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Relaxation Equations for Depolarized Rayleigh and Brillouin Scattering in Liquids*

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The spectral distributions of light scattered under various polarization conditions in liquids composed of optically anisotropic molecules are analyzed. Macroscopic equations are derived using analogous electric circuits which simulate the viscoelastic behavior due to shear stress, reorientations, and coupling with internal degrees of freedom. The equations describe the long-wavelength thermal fluctuations in the liquid and form the basis of a unified calculation of depolarized and Brillouin scattering. Under the condition that shear relaxation takes place more rapidly than reorientational processes, the sharp component and broad background in the depolarized spectrum are shown to depend primarily on the fluctuations in orientations and shear stress, respectively. Our results also provide a simple interpretation of the recently observed doublet structure. The Brillouin spectrum, on the other hand, shows the well-known effects of thermal relaxation as well as the effects of coupling with shear stress and reorientations. Numerical results on quinoline and nitrobenzene are presented, and the computed depolarized spectra are in good agreement with the experimental data of Stegeman and Stoicheff.

I. INTRODUCTION

Recent high-resolution measurements of the depolarized spectra of light scattered in molecular liquids have revealed a number of interesting features.[1-3] In general, the profile of a depolarized spectrum is known to consist of a central component, called the diffuse line or Rayleigh "wings," superimposed on a broad background. Detailed features of the sharp component, however, vary with the polarization arrangement and in special cases also with the scattering angle. For example, if the incident- and scattered-photon polarizations are normal and parallel to the scattering plane (*VH* geometry), a splitting in the sharp component is observed which gives rise to a narrow doublet. The splitting frequency is several times smaller than the familiar Brillouin shift. In the backward scattering spectrum the doublet is not observed. In the case of *HH* geometry, two broad peaks also appear in the spectrum, but now in the vicinity of the Brillouin frequency.

The experimental observations have stimulated considerable theoretical interest, as several attempts have been made recently to analyze these phenomena. From the early work of Leontovich,[4,5] it is known that the sharp component arises from anisotropic fluctuations due to molecular reorientations. A more general formulation by Rytov led to essentially similar results.[6] Recently, Volterra[7] has extended the Leontovich approach by considering explicitly two relaxation mechanisms, reorientations and shear diffusion, and in this way he was able to treat both the sharp component and the background in a single calculation. On the basis of these calculations, Stegeman and Stoicheff interpreted the narrow doublet in the depolarized spectrum as a direct indication of shear-wave propagation.[2,3] The different features of the sharp component also have been analyzed by Ailawadi, Berne, and Forster by studying the effects of angular momentum fluctuations.[8] These authors considered explicitly the effects of angular momentum fluctuations which give rise to an antisymmetric contribution to the stress tensor. On the other hand, Andersen and Pecora[9] have derived kinetic equations which take into account shear and orientation relaxations. They obtained results which reduce to those of Leontovich or Volterra when the stress tensor is assumed to be symmetric.

In contrast to the approach using macroscopic equations and dielectric constant, direct calculations of the molecular polarizability also have been made.[10-12] Ben-Reuven and Gershon have shown that by coupling the orientational motions to sound waves one obtains a frequency-dependent damping constant which will lead to a doublet in the depolarized spectrum.[11] In a related analysis, Keyes and Kivelson concluded that the existence of the narrow doublet indicates coupling effects are related to dissipative motions and not wavelike propagations.[12]

The purpose of this paper is to present an analysis of light scattering in liquids composed of optically anisotropic molecules. We adopt a macroscopic approach in which the liquid is treated as a viscoelastic medium which exhibits shear, reorientation, and thermal relaxations. Phenomenological electric circuits are used to simulate the behavior of fluctuations in the presence of multiple relaxations, and from these circuits we derive model equations by making the analogy between pressure or stress and voltage, and between density or deformation and charge.

The model equations, derived in Sec. II, are similar to those used by Volterra. However, in carrying out the analysis, Volterra has assumed that the relaxation times for reorientations are shorter than those associated with the shear modes. We believe that the opposite situation is generally more realistic and propose initial conditions consistent with this assumption. Section III contains the analysis of depolarized light scattering. By assuming that the isotropic and anisotropic components of the dielectric tensor have the same time dependence as the fluctuations in density and stress tensor, we obtain a unified calculation of depolarized and Brillouin scattering. The treatment of depolarized spectra takes into account both the sharp component and the background, and we find the observed "doublet" behavior in our results. The Brillouin spectrum, discussed in Sec. IV, shows the effects of thermal relaxation; in addition, the effects of coupling with shear modes and reorientations are also present. The depolarized spectra of liquid quinoline and nitrobenzene are analyzed in Sec. V. The calculations are seen to be in quantitative agreement with experiment. We then summarize the essential features of our work in Sec. VI and discuss them in the context of several recent theoretical investigations.

II. FRENKEL MODEL

In this section we obtain a system of macroscopic equations which describe the long-wavelength isotropic and anisotropic fluctuations in molecular liquids. These equations are basically the linearized equations of fluid dynamics except that the stress tensor is specified by a model equation which takes into account shear and orientation relaxations. Another model equation which considers thermal relaxation is used to relate the pressure and density fluctuations. Both equations are derived by analogy with phenomenological electric circuits.[13, 14]

