsilon_{xz}(q, t)] \ ; \quad (4c)$$
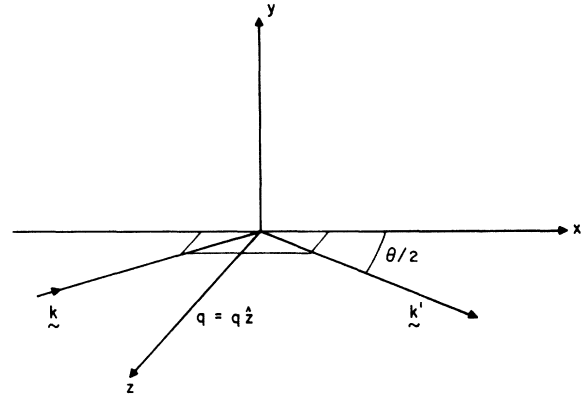
$$\theta = \pi:$$

FIG. 1. Scattering geometry adopted in this paper. x-z plane is called the scattering plane since the vectors $\vec{k}$ and $\vec{k}'$ (specifying the propagation directions of the incident and observed beams) lie entirely within this plane.
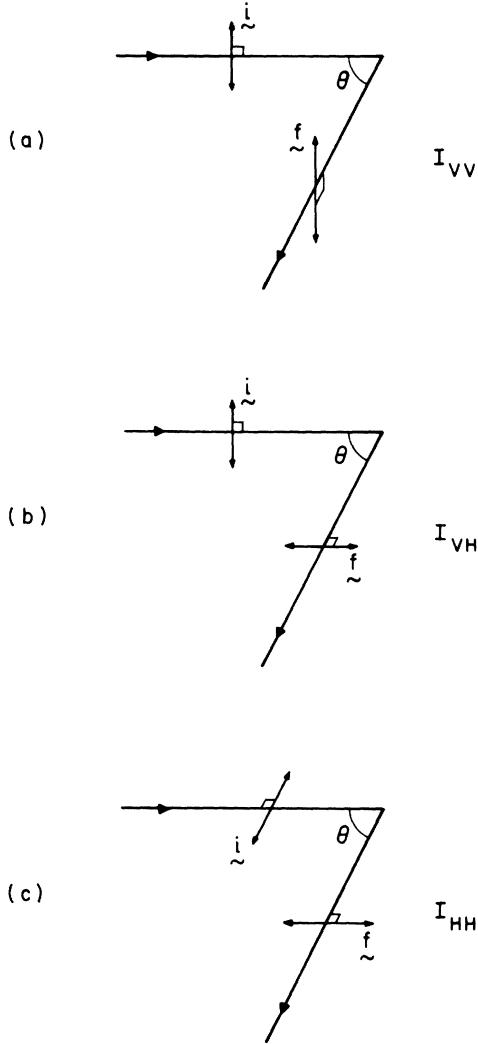
FIG. 2. Four different pairs of polarization directions considered: (a) fully polarized scattering; (b) depolarized scattering with either the initial or scattered polarization perpendicular to the scattering plane, $I_{VH} = I_{HV}$; (c) depolarized scattering with both $\hat{i}$ and $\hat{f}$ in the scattering plane.

$$\delta\epsilon_{VV}(q, t) = \delta\epsilon_{yy}(q, t) \quad , \tag{5a}$$

$$\delta\epsilon_{VH}(q, t) = \delta\epsilon_{yx}(q, t) \quad , \tag{5b}$$

$$\delta\epsilon_{HH}(q, t) = \delta\epsilon_{xx}(q, t) \quad . \tag{5c}$$

Thus we see that if the dielectric fluctuation is a scalar ($\delta\epsilon_{\alpha\beta} = \delta\epsilon_0 \delta_{\alpha\beta}$), as is usually assumed for monatomic fluids, the scattering is determined by the terms

$$\delta\epsilon_{VV}(q, t) = \delta\epsilon_0(q, t) \quad , \tag{6a}$$

$$\delta\epsilon_{VH} \equiv 0 \quad , \tag{6b}$$

$$\delta\epsilon_{HH}(q, t) = [\sin^2\tfrac{1}{2}\theta - \cos^2\tfrac{1}{2}\theta]\delta\epsilon_0 = -\cos\theta\,\delta\epsilon_0(q, t) \, . \tag{6c}$$

For 90° scattering only I_{VV} is nonzero, whereas for 180° scattering $I_{VV} = I_{HH}$ are both observed.

So far we only know that those thermal fluctuations in the medium which give rise to fluctuations in the dielectric tensor can scatter light. Thus the first thing that we must discuss is just what kinds of fluctuations in a medium can produce dielectric fluctuations.

In this paper we explore a phenomenological model for the dielectric fluctuations and the mechanical collective motions in the liquid from which they arise. Let us review a little background here. It is well known that the macroscopic dielectric constant of a one-component isotropic fluid in equilibrium is a scalar function of the density and the temperature:

$$\epsilon = \epsilon(\rho, T) \quad .$$

The actual density and temperature dependence of ϵ has been measured in a number of systems. It is obvious, therefore, that long-wavelength fluctuations $\delta\rho$ and δT of density and temperature will produce only scalar fluctuations in the dielectric constant, and thereby give rise only to I_{VV} and I_{HH} and not to I_{VH} components in the scattered light spectrum. If these are the only fluctuations considered, then we have

$$\delta\epsilon_{\alpha\beta}(q, t) = \left[\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T_0}\delta\rho(q, t) + \left(\frac{\partial\epsilon}{\partial\rho}\right)_{\rho_0}\delta T(q, t)\right]\delta_{\alpha\beta} \quad . \tag{7}$$

Usually, temperature fluctuations can be ignored compared with density fluctuations and Eq. (1) becomes

$$I_{VV}(q, \Omega) = \left(\frac{\partial\epsilon}{\partial\rho}\right)^2 S(q, \Omega) \quad ,$$

$$I_{HH}(q, \Omega) = (1 - \sin^2\theta)\left(\frac{\partial\epsilon}{\partial\rho}\right)^2 S(q, \Omega) \quad , \tag{8}$$

$$I_{VH}(q, \Omega) \equiv 0 \quad ,$$

where

$$S(q, \Omega) = \tfrac{1}{2}\int_{-\infty}^{+\infty} dt\, e^{-i\Omega t}\langle\delta\rho^*(q, 0)\delta\rho(q, t)\rangle$$

is the spectrum of density fluctuations of wave vector q. These equations have been very successful in describing the isotropic Brillouin spectrum observed in many simple liquids.[15]

Similar arguments can be developed to provide a reasonable guess at the form of the off-diagonal elements in the dielectric tensor. It is well known[14] that a fluid in steady flow possesses an anisotropic macroscopic dielectric constant which depends linearly on the velocity flow gradients:

$$\epsilon_{\alpha\beta} = \epsilon^{(0)}(\rho, T)\delta_{\alpha\beta} + X_0(\rho, T)v_{\alpha\beta}{}^{(0)} + X_2(\rho, T)v_{\alpha\beta}{}^{(2)} \quad , \tag{9a}$$

where

$$v_{\alpha\beta}^{(2)} \equiv \nabla_\alpha v_\beta + \nabla_\beta v_\alpha - \tfrac{2}{3}(\vec{\nabla}\cdot\vec{v})\delta_{\alpha\beta} \; , \tag{9b}$$

$$v_{\alpha\beta}^{(0)} \equiv (\vec{\nabla}\cdot\vec{v})\delta_{\alpha\beta} \tag{9c}$$

are the symmetric irreducible parts of the velocity flow gradient $\vec{\nabla}\vec{v}$. This represents the first terms in the expansion of $\epsilon_{\alpha\beta}$ in derivatives of the velocity. Equations (9a)–(9c) have often been used to analyze flow birefringence experiments. For a system in local equilibrium, Eqs. (9a)–(9c) are presumably also applicable if $\vec{v} = \vec{v}(\vec{q}, t)$ is (the Fourier transform of) the local velocity.