The linearized equations of motion of a fluid are[15]

$$\rho_0 \frac{\partial}{\partial t} v_\alpha(\vec{r}, t) = -\nabla_\alpha p(\vec{r}, t) + \nabla_\beta \sigma_{\alpha\beta} , \qquad (1)$$

where ρ_0 is the equilibrium mass density, v the local velocity, p the pressure deviation, and $\sigma_{\alpha\beta}$ is the traceless stress tensor. Vector indices are denoted by Greek letters and summation over repeated indices is understood. We will consider a linear relation between p and the deviations in density (or volume) n and in temperature T,

$$-p(\vec{r}, t) = Ln(\vec{r}, t) - \beta_T\, \alpha T(\vec{r}, t) , \qquad (2)$$

where $n = \Delta\rho/\rho_0$, β_T is the isothermal compressibility, and α is the thermal-expansion coefficient. The coefficient L depends on the model used and may appear as an operator. Another relation between T and n is the Fourier law of heat conduction

$$\frac{\partial T(\vec{r}, t)}{\partial t} = a\nabla^2 T(\vec{r}, t) - \frac{\gamma - 1}{\alpha}\, \frac{\partial n(\vec{r}, t)}{\partial t} , \qquad (3)$$

where $a = \lambda/\rho_0 c_v$ is the thermal diffusivity, λ is the conductivity coefficient, c_v the constant-volume specific heat, and $\gamma = c_p/c_v$. We also define the traceless deformation (strain) tensor as

$$\frac{\partial u_{\alpha\beta}(\vec{r}, t)}{\partial t} = \frac{1}{2}\left(\frac{\partial v_\alpha(\vec{r}, t)}{\partial x_\beta} + \frac{\partial v_\beta(\vec{r}, t)}{\partial x_\alpha} \right) . \qquad (4)$$

To complete our description we need to specify L and the relation between $\sigma_{\alpha\beta}$ and $u_{\alpha\beta}$.

As a simple example we recall the classical hydrodynamics model where

$$-p(\vec{r}, t) = \beta_T\, [n(\vec{r}, t) - \alpha T(\vec{r}, t)] , \qquad (5)$$

$$\sigma_{\alpha\beta}(\vec{r}, t) = 2\eta\, \frac{\partial u_{\alpha\beta}(\vec{r}, t)}{\partial t} , \qquad (6)$$

and η is the shear viscosity coefficient. It is well known that these expressions are not adequate in the presence of dispersion effects. We can easily modify (6) in a phenomenological manner to include shear relaxation.[13] This can be accomplished by making an analogy with an electric circuit consisting of a capacitance C placed in parallel with a resistance R. From this circuit we obtain an equation between voltage and charge, and if we now replace them by $\sigma_{\alpha\beta}$ and $u_{\alpha\beta}$, respectively, the result is

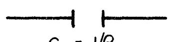
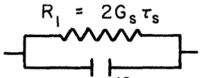
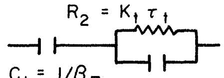
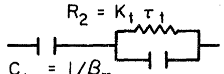
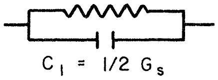
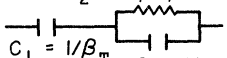
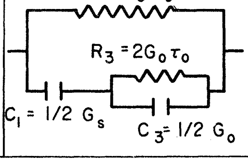
$$\left(\frac{\partial}{\partial t} + \frac{1}{\tau_s}\right) \sigma_{\alpha\beta}(\vec{r}, t) = 2G_s\, \frac{\partial u_{\alpha\beta}(\vec{r}, t)}{\partial t} , \qquad (7)$$

where we have identified C and R with the elastic and viscous properties of the fluid, $C = 1/2G_s$, and $R = 2G_s\tau_s$. Here G_s is the shear modulus and $\tau_s = \Gamma_s^{-1}$ is the shear-relaxation time. The viscosity is given by the usual Maxwell relation, $\eta = G_s\tau_s$.

A number of interesting equations can be represented by similar circuits. Also, the voltage and charge in the circuit equation are analogous to the pressure and density deviations. For example, using a RC circuit in series with a capacitance, we obtain an equation which takes into account thermal-relaxation effects. Such an equation has been used by Mountain in his analysis of Brillouin scattering by molecules with internal degrees of freedom.[16] Several models of this type are illustrated in Table I. The damping function $D(q, w)$ arises in connection with Brillouin scattering and therefore will be discussed later. It should be remembered that in the circuits relating p and n, a term $-\beta_T\alpha T$ should be added to the final expression for p; otherwise, one should at least replace β_T by β_s, the adiabatic compressibility.[13]

The circuits shown in Table I are arranged in the

TABLE I. Phenomenological analogous electric circuits and damping functions.

Model	$-P$	$\sigma_{\alpha\beta}$	$D(q,\omega)$
Classical Hydrodynamics	 $C_1 = 1/\beta_T$	 $R_1 = 2\eta = 2G_s\tau_s$	$4\eta/3\rho_0 + \frac{v_0^2(1-\gamma^{-1})aq^2}{\omega^2+(aq^2)^2}$
Maxwell	 $C_1 = 1/\beta_T$	$R_1 = 2G_s\tau_s$  $C_1 = 1/2G_s$	$\frac{4\eta/3\rho_0}{1+(\omega\tau_s)^2} + \frac{v_0^2(1-\gamma^{-1})aq^2}{\omega^2+(aq^2)^2}$
Kneser—Mountain	$R_2 = K_t\tau_t$  $C_1 = 1/\beta_T$ $C_2 = 1/K_t$	 $R_1 = 2G_s\tau_s$	$4\eta/3\rho_0 + \frac{v_0^2(1-\gamma^{-1})aq^2}{\omega^2+(aq^2)^2} + \frac{K_t\tau_t/\rho_0}{1+(\omega\tau_t)^2}$
Maxwell—Mountain	$R_2 = K_t\tau_t$  $C_1 = 1/\beta_T$ $C_2 = 1/K_t$	$R_1 = 2G_s\tau_s$  $C_1 = 1/2G_s$	$\frac{4\eta/3\rho_0}{1+(\omega\tau_s)^2} + \frac{v_0^2(1-\gamma^{-1})aq^2}{\omega^2+(aq^2)^2} + \frac{K_t\tau_t/\rho_0}{1+(\omega\tau_t)^2}$
Frenkel	$R_2 = K_t\tau_t$  $C_1 = 1/\beta_T$ $C_2 = 1/K_t$	$R_1 = 2G_s\tau_s$  $R_3 = 2G_0\tau_0$ $C_1 = 1/2G_s$ $C_3 = 1/2G_0$	$\frac{4G_s\,\omega^2\Gamma(1+\Delta)+\Gamma_0(\Gamma_s\Gamma_0-\omega^2)}{3\rho_0\,(\omega^2-\Gamma_s\Gamma_0)^2+\omega^2\Gamma^2} + \frac{v_0^2(1-\gamma^{-1})aq^2}{\omega^2+(aq^2)^2} + \frac{K_t\tau_t/\rho_0}{1+(\omega\tau_t)^2}$

order of increasing complexity. The circuits which describe shear and thermal relaxations may be called the Maxwell- and Kneser-Mountain models, respectively. The Maxwell-Mountain model, which treats both relaxations, also has been studied by Bhatia and Tong.[17] The most complicated circuit in Table I treats two relaxation processes. Such a circuit has been discussed by Frankel in connection with viscoelastic effects arising from structural changes. We will henceforth refer to the corresponding model as the Frankel model. Notice that the R_3C_3 circuit simulating reorientations appears in series with the capacitance representing shear modulus. This is because the shear relaxation is taken to be the more fundamental process.

From the analogous circuits we find the following equation for the Frenkel model:

$$-\left(\frac{\partial}{\partial t}+\Gamma_t\right)p(\vec{r},t)=\left((\beta_T+K_t)\frac{\partial}{\partial t}+\beta_T\Gamma_t\right)n(\vec{r},t)\ , \tag{8}$$

$$\left(\frac{\partial^2}{\partial t^2}+\Gamma\frac{\partial}{\partial t}+\Gamma_s\Gamma_0\right)\sigma_{\alpha\beta}(\vec{r},t)=2G_s\left((1+\Delta)\frac{\partial^2}{\partial t^2}+\Gamma_0\frac{\partial}{\partial t}\right)u_{\alpha\beta}(\vec{r},t)\ , \tag{9}$$

where

$$\Gamma=\Gamma_0+\Gamma_s(1+\Delta)\ , \tag{10}$$

$$\Delta=G_0/G_s\ . \tag{11}$$

Here G_0 is the orientational modulus, which describes the elastic part of the shear stress due to the reorientation of anisotropic molecules, and $\tau_0=\Gamma_0^{-1}$ is the corresponding relaxation time. The thermal-relaxation modulus K_t may be evaluated from the expression[18]

$$K_t=\rho_0^2v_0^2\,\frac{c_i(c_p-c_v)}{c_p(c_v-c_i)}\ , \tag{12}$$

where c_i is the internal specific heat. The product $K_t\tau_t$, where $\tau_t=\Gamma_t^{-1}$ is the thermal-relaxation time, gives the excess-bulk viscosity.

Equations (8) and (9), supplemented by (1) and (3) and appropriate initial conditions, provide the description of fluctuations in molecular liquids which we will use to study Brillouin and depolarized light scattering. It is tempting to regard this system of equations as hydrodynamic equations modified to include viscoelastic effects of shear, orientation, and thermal (or structural) relaxations. However, in conventional hydrodynamic theories, $\sigma_{\alpha\beta}$ is usually the Newtonian stress tensor which is symmetric and proportional to the velocity gradients. In the presence of fluctuations, spontaneous local stresses can exist and these are not related to the velocity gradient.[15] For example, angular momentum fluctuations are known to give rise to an antisymmetric component in $\sigma_{\alpha\beta}$.[19] For the purpose of our calculations, we therefore consider $\sigma_{\alpha\beta}$ to be an effective stress tensor which has a non-Newtonian contribution, but we make no assumptions regarding its symmetry at this point.

It is instructive to compare Eq. (9) with similar equations which have been employed by Leontovich and by Volterra. Leontovich assumed that the local strain in a liquid is relieved by the reorientation of molecules and proposed an equation identical to (7) except that τ_s is replaced by a relaxation time τ_L.[4,5] The latter is usually taken to be

$$\tau_L = \tfrac{1}{3}\tau_D = \tfrac{4}{3}(\pi/k_B T)\eta a^3 , \qquad (13)$$

where τ_D is the Debye-relaxation time and a is the radius of a molecule assumed to be spherical. The corresponding equations in Volterra's formulation consist of two coupled equations involving $\sigma_{\alpha\beta}$ and an anisotropic tensor [Eqs. (A1) and (A2) in Ref. 7]. They may be combined to give

$$\left(\frac{\partial^2}{\partial t^2} + [\Gamma_s + \gamma_0(1+D)]\frac{\partial}{\partial t} + \Gamma_s\gamma_0\right)\sigma_{\alpha\beta}(\vec{r}, t) = 2G_s\left(\frac{\partial^2}{\partial t^2} + \gamma_0\frac{\partial}{\partial t}\right)u_{\alpha\beta}(\vec{r}, t) , \qquad (14)$$

where D is a parameter and γ_0^{-1} is a reorientation time constant not necessarily identical to the above τ_0. This equation evidently has a structure similar to (9). Since both Leontovich and Volterra consider reorientations, we must conclude that the stress tensors calculated by their models also have a non-Newtonian contribution.

III. DEPOLARIZED LIGHT SCATTERING

It is well known that the spectral distributions of light scattered under various polarization conditions are determined by the fluctuations $\delta\epsilon_{\alpha\beta}$ in the dielectric tensor[20]

$$I_{\alpha\beta}(\vec{q}, \omega) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle \delta\epsilon_{\alpha\beta}(\vec{q}, t)\,\delta\epsilon^*_{\alpha\beta}(\vec{q}, 0)\rangle , \qquad (15)$$

where

$$\delta\epsilon_{\alpha\beta}(\vec{q}, t) = \int d^3r\, e^{i\vec{q}\cdot\vec{r}}\,\delta\epsilon_{\alpha\beta}(\vec{r}, t) \qquad (16)$$

and $\langle\ \rangle$ indicates an equilibrium ensemble average. The indices α and β now specify the polarization directions of the incident and scattered light. The frequency and wave-vector transfers are defined by $\omega = \omega_i - \omega_f$ and $\vec{q} = \vec{k}_i - \vec{k}_f$, where subscripts i and f refer to incident and scattered conditions. To a good approximation we have $q = 2k_i \sin\frac{1}{2}\theta$, where θ is the scattering angle.