However, as we shall see below (Sec. V), Eqs. (9a)–(9c) are not yet sufficient to explain the observed spectra. Apparently, depolarized light scattering probes at least some fluctuations which describe the approach toward, but vanish at, local equilibrium. We suggest that the relevant fluctuations are those of $(\vec{\nabla}\times\vec{v} - 2\vec{\omega})$, where $\vec{\omega}(\vec{r}t)$ is the local average density of the molecular angular velocity at the space-time point $(\vec{r}, t)$. In local equilibrium, the liquid rotates locally like a rigid body so that $\vec{\nabla}\times\vec{v} - 2\vec{\omega} = 0$. Away from local equilibrium, this quantity produces frictional torques, and thus presumably also an antisymmetric contribution to the dielectric tensor of the form

$$\epsilon_{\alpha\beta} = X_1 v_{\alpha\beta}^{(1)} \; , \tag{10a}$$

where we have

$$v_{\alpha\beta}^{(1)} = \epsilon_{\alpha\beta\gamma}(\vec{\nabla}\times\vec{v} - 2\omega)_\gamma \tag{10b}$$

and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol. Thus we expect that

$$\epsilon_{\alpha\beta} \equiv \epsilon_{\alpha\beta}[\rho, T, v_{\alpha\beta}^{(0)}, v_{\alpha\beta}^{(1)}, v_{\alpha\beta}^{(2)}] \; . \tag{11}$$

Consequently, we expect that in an equilibrium system containing polyatomic molecules, fluctuations in $\{\rho, T, v_{\alpha\beta}^{(j)}(j = 0, 1, 2)\}$ will produce anisotropic fluctuations in the dielectric constant and thereby produce depolarized spectra. Thus in analogy with the theory of isotropic scattering we write

$$\delta\epsilon_{\alpha\beta} = \frac{\partial\epsilon}{\partial\rho}\delta\rho\delta_{\alpha\beta} + \sum_{j=0,1,2} X_j v_{\alpha\beta}^{(j)} \; , \tag{12}$$

where X_j's represent coupling coefficients. While there is room for letting these coefficients depend on q and Ω, we assume them to be constant. The dynamics is then fully contained in the explicitly treated fluctuation spectrum.

III. ANGULAR MOMENTUM FLUCTUATIONS: A NEW MECHANISM FOR LIGHT SCATTERING

In Sec. II we adopted the point of view that only flucutations in the density, temperature, and velocity gradients couple to the radiation field. In fact, we adopted a specific form for this coupling given by Eq. (12). This form is based on the observation that a structured molecule experiences an aligning torque when placed in an inhomogeneous

velocity field (velocity gradients are nonzero). Moreover, this form of the dielectric fluctuation is the simplest form that can be assumed consistent with small gradients, with small departures from equilibrium, and with rotational invariance.

We have shown elsewhere[11] that when a fluid contains structured molecules, the angular momentum should be considered in addition to mass, linear momentum, and energy appearing in ordinary hydrodynamics. In this section we consider the consequences of this modified hydrodynamics on light scattering.

The stress tensor $\tau_{\alpha\beta}$ in a fluid of structured molecules contains, in addition to the usual symmetric (Newtonian) part, an antisymmetric part[12]:

$$\tau_{\alpha\beta} = \eta_s[\nabla_\alpha v_\beta + \nabla_\beta v_\alpha - \tfrac{2}{3}(\vec{\nabla}\cdot\vec{v})\delta_{\alpha\beta}] + \eta_v(\vec{\nabla}\cdot\vec{v})\delta_{\alpha\beta}$$
$$+ \eta_r\epsilon_{\alpha\beta\gamma}[(\vec{\nabla}\times\vec{v})_\gamma - 2\omega_\gamma] \; . \tag{13}$$

Comparison with the Newtonian stress tensor of hydrodynamics shows that the shear and volume viscosity parts are unchanged. The new feature is the antisymmetric part of the stress tensor[12]

$$\tau_{\alpha\beta}^{(1)} = \eta_r\epsilon_{\alpha\beta\gamma}[(\vec{\nabla}\times\vec{v})_\gamma - 2\omega_\gamma] \; ,$$

where η_r is a new transport coefficient called the rotational viscosity, and $\vec{\omega}(\vec{r}, t)$ is the angular-velocity field. Consider the intrinsic angular momentum of a molecule (i.e., the angular momentum of a molecule due to its rotation about its own center of mass). If all the intrinsic angular momenta of the molecules in a small fluid element (centered on $\vec{r}$) are added, and the resultant is divided by the scalar part of the molecular moment of inertia tensor, the result is $\vec{\omega}(\vec{r}, t)$. This term in the stress tensor gives rise to a kind of Lenz's law for angular momenta: Intrinsic angular momentum density will always appear in such a way as to reduce vorticity $(\vec{\nabla}\times\vec{v})$ and vice versa. We will now discuss briefly the consequences of angular momentum on light scattering.

The linearized equations of hydrodynamic-fluctuation theory suitably modified to account for angular-momentum fluctuations are used to compute the spectra. These equations are[12]

$$\frac{\partial\delta\rho}{\partial t} + \rho_0\nabla_\alpha v_\alpha = 0 \; , \tag{14a}$$

$$m\rho_0\frac{\partial v_\alpha}{\partial t} = -\nabla_\alpha\delta P + \nabla_\beta\tau_{\alpha\beta} + f_\alpha \; , \tag{14b}$$

$$\rho_0 T_0\frac{\partial\delta S}{\partial t} = K\nabla^2\delta T + g \; , \tag{14c}$$

$$I\rho_0\frac{\partial\omega_\alpha}{\partial t} = 2\eta_r[(\vec{\nabla}\times\vec{v})_\alpha - 2\omega_\alpha] + n_\alpha \; , \tag{14d}$$

$$\delta P = \left(\frac{\partial P}{\partial\rho}\right)_{T_0}\delta\rho + \left(\frac{\partial P}{\partial T}\right)_{\rho_0}\delta T \; , \tag{15a}$$

$$\delta S = \left(\frac{\partial S}{\partial \rho}\right)_{T_0} \delta \rho + \left(\frac{\partial S}{\partial T}\right)_{\rho_0} \delta T \quad , \tag{15b}$$

where $\tau_{\alpha\beta}$ is given by Eq. (13). Here $\{\delta\rho, \delta P, \vec{v}, \vec{\omega},$ $\delta T, \delta S\}$ are fluctuations in the density, pressure, velocity, angular velocity, temperature, and entropy at the space-time point $(\vec{r}, t)$. The subscript 0 indicates an equilibrium value, i.e., the number density is $\rho_0 + \delta\rho(\vec{r}, t)$. Equations (14a)–(14d) are closed by the local-equilibrium assumption expressed in Eqs. (15a) and (15b). The terms f_α, g, and n_α are the "random" forces, force density, heat flow, and torque density acting on a fluid element at the space-time point $(\vec{r}, t)$. These are just the "random forces" that appear in the Mori formalism.[16] The product of any of these random forces with the hydrodynamic variables averages to zero in an equilibrium ensemble; thus, for example, we have

$$\langle v_\alpha^*(q, 0) f_\beta(q, t) \rangle \equiv 0 \quad .$$

According to the second fluctuation-dissipation theorem, the transport coefficients in Eqs. (14a)–(14d) are related to the time-correlation functions of these "random forces," and moreover, for Eqs. (14a)–(14d) to be valid these "forces" must have white spectra. A most important consequence of this theorem is that the random forces do not couple any of the variables together that would not ordinarily be coupled in the usual linear phenomenological equations. Thus, for example, the presence of random forces does not destroy the dynamical independence of v_x, v_y, and v_z.