In the macroscopic approach to light scattering, it is conventional to assume that $\delta\epsilon_{\alpha\beta}$ can be expressed in terms of the thermal fluctuations in the medium. We will follow Leontovich in introducing an anisotropic (traceless) tensor $\zeta_{\alpha\beta}$, and write[7]

$$\delta\epsilon_{\alpha\beta}(\vec{r}, t) = An(\vec{r}, t)\,\delta_{\alpha\beta} + B\zeta_{\alpha\beta}(\vec{r}, t) \qquad (17)$$

with coupling constants A and B. One usually ignores the dependence of the dielectric constant on temperature at constant density; thus $A = \rho_0(\partial\epsilon/\partial\rho)_T$. The constant B is less well defined. If we consider a crystal and take $\zeta_{\alpha\beta}$ to be the elastic strain, then B would be a fourth-rank tensor with components given by the Pockel elasto-optical constants.[21] In the present work we will treat B as a scalar constant, and as we shall see, its evaluation is not needed for the analysis of the frequency profile of certain depolarized spectra.

In general the dielectric tensor $\delta\epsilon_{\alpha\beta}(\vec{r}, t)$ is symmetric,[20,22] so the anisotropic tensor is also symmetric. In applying the Frenkel model to light scattering we assume that the spatial and temporal behavior of the anisotropic fluctuations are the same as those of the traceless stress tensor. Specifically, their Fourier components are related by

$$\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle\zeta_{\alpha\beta}(\vec{q}, t)\zeta^*_{\alpha\beta}(\vec{q}, 0)\rangle[\langle|\zeta_{\alpha\beta}(\vec{q})|^2\rangle]^{-1} = \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle\sigma_{\alpha\beta}(\vec{q}, t)\sigma^*_{\alpha\beta}(\vec{q}, 0)\rangle[\langle|\sigma_{\alpha\beta}(\vec{q})|^2\rangle]^{-1} = 2\,\mathrm{Re}[\sigma_{\alpha\beta}(\vec{q}, s)/\sigma_{\alpha\beta}(\vec{q})]_{s=i\omega} \equiv 2\tilde{\sigma}_{\alpha\beta}(\vec{q}, \omega) , \qquad (18)$$

where $\sigma_{\alpha\beta}(\vec{q}, s)$ is the Fourier-Laplace transformed solution to (9). It seems to be conventional to regard the spatial Fourier transform of $\delta\epsilon_{\alpha\beta}(\vec{r}, t)$ to be Hermitian. Then it is reasonable to assume that the effective stress tensor satisfies

$$\sigma_{\alpha\beta}(\vec{q}, t) = \sigma^*_{\beta\alpha}(\vec{q}, t) . \qquad (19)$$

This does not necessarily imply that $\sigma_{\alpha\beta}(\vec{r}, t)$ is symmetric. However, the Hermitian property does require

$$\begin{aligned} \sigma^S_{\alpha\beta}(\vec{r}, t) &= \sigma^S_{\alpha\beta}(-\vec{r}, t) , \\ \sigma^A_{\alpha\beta}(\vec{r}, t) &= -\sigma^A_{\alpha\beta}(-\vec{r}, t) , \end{aligned} \qquad (20)$$

where superscripts S and A denote the symmetric and antisymmetric components of the stress tensor, respectively. Given that $\zeta_{\alpha\beta}(\vec{q}, t)$ and $\sigma_{\alpha\beta}(\vec{q}, t)$ are Hermitian and traceless, each matrix is specified by five independent components.

We now specify the scattering geometry. As shown in Fig. 1, the scattering plane which contains $\vec{k}_i$ and $\vec{k}_f$ is chosen to be the xz plane with $\vec{q}$ directed along the z axis. With this arrangement, we can take the five independent components of $\zeta_{\alpha\beta}$ to be[7]

$$\zeta_{xy},\ \zeta_{xz},\ \zeta_{yz},\ X = \tfrac{1}{2}(\zeta_{xx} - \zeta_{yy}),\ \zeta_{zz} = -(\zeta_{xx} + \zeta_{yy}) .$$

We expect the fluctuations ζ_{xy} and X will not couple to longitudinal waves, whereas the effects of such waves should appear in ζ_{zz}. Excitations propagating along the z direction but polarized along the x

or y direction may be called shear waves. Their effects should appear in ζ_{xz} and ζ_{yz}.

We restrict our analysis further by considering only light polarizations which are parallel (H) or normal (V) to the scattering plane. The spectral distributions of interest are therefore[23]

$$I_H^V(\theta,\omega)=I_V^H(\theta,\omega)=B^2[S(\zeta_{yz})\cos^2\tfrac{1}{2}\theta+S(\zeta_{xy})\sin^2\tfrac{1}{2}\theta], \tag{21}$$

$$\begin{aligned}I_H^H(\theta,\omega)=A^2S(n)(\cos^2\tfrac{1}{2}\theta-\sin^2\tfrac{1}{2}\theta)^2+AB[S(n,\zeta_{zz})+S(\zeta_{zz},n)](\cos^2\tfrac{1}{2}\theta-\sin^2\tfrac{1}{2}\theta)\\ \times(\cos^2\tfrac{1}{2}\theta+\tfrac{1}{2}\sin^2\tfrac{1}{2}\theta)+B^2S(\zeta_{zz})(\cos^2\tfrac{1}{2}\theta+\tfrac{1}{2}\sin^2\tfrac{1}{2}\theta)+B^2S(X)\sin^4\tfrac{1}{2}\theta\,,\end{aligned} \tag{22}$$