Let us now use hydrodynamic fluctuation theory to derive expressions for the components I_{VV}, I_{VH}, and I_{HH} of the spectrum based on Eq. (12) for the dielectric fluctuations. It should be noted that the space-time transforms of the components of the stress tensor are

$$\tau_{\alpha\beta}^{(0)}(q, \Omega) = -i\eta_v \vec{q} \cdot \vec{v}(q, \Omega) \delta_{\alpha\beta} \quad , \tag{16a}$$

$$\tau_{\alpha\beta}^{(2)}(q, \Omega) = -i\eta_s [q_\alpha v_\beta(q, \Omega) + q_\beta v_\alpha(q, \Omega)$$

$$- \tfrac{2}{3}\vec{q} \cdot \vec{v}(q, \Omega) \delta_{\alpha\beta}] \quad , \tag{16b}$$

$$\tau_{\alpha\beta}^{(1)}(q, \Omega) = \eta_r \epsilon_{\alpha\beta\gamma} \{-i[\vec{q} \times \vec{v}(q, \Omega)]_\gamma - 2\vec{\omega}_\gamma(q, \Omega)\} \quad . \tag{16c}$$

We investigate some of the consequences of these equations, without introducing viscoelastic effects, i.e., frequency dependence in the transport coefficients. In the first place, let us see whether or not these equations predict backscattering in the I_{VH} spectrum as observed experimentally. It is easy to show for $\theta = \pi$ that

$$I_{VH}(q, \Omega) = |X_1|^2 C_\parallel^{(\omega)}(q, \Omega) \quad , \tag{17}$$

where $C_\parallel^{(\omega)}(q, \Omega)$ is the spectral density of the longitudinal angular-velocity correlation function

$$C_\parallel^{(\omega)}(q, \Omega) = \tfrac{1}{2} \int_{-\infty}^{+\infty} dt\, e^{-i\Omega t} \langle \omega_z^*(q, 0) \omega_z(q, t) \rangle \quad , \tag{18}$$

and X_1 is the coupling coefficient in Eq. (12). From Eq. (14d) it follows that

$$C_\parallel^{(\omega)}(q, \Omega) = \frac{1}{I\beta} \frac{\tau}{1 + \Omega^2 \tau^2} \quad , \tag{19a}$$

where

$$1/\tau = 4\eta_r/I\rho_0 \tag{19b}$$

is the relaxation rate for the collective angular momentum. Thus we see that at least one feature of the observed spectrum is accounted for. Similarly, it can be shown that there will be also a central line in the I_{HH} scattering at $\theta = \tfrac{1}{2}\pi$ which is observed in the laboratory.

The addition of angular momentum variables to the linear hydrodynamic equations will have absolutely no effect on the fully polarized spectrum $I_{VV}(q, \Omega)$, which will still be correctly determined by $S(q, \Omega)$, as in Eq. (8). They will, however, have an enormous effect on the characteristics of the depolarized spectra. Since the tensor $\delta\epsilon_{\alpha\beta}$ is Hermitian $(\delta\epsilon_{\alpha\beta}^* = \delta\epsilon_{\beta\alpha})$ it follows that the spectrum I_{VH} is always equal to I_{HV}. In order to treat the data systematically we define a constant κ such that

$$X_1 = \kappa X_2 \quad .$$

From Eqs. (4), (13), (14a)–(14d), and (15a) and (15b), we can write down expressions for the scattered intensities for arbitrary scattering angle θ. For 90° scattering in particular, we find that

$$I_{VH}(q, \Omega) = \frac{C}{2} \left(\frac{1}{1 + \Omega^2 \tau^2} + \frac{\Omega_T^2 [\tau v q^2 + (\lambda/\kappa^2)] + \Omega^2 [1 + 3\lambda^2 + (\lambda/\kappa^2)\tau v q^2]}{(\Omega^2 - \Omega_T^2)^2 \tau^2 + \Omega^2 (1 + \tau v q^2)^2} \right) \quad , \tag{20a}$$

and

$$I_{HH}(q, \Omega) = C \left(\frac{\Omega_T^2 (v\tau q^2 + 3\lambda) + \Omega^2 (1 - 2\lambda + \lambda\tau v q^2)}{(\Omega^2 - \Omega_T^2)^2 \tau^2 + \Omega^2 (1 + \tau v q^2)^2} + \frac{(\lambda/\kappa^2)}{\tau} \frac{C_\parallel^{(v)}(q, \Omega)}{C_\parallel^{(v)}(q, t = 0)} \right) \quad , \tag{20b}$$

where

$$C = 4|X_2|^2 \kappa^2 \tau/I\beta, \qquad \lambda = Iq^2/4m \quad ,$$

$$\tau = I\rho_0/4\eta_r, \qquad v = \eta_s/m\rho_0 \quad ,$$

$$\Omega_T^2 = (4\eta_s\eta_r/Im\rho_0^2)q^2 = vq^2/\tau \quad .$$

$C_\parallel^{(v)}(q, \Omega)$ is the spectral density of the longitudinal current-correlation function

$$C_\parallel^{(v)}(q, \Omega) = \tfrac{1}{2} \int_{-\infty}^{+\infty} dt\, e^{-i\Omega t} \langle v_z^*(q, 0) v_z(q, t) \rangle \quad ,$$

and is related to the dynamic structure factor

$S(q, \Omega)$ by

$$q^2 C_{\parallel}^{(v)}(q, \Omega) = \Omega^2 S(q, \Omega) \quad . \tag{20c}$$

Now $C_{\parallel}^{(v)}(q, \Omega)$ can be calculated, as in Ref. 15, from ordinary hydrodynamics (there is no coupling with "intrinsic" angular momentum), and is given by

$$\frac{C_{\parallel}^{(v)}(q, \Omega)}{C_{\parallel}^{(v)}(q, t = 0)}$$

$$= \frac{aq^2\Omega^2(\Omega_L^2 + abq^4 - \Omega^2) - \Omega^2[(aq^2/\gamma)\Omega_L^2 - (a + b)q^2\Omega^2]}{[(ak^2/\gamma)\Omega_L^2 - (a + b)q^2\Omega^2]^2 + \Omega^2(\Omega_L^2 + abq^4 - \Omega^2)^2} \quad , \tag{20d}$$

where

$$a = K/m\rho_0 c_v \quad , \qquad \gamma = C_p/C_v \quad , \qquad b = (\tfrac{4}{3}\eta_s + \eta_v)/m\rho_0$$

and $\Omega_L^2 = q^2 C_0^2$, C_0 being the low-frequency limit of the sound velocity (the other symbols have their usual meanings).

The integrated intensity ratio $I_{VH}(q)/I_{HH}(q)$ is given by

$$\frac{I_{VH}(q)}{I_{HH}(q)} = \frac{1 + \tfrac{1}{2}\lambda(1 + \kappa^{-2})}{1 + \lambda(1 + \kappa^{-2})} \quad . \tag{21}$$

For anisotropic molecular liquids like quinoline and nitrobenzene studied experimentally by Stegeman and Stoicheff,[4,7] the integrated intensities of I_{VH} and I_{HH} are equal. Since $\lambda \ll 1$, this puts a restriction on κ, namely, $\lambda\kappa^{-2} \ll 1$, or in terms of κ^2 we have

$$\kappa^2 \gg q^2 I/m \sim 10^{-5} \quad .$$

IV. COMPARISON WITH EXPERIMENT

We have computed $I_{VH}(q, \Omega)$ and $I_{HH}(q, \Omega)$ at 90° scattering for quinoline at $T = 22.3$ °C, and compared with the experimental results. The value of q is 1.4×10^5 cm^{-1}, and the numerical values of the various parameters in Eqs. (20a)–(20d) were chosen to be

(a) $I = 373$ amu Å^2 , $\Omega_L = 6.2$ GHz ,

    $m\rho_0 = 1.1$ g cm^{-1} , $\eta_s = 7.2 \times 10^{-2}$ P ,

(b) $\tau = 3.47 \times 10^{-11}$ sec , $\Omega_T = 0.95$ GHz,

    $\eta_r = 2.3 \times 10^{-6}$ P .

The parameters in group (a) are those which are independently known. τ determines Ω_T and η_r,[17] and has been chosen so as to give the correct width for the diffuse peak observed in I_{VH} backscattering, cf. Eqs. (19a) and (19b). Suitable approximate values for η_v and the thermal conductivity K were chosen to compute $C_{\parallel}^{(v)}(q, \Omega)$; these values are not very critical and were estimated such that $aq^2/\Omega_L = 10^{-2}$ and $bq^2/\Omega_L = 4 \times 10^{-2}$ [Eq. (20d)].

This leaves the coupling-constant ratio $\kappa = X_1/X_2$ as an adjustable parameter. The results are plotted

in Figs. 3 and 4 for two different values, $\kappa^2 = 10^{-4}$ and 10^{-3}. The spectrum of $I_{VH}(q, \Omega)$ has a maximum at $\Omega = 0.8$ GHz, and consequently we obtain a splitting which is in qualitative agreement with that observed experimentally where the maximum is at $\Omega = 0.95$ GHz. It should be clear that by choosing slightly different values of the various parameters which are not known very accurately, we could obtain a much better fit. The width of both the I_{VH} and I_{HH} spectra is given by $1/\tau$, theoretically and experimentally. Also we find a small Brillouin peak in the $I_{HH}(q, \Omega)$ spectrum at $\Omega = 6.2$ GHz. Note that the intensity of the peak can be adjusted by the parameter κ, and should be close to $\kappa^2 = 10^{-3}$. Note also that this value of κ is well within the bounds imposed by Eq. (21), namely, the observed equality of integrated intensities $I_{VH}(q)$ and $I_{HH}(q)$.

V. ORDINARY HYDRODYNAMICS AND GENERALIZED HYDRODYNAMICS

In this section we study what happens when the angular momentum is left out of the hydrodynamics. All that has to be done is to formally set $\eta_r = 0$ and $X_1 = 0$. An immediate consequence of this is that no antisymmetric terms will appear in either the stress tensor or in the dielectric fluctuations. The spectra then immediately reduce to

$$\theta = \pi \text{ (backscattering)}: \quad I_{VH}(q, \Omega) = 0 \quad ;$$

$$\theta = \tfrac{1}{2}\pi:$$

$$I_{VH}(q, \Omega) = \tfrac{1}{2}|X_2|^2 q^2 C_{\perp}^{(v)}(q, \Omega),$$

$$I_{HH}(q, \Omega) = |X_2|^2 \Omega^2 S(q, \Omega) \quad ,$$

where $C_{\perp}^{(v)}(q, \Omega)$ is the spectral density of the transverse velocity (v_x or v_y),

$$C_{\perp}^{(v)}(q, \Omega) = \tfrac{1}{2} \int_{-\infty}^{+\infty} dt \, e^{-i\Omega t} \langle v_y^*(q, 0) v_y(q, t) \rangle \quad .$$

Here we have

$$C_{\perp}^{(v)}(q, \Omega) = \frac{1}{m\beta} \frac{\nu q^2}{\Omega^2 + (\nu q^2)^2} \quad , \tag{22}$$

where ν is the kinematic viscosity (equal to $\eta_s/m\rho_0$).

These formulas are at variance with the experiment for the following reasons:

(a) They predict no backscattering, yet experimentally there is I_{VH} backscattering.

(b) They predict (when typical values are substituted for ν) much narrower lines than are observed.

(c) They do not account for the splittings observed in some fluids.

(d) They predict that there will be no central line in I_{HH} for $\theta = \tfrac{1}{2}\pi$, yet experimentally there is such a line.

When angular momentum is included, these objections are removed. It is legitimate to ask whether a generalized hydrodynamic theory can be devised which would account for the characteristics of the
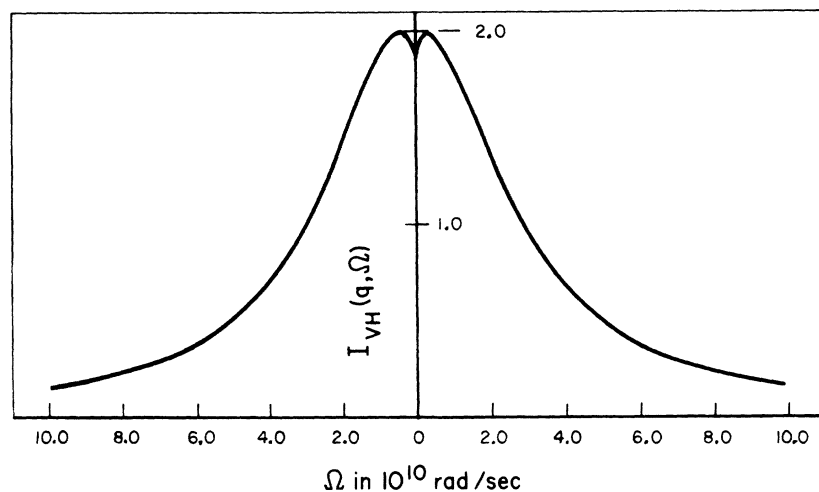
FIG. 3. $I_{VH}(q, \Omega)$ and $I_{HH}(q, \Omega)$ spectra calculated from Eqs. (20a)–(20d) for $\kappa^2 = 10^{-4}$.
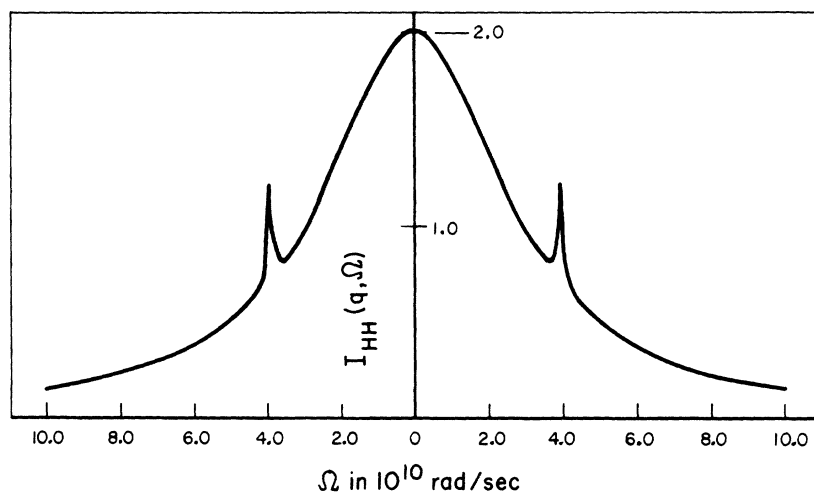
observed spectrum without adding any "nonhydro-dynamic" terms like angular momentum.