$$I_V^V(\theta,\omega)=A^2S(n)-\tfrac{1}{2}AB[S(n,\zeta_{zz})+S(\zeta_{zz},n)]+\tfrac{1}{4}B^2S(\zeta_{zz})+B^2S(X)\,, \tag{23}$$

where

$$S(a,b)\equiv 2\int_0^\infty dt\cos\omega t\langle a(\vec{q},t)b^*(\vec{q},0)\rangle\,, \tag{24}$$

and in the case of autocorrelation only one argument is indicated in S. In arriving at these results we have assumed that the density fluctuation and the five components of $\zeta_{\alpha\beta}$ chosen above are uncorrelated except in the case of n and ζ_{zz}. The superscript and subscript in I are intended to denote incident and scattered polarizations, but the distinction is not really necessary if (19) is valid and only V and H polarizations are considered. The explicit angular dependence in the intensity expressions arises purely from geometric factors. In addition, there is an intrinsic, though weaker, angular dependence in the spectra because the various correlation functions are q dependent.

The present choice of polarizations and scattering geometry corresponds to the experimental arrangement of Stegeman and Stoicheff. Although measurements have been made at several scattering angles, we will carry out a detailed analysis only for the case of $\theta=\frac{1}{2}\pi$. From (21) and (22) we obtain

$$I_H^V(\tfrac{1}{2}\pi,\omega)=\tfrac{1}{2}[B^2\langle|X(\vec{q})|^2\rangle]\left(\frac{S(\zeta_{xy})}{\langle|\zeta_{xy}(\vec{q})|^2\rangle}+\frac{S(\zeta_{yz})}{\langle|\zeta_{yz}(\vec{q})|^2\rangle}\right), \tag{25}$$

$$I_H^H(\tfrac{1}{2}\pi,\omega)=\tfrac{1}{4}[B^2\langle|X(\vec{q})|^2\rangle]\left(\frac{S(\zeta_{zz})}{\langle|\zeta_{zz}(\vec{q})|^2\rangle}+\frac{S(X)}{\langle|X(\vec{q})|^2\rangle}\right), \tag{26}$$

where we have used the relations[7]

$$\langle|\zeta_{xy}(\vec{q})|^2\rangle=\langle|\zeta_{yz}(\vec{q})|^2\rangle=\tfrac{3}{4}\langle|\zeta_{zz}(\vec{q})|^2\rangle=\langle|X(\vec{q})|^2\rangle\,. \tag{27}$$

If we are not concerned with integrated intensities, then there is no need to evaluate the coupling constant B or $\langle|\vec{X}|\rangle^2$. Of course it is only at 90° that I_H^H arises entirely from anisotropic fluctuations and can be properly called a depolarized spectrum. The effects of density fluctuations and cross correlations, always present in I_V^V, appear in I_H^H at all other scattering angles. We will consider these effects briefly in Sec. IV.

The correlation functions which appear in (25) and (26) will now be computed according to (18). Taking Fourier and Laplace transforms of model equations (8) and (9) we find

$$\begin{aligned}p(\vec{q},s)=\frac{p(\vec{q})}{s+\Gamma_t}+\left(\beta_T+\frac{K_ts}{s+\Gamma_t}\right)n(\vec{q},S)\\ -\frac{\beta_T+K_t}{s+\Gamma_t}\,n(\vec{q})-\beta_T\alpha T(\vec{q},s)\,,\end{aligned} \tag{28}$$

$$\begin{aligned}(s^2+s\Gamma+\Gamma_0\Gamma_s)\sigma_{\alpha\beta}(\vec{q},s)=\left(\frac{\partial}{\partial t}\,\sigma_{\alpha\beta}(\vec{q},t)\right)_{t=0}\\ +(s+\Gamma)\sigma_{\alpha\beta}(\vec{q})+2sG_s[s(1+\Delta)+\Gamma_0]u_{\alpha\beta}(\vec{q},s)\,.\end{aligned} \tag{29}$$

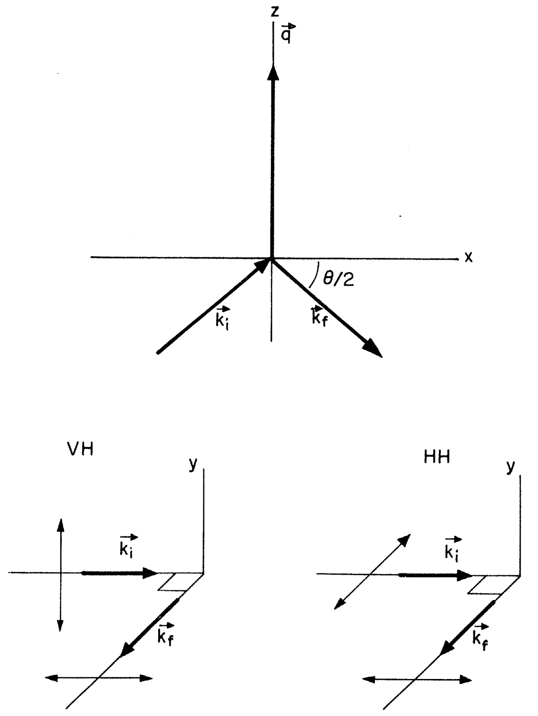


FIG. 1. Scattering geometry with wave-vector transfer $\vec{q}$ in the xz plane. Polarization arrangements shown are for VH and HH scattering at $\theta=90°$.