Recently, much progress has been made with regard to understanding collective behavior of monatomic liquids.[18-20] It was found that if the hydrodynamic equations are modified to take into account memory effects (frequency-dependent transport coefficients), both the microscopic and macroscopic behavior of the collective variables $\delta\rho(\vec{q}, t)$, $\vec{v}(\vec{q}, t)$, $\delta T(\vec{q}, t)$ can be understood on the basis of one comprehensive theory. This theory can be derived from first principles by methods first developed by Zwanzig[21] and Mori.[16] For long times, the behavior of these variables is just that expected from Eqs. (14a)–(14d), (15a) and (15b), and (16a) and (16b). This theory is now commonly called generalized hydro-dynamics. For monatomic liquids it has been shown experimentally that the linear hydrodynamic theory of fluctuations works for wave numbers as high as 10^6 cm^{-1} and for frequencies as high as 10^{10} sec^{-1}. Thus for simple liquids like argon and xenon, hydrodynamic fluctuation theory suffices for a prediction of the spectrum (except for collision-induced scattering). For molecular liquids, the situation is much more complex. From ultrasonics[22] it is known that there are at least three time regimes in the attenuation of sound corresponding to vibrational, rotational, and translational relaxation. According to experiments, there is marked frequency dependence in the attenuation coefficient of sound. This has lead many investigators to assume that transport coefficients such as η_s and η_v depend on

the frequency. Mountain,[23] for example, has attributed observed deviations from the Landau-Placzek ratio in the Brillouin scattering from CS_2, to frequency dependence in the bulk viscosity which he claims reflects the vibrational relaxation of these molecules. By allowing η_v to depend on a single relaxation time, Mountain accounts for the observed scattering and, moreover, predicts the existence of a new broad band in liquids. Now there is absolutely no reason not to put frequency dependence into the shear viscosity as well. After all, rotations and asymmetric molecular vibrations can couple to transverse modes in liquids. One way to modify the equations is to put memory effects into the hydrodynamics (these can be attributed to vibrational and rotational relaxation). Then, for example, the stress tensor will become

$$\tau_{\alpha\beta}(\vec{r}, t) = \int_0^t dt_1\, \eta_s(t_1)[\nabla_\alpha v_\beta(\vec{r}, t - t_1)$$

$$+ \nabla_\beta v_\alpha(\vec{r}, t - t_1) - \tfrac{2}{3}\vec{\nabla} \cdot \vec{v}(\vec{r}, t - t_1)\delta_{\alpha\beta}]$$

$$+ \int_0^t dt_1\, \eta_v(t_1)\, \vec{\nabla} \cdot \vec{v}(\vec{r}, t - t_1)\delta_{\alpha\beta} \quad , \quad (23)$$

where we ignore spatial dispersion in $\eta_s(\tau)$ and $\eta_v(\tau)$ (because in light scattering, relatively small values of q are examined) and angular momentum fluctuations are ignored. A similar expression can be written for the entropy. Now it is anybody's guess what the time dependence of $\eta_s(\tau)$ should be. We suspect that a reasonable form for $\eta_s(\tau)$ is
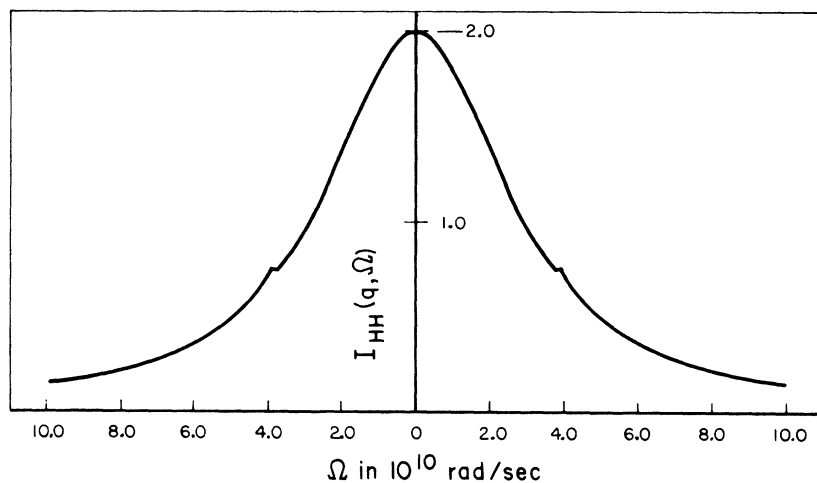
$$\eta_s(\tau) = (\eta_1/\tau_1)\, e^{-t/\tau_1} + (\eta_2/\tau_2)e^{-t/\tau_2} + \cdots \quad , \quad (24a)$$

where each term corresponds to a different relaxing degree of freedom that couples to transverse modes
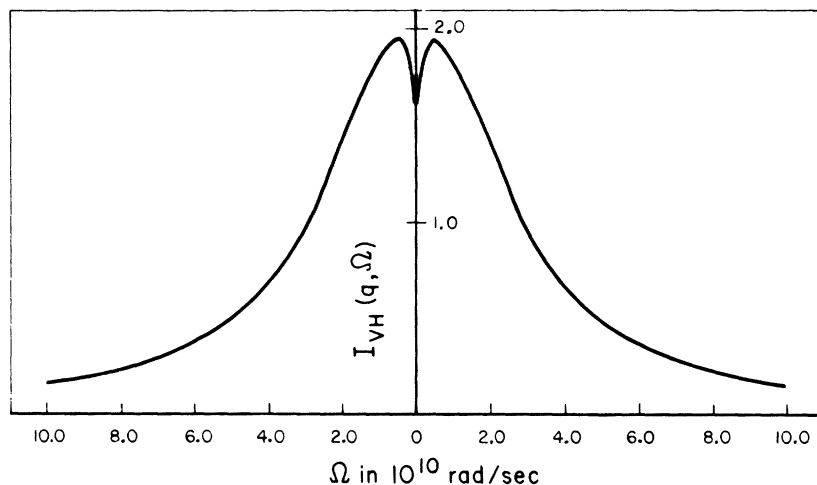
$$\kappa^2 = 10^{-3}$$

FIG. 4. $I_{VH}(q, \Omega)$ and $I_{HH}(q, \Omega)$ spectra calculated from Eqs. (20a)–(20d) for $\kappa^2 = 10^{-3}$.

in the fluid (rotations, asymmetric molecular vibrations, etc.). Some possible choices of η_s are

single relaxation time:

$$\eta_s(t) = (\eta_s/\tau)\, e^{-t/\tau} \quad (\eta_s = \text{shear viscosity}); \quad (24b)$$

one fast and one slow relaxation process:

$$\eta_s(t) = \eta_\infty \delta(t) + [(\eta_s - \eta_\infty)/\tau]\, e^{-t/\tau} . \quad (24c)$$

We are interested in computing I_{VH} so that at this point it is not necessary to specify the time dependence of the volume viscosity.

The only modification in the I_{VH} spectrum introduced by memory effects is the replacement of $C_\perp^{(v)}(q, \Omega)$ in Eq. (22) by

$$C_\perp^{(v)}(q, \Omega) = \frac{1}{m\beta}\, \frac{\nu_r(\Omega)q^2}{[\Omega + \nu_i(\Omega)q^2]^2 + [\nu_r(\Omega)q^2]^2} , \quad (25a)$$

where $\nu_r(\Omega)$ and $\nu_i(\Omega)$ are the real and imaginary parts of the frequency-dependent kinematic viscosity

$$\nu(i\Omega) = \nu_r(\Omega) + i\nu_i(\Omega) = \int_0^\infty dt\, e^{-i\Omega t} \nu(t) , \quad (25b)$$

where $\nu(t) = \eta_s(t)/m\rho_0$. The line shape of $I_{VH}(q, \Omega)$ will depend critically, therefore, on what form we take for $\nu(t)$. For example, if the single relaxation-time approximation [Eq. (24b)] is used, the transverse mode has the spectrum

$$C_\perp^{(v)}(q, \Omega) = \frac{\tau}{m\beta}\, \frac{\Omega_T^2}{(\Omega^2 - \Omega_T^2)^2 \tau^2 + \Omega^2} , \quad (25c)$$

where the quantity Ω_T is

$$\Omega_T = q(\nu/\tau)^{1/2} = 2k(\nu/\tau)^{1/2} \sin\tfrac{1}{2}\theta . \quad (25d)$$

Only when $\Omega_T \gg \tau^{-1}$ or $q^2\nu\tau \gg 1$ would this give rise to a splitting which varies linearly with $\sin\tfrac{1}{2}\theta$. However, the q values used in the experiment are so small that we have $q^2\nu\tau \ll 1$ in fact. If, on the other hand, Eq. (24c) is used, we get

$$C_\perp^{(v)}(q, \Omega) = \frac{\tau}{m\beta}\, \frac{\Omega_T^2 + \Omega^2\Omega_\infty^2\tau^2}{(\Omega^2 - \Omega_T^2)^2\tau^2 + (1 + \Omega_\infty^2\tau^2)\Omega^2} , \quad (26a)$$

where

$$\Omega_T = q(\nu/\tau)^{1/2}, \quad \Omega_\infty = q(\eta_\infty/m\rho_0\tau)^{1/2} . \quad (26b)$$

This will account for the observed splitting in I_{VH}. Both of these models do not predict backscattering in the I_{VH} spectrum, however. Thus, a purely generalized hydrodynamic theory will not account for the observations.

VI. RYTOV'S THEORY

We have adopted the point of view that the dielectric fluctuations could be assumed from the form of the optical anisotropies of a fluid in steady flow. Let us now look a little more deeply into the origin of such terms. The reason for the appearance of these optical anisotropies lies in the fact that a non-

spherical molecule experiences an aligning torque in a moving fluid. Since the divergence of the stress tensor $(\nabla_\beta \tau_{\alpha\beta})$ gives the force F_α acting on a fluid element at each point in the fluid, and thereby on each point of a body immersed in the fluid, it follows that the moment of this force is an aligning torque. If this argument is carried through to its logical conclusion, it is found that the degree of alignment of the molecules in steady flow, and therefore the anisotropic part of the dielectric tensor, depends on the viscous stress tensor $\tau_{\alpha\beta}$ and only indirectly on the velocity gradients. Then it is reasonable to assume that

$$\delta\epsilon_{\alpha\beta}(q, t) = \frac{\partial\epsilon}{\partial\rho}\, \delta\rho(q, t)\delta_{\alpha\beta} + \sum_{j=0,1,2} Y_j \tau_{\alpha\beta}^{(j)}(q, t), \quad (27a)$$

where $\tau_{\alpha\beta}^{(0)}$, $\tau_{\alpha\beta}^{(1)}$, and $\tau_{\alpha\beta}^{(2)}$ are the scalar, antisymmetric, and symmetric parts of the viscous stress tensor, respectively, and Y_j are the coupling coefficients. If noncentral intermolecular forces are ignored, the antisymmetric part $\tau_{\alpha\beta}^{(1)}$ of the viscous stress tensor vanishes; the viscous stress tensor has now only six components and Eq. (27a) becomes

$$\delta\epsilon_{\alpha\beta}(q, t) = \frac{\partial\epsilon}{\partial\rho}\, \delta\rho(q, t)\delta_{\alpha\beta} + Y_0 \tau_{\alpha\beta}^{(0)}(q, t) + Y_2 \tau_{\alpha\beta}^{(2)}(q, t). \quad (27b)$$

For 90° depolarized scattering, Eqs. (4) reduce to

$$\delta\epsilon_{VH}(q, t) = 2^{1/2}[\delta\epsilon_{yx}(q, t) - \delta\epsilon_{yz}(q, t)],$$
$$\delta\epsilon_{HH}(q, t) = \tfrac{1}{2}[\delta\epsilon_{xx}(q, t) - \delta\epsilon_{zz}(q, t)] . \quad (28)$$

It is our intention, in this section, to show that what Rytov[9] has calculated is just the viscous stress tensor correlation functions. This has also been pointed out by Volterra.[10] Akcasu and Daniels,[18] in a recent paper on current-current correlations, have derived generalized Langevin equations for the viscous stress tensor. They choose a set of variables

$$\rho(q) = m \sum_{j=1}^N e^{iq\cdot x^j} , \quad (29a)$$

$$J_\alpha(q) = m \sum_{j=1}^N v_\alpha^j(t)\, e^{iq\cdot x^j} , \quad (29b)$$

$$\Pi_{\alpha\beta}(q) = \sum_{j=1}^N \left(mv_\alpha^j v_\beta^j + \tfrac{1}{2} \sum_{\substack{l=1 \\ (l\neq j)}}^N \frac{x_\alpha^{jl} x_\beta^{jl}}{|x^{jl}|^2} p^{jl}(q)\right) e^{iq\cdot x^j} , \quad (29c)$$

where

$$x^{jl} = x^j - x^l ,$$

$$p^{jl}(q) = R\, \frac{dv(R)}{dR}\, \frac{1 - e^{-iq\cdot R}}{iq\cdot R}\bigg|_{R=x^{jl}} , \quad (29d)$$

and where $\rho(q)$, $J_i(q)$, and $\Pi_{\alpha\beta}(q)$ are, respectively, the mass density, mass current density, and microscopic stress tensor. In these definitions, x^j, v^j denote the position and velocity of jth molecule in the system. Akcasu and Daniels also consider tem-

perature fluctuations, which we will ignore in the present discussion. The viscous stress tensor is now defined as

$$\tau_{\alpha\beta}(q) = \Pi_{\alpha\beta}(q) - \frac{\langle \rho^*(q)\Pi_{\alpha\beta}(q)\rangle}{\langle |\rho(q)|^2\rangle}\ \rho(q)\ . \qquad (29e)$$

By using projection-operator techniques developed by Zwanzig[21] and Mori,[16] these authors derive generalized Langevin equations for the variables $\rho(q)$, $J_\alpha(q)$, and $\tau_{\alpha\beta}(q)$.