For initial conditions we have set

$$u_{\alpha\beta}(\vec{q}, t=0) \equiv u_{\alpha\beta}(\vec{q}) = 0 \ .$$

However, because the phenomenological stress tensor contains a non-Newtonian component, we will assume $\sigma_{\alpha\beta}(\vec{q}, t)$ and its first time derivative do not vanish at $t=0$. The model equations have to be supplemented by the transforms of (1), (3), and (4):

$$\rho_0 s v_\alpha(\vec{q}, s) = iqp(\vec{q}, s)\, \delta_{\alpha z} + iq\sigma_{\alpha\beta}(\vec{q}, s)\, \delta_{\beta z} \ , \tag{30}$$

$$T(\vec{q}, s) = -(s^2 + aq^2)^{-1}\, [(\gamma - 1)/\alpha]\, [sn(\vec{q}, s) - n(\vec{q})] \ , \tag{31}$$

$$su_{\alpha\beta}(\vec{q}, s) = \tfrac{1}{2} iq\, [v_\alpha(\vec{q}, s)\, \delta_{\beta z} + v_\beta(\vec{q}, s)\, \delta_{\alpha z}] \ , \tag{32}$$

with $\vec{v}(\vec{q}) = 0$ and $T(\vec{q}) = 0$.

Solutions to the system of Eqs. (28)–(32) are easily found once the initial values for the pressure fluctuation and the stress tensor are specified. We will assume that at $t=0$ the effects of thermal relaxation have not set in, thus $p(\vec{q}) = -\beta T n(\vec{q})$. Similarly, it will be assumed that the slower of the two relaxation processes which govern the decay of the stress tensor can be ignored at $t=0$. Although the magnitudes of shear and orientation relaxation times can have a wide range of variations depending on the liquid, we feel it is more realistic to assume

$$\tau_s \ll \tau_0 \ , \tag{33}$$

$$\left(\frac{\partial}{\partial t}\sigma_{\alpha\beta}(\vec{q}, t)\right)_{t=0} = -\frac{\sigma_{\alpha\beta}(\vec{q})}{\tau_s} \ . \tag{34}$$

Using these initial conditions we find the correlation functions defined in (18) are given by

$$\tilde{\sigma}_{xy}(\vec{q}, \omega) = \tfrac{1}{2}\, [\tilde{\sigma}_{xx}(\vec{q}, \omega) - \tilde{\sigma}_{yy}(\vec{q}, \omega)]$$

$$= \frac{\omega^2 \Gamma_s + \delta \Gamma_s \Gamma_0}{(\omega^2 - \Gamma_s \Gamma_0)^2 + (\omega\Gamma)^2} \ , \tag{35}$$

$$\tilde{\sigma}_{xz}(\vec{q}, \omega) = \tilde{\sigma}_{yz}(\vec{q}, \omega)$$

$$= \frac{\omega^4 \Gamma_s + \omega^2(\delta\Gamma_s\Gamma_0 + \Delta\Gamma\Omega_T^2)}{(\omega^2\Gamma - \Omega_T^2\Gamma_0)^2 + \omega^2[\omega^2 - \Gamma_s\Gamma_0 - (1+\Delta)\Omega_T^2]^2} \ , \tag{36}$$

$$\tilde{\sigma}_{zz}(\vec{q}, \omega) = \frac{c_1[\delta\Omega_L^2 - \omega^2(\delta + \Omega_1)] + c_2\omega^2(\delta\Omega_1 + \Omega_L^2 - \omega^2)}{c_1^2 + c_2^2\omega^2} \ , \tag{37}$$

where

$$\delta = \Gamma_0 + \Delta\Gamma_s \ , \tag{38}$$

$$\Omega_T = (G_s/\rho_0)^{1/2} q \ , \tag{39}$$

$$c_1 = \omega^4 - \omega^2[\Omega_L^2 + \Gamma_s\Gamma_0 + \Gamma_s\Omega_1 + \tfrac{4}{3}\Omega_T^2(1+\Delta)] \ , \tag{40}$$

$$c_2 = -\omega^2(\Gamma_s + \Omega_1) + \Gamma_s\Omega_L^2 + \Omega_1\Gamma_s\Gamma_0 + \tfrac{4}{3}\Omega_T^2\Gamma_0 \ , \tag{41}$$

$$\Omega_1 = \frac{\Gamma_t q^2(v_\infty^2 - v_0^2)}{\omega^2 + \Gamma_t^2} + \frac{a v_0^2 q^4(1 - \gamma^{-1})}{\omega^2 + (aq^2)^2} \ , \tag{42}$$

$$\Omega_L^2 = \frac{v_0^2 q^2}{\gamma} + \omega^2 q^2\left(\frac{v_\infty^2 - v_0^2}{\omega^2 + \Gamma_t^2} + \frac{v_0^2(1 - \gamma^{-1})}{\omega^2 + (aq^2)^2}\right)$$

$$\simeq v_0^2 q^2 + \omega^2 q^2(v_\infty^2 - v_0^2)/(\omega^2 + \Gamma_t^2) \ . \tag{43}$$

We have denoted the shear-wave frequency by Ω_T, the low- and high-frequency sound speeds by $v_0 = (\beta_s/\rho_0)^{1/2}$, and $v_\infty = (v_0^2 + K_t/\rho_0)^{1/2}$, respectively. The longitudinal-wave frequency (Brillouin shift) is Ω_L and is dispersive because of thermal relaxation. Notice that the presence of Ω_L in (37) indicates a coupling between longitudinal waves and anisotropic fluctuations.