Assuming that the relaxation times of the longitudinal viscosity and shear viscosity are the same, and further ignoring the coupling between τ_{xx}, τ_{yy}, and τ_{zz} [cf. Eqs. (4.21) and (4.56a), Ref. 18], the equations of motion are

$$\dot{\rho}(q, t) = iq\, J_z(q, t), \quad \dot{J}_x(q, t) = iq\,\tau_{xz}(q, t),$$

$$\dot{J}_z(q, t) - (i/q)\,\Omega_L^2\rho(q, t) = iq\,\tau_{zz}(q, t),$$

$$\dot{\tau}_{xx}(q, t) - (i/q)\,(\Omega_S^2 - \Omega_L^2 - 2\Omega_T^2)J_z(q, t)$$
$$+ (1/\tau)\,\tau_{xx}(q, t) = F_{xx}(q, t),$$

$$\dot{\tau}_{yy}(q, t) - (i/q)\,(\Omega_S^2 - \Omega_L^2 - 2\Omega_T^2)J_z(q, t) \qquad (30)$$
$$+ (1/\tau)\,\tau_{yy}(q, t) = F_{yy}(q, t),$$

$$\dot{\tau}_{zz}(q, t) - (i/q)\,(\Omega_S^2 - \Omega_L^2)J_z(q, t)$$
$$+ (1/\tau)\,\tau_{zz}(q, t) = F_{zz}(q, t),$$

$$\dot{\tau}_{xz}(q, t) - (i/q)\,\Omega_T^2\, J_x(q, t) + (1/\tau)\,\tau_{xz}(q, t) = F_{xz}(q, t),$$

$$\dot{\tau}_{yz}(q, t) - (i/q)\,\Omega_T^2\, J_y(q, t) + (1/\tau)\,\tau_{yz}(q, t) = F_{yz}(q, t),$$

$$\dot{\tau}_{xy}(q, t) + (1/\tau)\,\tau_{xy}(q, t) = F_{xy}(q, t),$$

where $F_{\alpha\beta}(q, t)$ is a random force with a white spectrum and

$$\Omega_L^2 = q^2\, K_0/\rho_0, \quad \Omega_T^2 = q^2\mu_\infty/\rho_0,$$
$$\Omega_S^2 = q^2\, (K_\infty + \tfrac{4}{3}\mu_\infty)/\rho_0 \simeq \Omega_L^2 + \tfrac{4}{3}\,\Omega_T^2\ . \qquad (31)$$

Note that in writing down Eqs. (30), a single-relaxation-time approximation has been made for shear and bulk viscosities

$$\eta_s(i\Omega) = \frac{\mu_\infty\tau}{1 + i\Omega\tau}, \quad \eta_v(i\Omega) = \frac{(K_\infty - K_0)\tau}{1 + i\Omega\tau}, \qquad (32)$$

where the symbols have the usual meaning. For further details, see Akcasu and Daniels.[18]

It is straightforward now to calculate the depolarized scattered intensities $I_{VH}(q, \Omega)$ and $I_{HH}(q, \Omega)$ and from Eqs. (1) and (28):

$$I_{VH}(q, \Omega) = \tfrac{1}{4}\left|\, Y_2\right|^2 \int_{-\infty}^{+\infty} dt\, e^{-i\Omega t}$$

$$\times\langle[\tau_{yx}(q) - \tau_{yz}(q)]^*\,[\tau_{yx}(q, t) - \tau_{yz}(q, t)]\rangle$$

$$= \frac{C}{2}\left(\frac{1}{1 + \Omega^2\tau^2} + \frac{\Omega^2}{\Omega^2 + (\Omega^2 - \Omega_T^2)^2\tau^2}\right), \qquad (33a)$$

where

$$C = \tfrac{1}{2}\left|\, Y_2\right|^2 Vk_B T\mu_\infty\tau\ .$$

Similarly we have

$$I_{HH}(q, \Omega) = \frac{C}{4}\left(\frac{1}{1 + \Omega^2\tau^2} + \frac{3(\Omega^2 - \Omega_L^2)^2}{(\Omega^2 - \Omega_L^2)^2 + \Omega^2\tau^2\,(\Omega^2 - \Omega_S^2)^2}\right). \qquad (33b)$$

Note that Eqs. (33a) and (33b) are exactly those derived by Leontovich[8] and by Rytov[9] in his last paper. Rytov, of course, has discussed a more general frequency dependence for Y_2. Moreover, in this calculation, angular momentum has been completely ignored. We believe it is quite possible to develop an analogous theory with angular momenta by studying the antisymmetric stress tensor.

These formulas have recently received experimental support from the work of Stegeman and Stoicheff.[4,7] Rytov's derivation of these results is somewhat confusing. It proceeds along the following lines:

(a) It is assumed that the dielectric fluctuations are

$$\delta\epsilon_{\alpha\beta} = Xu\delta_{\alpha\beta} + Yu'_{\alpha\beta}\ , \qquad (34)$$

where $u_{\alpha\beta}$ is the strain tensor in viscoelastic theory, u is the trace of $u_{\alpha\beta}$, and $u'_{\alpha\beta}$ is the symmetric traceless part of $u_{\alpha\beta}$.

(b) It is assumed that the coupling coefficients X and Y are frequency dependent and are, respectively, proportional to the frequency-dependent bulk $K(\Omega)$ and shear modulus $\mu(\Omega)$, i.e., that $X(i\Omega) = XK(i\Omega)$ and $Y(i\Omega) = Y\mu(i\Omega)$.

(c) The stress tensor $\tau_{\alpha\beta}(q, i\Omega)$ is

$$\tau_{\alpha\beta}(q, i\Omega) = K(i\Omega)\, u\,\delta_{\alpha\beta} + \mu(i\Omega)\, u'_{\alpha\beta} \qquad (35a)$$

and the displacements $s_\alpha(\alpha = 1, 2, 3)$ satisfy the equation of viscoelasticity

$$\rho_0\frac{\partial^2 s_\alpha}{\partial t^2} = \nabla_\beta \tau_{\alpha\beta} + f_\alpha\ , \qquad (35b)$$

where f_α is a random force.

(d) From the form of the stress tensor it follows that

$$u'_{\alpha\beta}(q, \Omega) = [1/\mu(i\Omega)]\,\tau_{\alpha\beta}^{(2)}(q, \Omega),$$

$$u(q, \Omega) = [1/K(i\Omega)]\,\tau_{\alpha\beta}^{(0)}(q, \Omega), \qquad (36)$$

where $\tau_{\alpha\beta}^{(0)}$ and $\tau_{\alpha\beta}^{(2)}$ are the scalar and symmetric traceless parts of the stress tensor. Substitution of Eq. (36) into Eq. (34) then gives

$$\delta\epsilon_{\alpha\beta} = X\,\tau_{\alpha\beta}^{(0)} + Y\tau_{\alpha\beta}^{(2)}\ ,$$

where $\tau_{\alpha\beta}$ is still of the form given in Eq. (35a).

(e) Rytov at this point calculates the stress-tensor correlation functions.

Our derivation springs naturally from a consideration of the microscopic events. We hope that our

derivation makes Rytov's basic idea more accessi-
ble to the reader. One advantage in our approach
is that we avoid introducing the notion of a displace-
ment of distortion field which we believe is mean-
ingless in connection with the liquid state.