The frequency spectra of I_H^V and I_H^H are obtained by replacing $[\langle \zeta_{\alpha\beta}(\vec{q}) |^2\rangle]^{-1} S(\zeta_{\alpha\beta})$ by $\tilde{\sigma}_{\alpha\beta}(\vec{q}, \omega)$. It is of interest to ask whether the experimental features briefly mentioned in the Introduction can be correlated with our results. For this purpose we find it most convenient to decompose the theoretical expressions into two parts, the sharp component and the broad background. In the case of VH (or HV) polarizations we have

$$I_H^V(\tfrac{1}{2}\pi, \omega) \cong B^2\langle | X(\vec{q})|^2\rangle\left(\frac{2M\Gamma_{sc}}{\omega^2 + \Gamma_{sc}^2} + \frac{L\Gamma_b}{\omega^2 + \Gamma_b^2} + L\,\frac{\omega^2\Gamma_b + \Delta\tau_0(1+\Delta)^2\Omega_T^2[\omega^2 - \Omega_T^2(1+\Delta)]}{[\omega^2 - \Omega_T^2(1+\Delta)]^2 + (\omega\Gamma_b)^2}\right) \ , \tag{44}$$

$$\Gamma_{sc} = \Gamma_0(1+\Delta)^{-1} \ ,$$

$$\Gamma_b = \Gamma_s(1+\Delta) + \Delta\Gamma_0(1+\Delta)^{-1} \ , \tag{45}$$

$$M = \Delta(1+\Delta)^{-1}, \ L = (1+\Delta)^{-1} \ .$$

In carrying out the approximate spectral decomposition we have made use of condition (33). The first term in (44) gives the sharp component while the remaining terms describe the broad background. The width of the sharp component Γ_{sc} is seen to be proportional to Γ_0, the reorientational-relaxation frequency, and the background width Γ_b is determined mainly by Γ_s, the shear-relaxation frequency.

By referring to (35) and (36) we see that $\tilde{\sigma}_{xy}$ gives a Lorentzian contribution to both the sharp component and the background. Half of the first term and the last term in (44) are the contributions from $\tilde{\sigma}_{xz}$. The last term is seen to be negative for

$$\omega^2 < \Omega_T^4\Delta(1+\Delta)^2[\Omega_T^2\Delta(1+\Delta) + \Gamma_b\Gamma_{sc}]^{-1}$$

$$\simeq \Omega_T^4\Delta(1+\Delta)^3/\Gamma_b\Gamma_0$$

and has a maximum around $\Omega_T(1+\Delta)^{1/2}$. At higher frequencies it decays like a Lorentzian of width

Γ_b. It is evident that the behavior of this term will give rise to a doublet which we will associate with the observed splitting in the central component. We expect the doublet will appear around the frequency $\Omega_T(1+\Delta)^{1/2}$, which depends on both the shear and orientational moduli. Equation (44) also predicts that the integrated intensity ratio of sharp component to background is Δ, the ratio of orientation and shear moduli. This ratio gives a measure of the relative importance of the two relaxation mechanisms and is consistent with the interpretation that Γ_{sc} and Γ_b be primarily governed by orientation and shear processes, respectively.

In a similar manner we can decompose the spectrum for the case of HH polarizations. We find

$$I_H^H(\tfrac{1}{2}\pi,\omega)$$

$$\cong \tfrac{1}{2}B^2\langle|X(\vec{q})|^2\rangle\left(4M\frac{\Gamma_{sc}}{\omega^2+\Gamma_{sc}^2}+L\frac{\Gamma_b}{\omega^2+\Gamma_b^2}+J\right), \tag{46}$$

$$J=3L\frac{(\omega^2-\Omega_L^2)^2\Gamma_b+\omega^2\Omega_1(\Omega^2-\Omega_L^2)}{\omega^2(\omega^2-\Omega^2)^2+[\omega^2(\Omega_1+\Gamma_b)-\Omega_L^2\Gamma_b]^2}, \tag{47}$$

with

$$\Omega^2=\Omega_L^2+\tfrac{4}{3}\Omega_T^2+\Gamma_b\Omega_1 . \tag{48}$$

Again one can distinguish the sharp component from the background. The term J comes from $\tilde{\sigma}_{zz}$, which is coupled to density fluctuations. We observe that since $\Omega_1 \ll \Gamma_b$, to a good approximation we have

$$J\simeq 3L\frac{(\omega^2-\Omega_L^2)^2\Gamma_b}{\omega^2(\omega^2-\Omega^2)^2+(\omega^2-\Omega_L^2)^2\Gamma_b^2}$$

$$=\frac{3L}{\Gamma_b}\left[1+\left(\frac{\omega}{\Gamma_b}\right)^2\left(\frac{\omega^2-\Omega^2}{\omega^2-\Omega_L^2}\right)^2\right]^{-1} . \tag{49}$$

Equation (49) shows that $(\Gamma_b/3L)J$ is always positive and has a maximum of unity at the origin and again at $\omega=\Omega$. It is zero at $\omega=\Omega_L<\Omega$ and for $\omega>\Omega$ it is essentially a Lorentzian of width Γ_b. Although the structure of J is different from the last term in (44), the cusp behavior around Ω_L will also give rise to a peak in the spectrum of I_H^H. Since Ω is not much greater than Ω_L, this peak in principle can be quite sharp, but is possibly considerably broadened by resolution effects. In any event, we see that (46) does reproduce the observed structure[3] in the vicinity of the Brillouin frequency.

The decomposed forms of the various correlation functions are also useful for the discussion of spectra at other scattering angles. For example, at $\theta\simeq\pi$ Eq. (21) shows that I_H^V and I_V^H are proportional to $\tilde{\sigma}_{xy}$, or

$$I_H^V(\pi,\omega)\simeq B\langle|X(\vec{q})|^2\rangle\left(M\frac{\Gamma_{sc}}{\omega^2+\Gamma_{sc}^2}+L\frac{\Gamma_b}{\omega^2+\Gamma_b^2}\right). \tag{50}$$

Indeed, Stegeman did not observe a doublet in his measurements at 176°.[3]

In Sec. V we will apply the above results to the experimental spectra of Stegeman and Stoicheff. Even though the decomposed expressions are found to be quite accurate, we will nevertheless use the original expressions (35)–(37) for numerical computations.