VII. DISCUSSION

Of central importance in this article is the obser-
vation that a purely hydrodynamic theory of fluctua-
tions does not suffice to explain depolarized light
scattering in liquids such as quinoline. Yet the ob-
served spectra occur at rather long wavelengths
$(q \sim 10^5 \text{ cm}^{-1})$ and small frequencies $(\Omega \sim 10^{10} \text{ sec}^{-1})$;
this suggests that it is probably unnecessary to con-
sider in detail the dynamics of close collisions; a
coarser description in terms of largely collective
modes should be sufficient. Apparently what is
probed in these experiments are the collective pro-
cesses towards the end of the kinetic stage which
describe the approach toward local equilibrium.
Moreover, we note that these not-quite-hydrody-
namic modes have to couple directly to the radia-
tion field. If we were to assume that the light is
scattered only from fluctuations of the density and
the velocity gradients (as would be appropriate in
local equilibrium) we would not obtain a backscat-
tered $I_{VH}(q, \Omega)$ spectrum, even if nonhydrodynamic
fluctuations of these variables were taken into ac-
count. This is quite clear from our rederivation of
the results obtained by Rytov.[9] His theory of depo-
larized light scattering starts from the observation
that a liquid responds to a perturbation of relatively
high frequency in much the same way as a glass
does. Like a glass or a solid, it is thus expected
that a liquid can support transverse high-frequency
waves. Rytov therefore starts out from the clas-
sical equations of viscoelasticity but assumes that the
shear viscosity has a frequency dependence deter-
mined by a single relaxation time. In order to de-
rive the frequency spectrum, Rytov introduces
"random forces" into his equations in much the
same way as Landau[14] does. Central in Rytov's
treatment is the notion of a "distortion" in the liquid
state. Whereas this concept is well defined in con-
nection with a glass, its meaning in a liquid is not
very clear. We presented in Secs. V and VI a visco-
elastic theory based on generalized hydroynamics
which avoids the concept of a distortion field. This
approach is different from Rytov's. It is based in
part on the rigorous body of theory connected to
memory functions and the second fluctuation-dissip-
ation theorem. The nonhydrodynamic fluctuations
are those of the stress tensor which are assumed to
decay with a simple, q-independent relaxation time.
Note that this modification of hydrodynamics does
not give a backscattered I_{HV} spectrum if the dielec-
tric tensor is coupled only to the Newtonian part of
the stress tensor, i.e., to velocity gradients. We

do find a backscattered I_{VH} spectrum of the right
shape if we assume that the dielectric fluctuations
couple to the microscopic stress tensor.

To account for some of the gross features that
are observed experimentally in molecular liquids,
then, Eq. (9) is inadequate, and must be modified
such that the dielectric fluctuations are of the form

$$\delta\epsilon_{\alpha\beta}(q, \Omega) = \frac{\partial\epsilon}{\partial\rho}\, \delta\rho(q, \Omega) + \sum_{j=0,2} X_j v_{\alpha\beta}^{(j)}(q, \Omega) + X_3 \zeta_{\alpha\beta}(q, \Omega).$$

In our version of Rytov's theory, $\zeta_{\alpha\beta}$ would be the
non-Newtonian part of the microscopic stress ten-
sor. Another possibility is to use for $\zeta_{\alpha\beta}$ a tensor
which describes the orientational ordering of single
molecules in the liquid, such as the order parame-
ter discussed in the work of Leontovich[8] and, more
recently, Volterra.[10] If it is assumed for simplici-
ty that $\zeta_{\alpha\beta}$ does not couple to $v_{\alpha\beta}^{(j)}$ and $\delta\rho$, then it is
found, for example, that

$$I_{VH}(q, \Omega) = |X_3|^2 \langle|\zeta_{yx}(q, \Omega)|^2\rangle + |X_2|^2 q^2 C_1^{(v)}(q, \Omega) \cos^2\tfrac{1}{2}\theta.$$

Thus for $\theta = \pi$, we have

$$I_{VH}(q, \Omega) = |X_3|^2 \langle|\zeta_{yx}(q, \Omega)|^2\rangle \neq 0.$$

This correlation function has been computed by
Pecora[24] for the case of asymmetric Brownian ro-
tation. It is, in general, a sum of five Lorentzians
with (essentially q-independent) widths which are de-
termined by the rotational diffusion coefficients
around the different molecular symmetry axes. For a
spherical-top molecule, these reduce to

$$I_{VH}(q, \Omega) = |A|^2 \left(\frac{q^2 D + 6\theta_{rot}}{\Omega^2 + (q^2 D + 6\theta_{rot})^2}\right) \ ,$$

where D and θ_{rot} are the translational and rotational
self-diffusion coefficients. This mechanism could
in principle describe both the broad background (if
the rotational diffusion tensor is very anisotropic)
and the central line. We have not considered it in
detail, but a more systematic analysis appears pos-
sible. Indeed, this kind of treatment is similar in
spirit to the theories of Leontovich and Volterra.

What is entirely new in this paper is the treatment
of angular-momentum fluctuations in connection with
depolarized light scattering. For this theory, the
nonhydrodynamic term in $\delta\epsilon_{\alpha\beta}$ is antisymmetric and
given by $\zeta_{\alpha\beta} = \epsilon_{\alpha\beta\gamma}(\vec{\nabla}\times\vec{v} - 2\vec{\omega})_\gamma$. We find it appealing
that a very small contribution of this form (of rela-
tive order $\kappa \sim 3\times 10^{-2}$) is sufficient to render most of
the qualitative features of the observed spectra.
The crucial parameter in this theory is then the ro-
tational viscosity η_r or, equivalently, the decay rate
$1/\tau$ in Eqs. (20a)–(20d). η_r is, in principle, suscepti-
ble to independent determination from flow measure-
ments; however, at present we know of no experi-
ments from which the value of η_r could be indepen-
dently obtained. τ is the decay time of collective
intrinsic angular momentum fluctuations in the li-

quid. It is important to note that the numerical value of τ required to give a reasonable fit to the light-scattering data ($\tau = 3.4 \times 10^{-11}$ sec) is several orders of magnitude larger than the relaxation time of a single molecule's angular momentum. This is, of course, consistent and desirable within our theory, which is based upon the assumption[11] that the inter-particle forces are relatively ineffective in destroy-ing collective spin-density excitations (by converting them into translational vortex motion).

We wish to end on a cautionary note: It is clear that a phenomenological theory like ours could be "improved" by allowing for frequency dependence in the transport coefficients η_s, η_v, and η_r. Similarly, the coupling coefficients X_j in Eq. (12) could be made frequency dependent as some authors have suggested in similar cases. While such frequency dependence is not without physical motivation, we have refrained from introducing it here, chiefly in

order to keep the number of adjustable parameters at a minimum. It seems to us that without a much more fundamental theory of light scattering in mo-lecular liquids, the experimental data available are not sufficient to allow a clear decision between sev-eral possible phenomenological models, and to in-troduce too many adjustable parameters would only becloud the issue. In this sense, we wish to present the considerations in this article as interesting in connection with depolarized light scattering, rather than as the definitive solution of what we regard as a still largely unsolved problem.[25]

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[25]*Footnote added in proof*. Several other theories on this subject have come to the authors' attention after this paper was submitted: N. D. Gershon and A. Ben Reuven, J. Chem. Phys. (to be published); T. Keyes and D. Kivel-son, *ibid*. (to be published); H. C. Anderson and R. Pecora, *ibid*. (to be published).