IV. BRILLOUIN SCATTERING

The isotropic component of the dielectric-tensor fluctuations is usually assumed to be proportional to the density fluctuations. This component gives rise to Brillouin scattering, and consequently attempts to study

$$S(n)\equiv S(q,\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,\frac{e^{-i\omega t}\langle n(\vec{q},t)\,n^*(\vec{q},0)\rangle}{S(q)}$$

$$=\frac{1}{\pi}S(q)\,\mathrm{Re}\left(\frac{n(\vec{q},s)}{n(\vec{q},0)}\right)_{s=i\omega} \tag{51}$$

in liquids[16, 24] and gases[25] have been made. Here $S(q)=1+\Gamma(q)$, where $\Gamma(q)$ is the Fourier transform of the equilibrium pair-distribution function. The density-correlation function $S(q,\omega)$ is also the quantity which governs the inelastic scattering of thermal neutrons,[26] although the values of q and ω involved are some three orders of magnitude greater.

In the calculation of $S(q,\omega)$, it is convenient to discuss various models in terms of a frequency- and wave-number-dependent damping function $D(q,\omega)$.[27,28] We define this quantity as

$$D(q,\omega)=\mathrm{Re}\,[D(q,s)]_{s=i\omega} , \tag{52}$$

where

$$\pi S(q,\omega)=-\frac{v_0^2q^2}{\gamma}\frac{1}{\omega}\,\mathrm{Im}\left(\omega^2-\frac{v_0^2q^2}{\gamma}+sq^2D(q,s)\right)^{-1}_{s=i\omega} . \tag{53}$$

The Frenkel model, (28)–(32), gives

$$\frac{n(q,s)}{n(q,0)}=Y^{-1}(s)\left[(s^2+s\Gamma+\Gamma_s\Gamma_0)\left(s+\frac{(v_\infty^2-v_0^2)q^2}{s+\Gamma_t}\right.\right.$$

$$\left.\left.+\frac{v_0^2q^2(1-\gamma^{-1})}{s+aq^2}\right)+\frac{4}{3}\Omega_T^2[\Gamma_0+s(1+\Delta)]\right] , \tag{54}$$

where

$$Y(s)=(s^2+s\Gamma+\Gamma_s\Gamma_0)\left(s^2+\frac{v_0^2q^2}{\gamma}+\frac{sq^2(v_\infty^2-v_0^2)}{s+\Gamma_t}\right.$$

$$\left.+\frac{sv_0^2q^2(1-\gamma^{-1})}{s+aq^2}\right)+\frac{4}{3}s\,\Omega_T^2\,[\Gamma_0+s\,(1+\Delta)]. \tag{55}$$

Thus we have

$$D(q,\omega)=\frac{av_0^2q^2(1-\gamma^{-1})}{\omega^2+(aq^2)^2}+\frac{(v_\infty^2-v_0^2)\tau_t}{1+(\omega\tau_t)^2}$$

$$+\frac{4G_s}{3\rho_0}\,\frac{\omega^2\Gamma(1+\Delta)+\Gamma_0(\Gamma_0\Gamma_s-\omega^2)}{(\omega^2-\Gamma_s\Gamma_0)^2+(\omega\Gamma)^2}\;. \qquad (56)$$

It is straightforward to interpret the various terms appearing in (56). The first term gives the familiar damping effects due to thermal-conduction processes.[20] The second term represents the effects of thermal relaxation.[16] The third term describes the coupled effects of shear relaxation and reorientation. The coupling is a consequence of the model, as is the dispersion effect due to thermal relaxation in the spectrum of anisotropic fluctuations. In the case of vanishing anisotropic fluctuations we expect $\Delta \to 0$ and $\Gamma_0 \to 0$. Then (56) reduces to the model discussed by Bhatia and Tong.[17] If we further ignore the shear relaxation by replacing the third term by $\frac{4}{3}\eta/\rho_0$, then (56) becomes identical to the so-called Mountain model.[16] The damping functions corresponding to the models discussed in Sec. II are given in Table I.

In terms of the notation of Sec. III, the polarization arrangements which enable $S(q,\omega)$ to be observed are VV and also HH for $\theta \neq \frac{1}{2}\pi$. Equations (22) and (23) show that in addition to $S(q,\omega)$ the measurement will always contain contributions from anisotropic fluctuations, $\tilde{\sigma}_{zz}$ and $\tilde{X}$, and cross correlations. The cross correlations can be obtained from the Frenkel model in a similar way. We find

$$S(n,\sigma_{zz})+S(\sigma_{zz},n)$$

$$=2\mathrm{Re}\left[Y^{-1}(s)\left(\frac{4}{3}\frac{G_s v_0^2 q^2}{\gamma}\;S(q)\left[\Gamma_0+s(1+\Delta)\right]\right.\right.$$

$$\left.\left.+\tfrac{1}{3}\langle|\sigma_{zz}(\vec{q})|^2\rangle\;\frac{4G_0^2q^2}{\rho_0}(s+\delta)\right)\right]. \qquad (57)$$

To determine the observed absolute intensity of Brillouin scattering, we must also have the numerical values of coupling constants A and B. Since we do not expect new features to emerge from such calculations, we will not pursue this calculation any further.

V. NUMERICAL RESULTS

Recently Stegeman and Stoicheff have made light-scattering measurements on several nonassociated organic liquids of rather high viscosity.[2,3] Among the observed spectra of I_V^H and I_H^H many showed the doublet feature discussed in Sec. III. As an application of the above analysis we will compute the 90° scattering spectra of quinoline and nitrobenzene, which are among the best resolved data. Although these two cases show similar features, their integrated intensity ratios of sharp component to background are quite different. The ratio is 0.54 for quinoline and 2.84 for nitrobenzene.[3]

TABLE II. Physical constants and parameters for quinoline and nitrobenzene.

	Quinoline	Nitrobenzene
T (°C)	22.3	20.0
ρ_0(gm/cm^3)	1.093	1.2
v_0(10^4cm/sec)	13.6	14.75
v_∞(10^4 cm/sec)	16.7	15.15
η(cp)	3.57	2.01
τ_t(10^{-11} sec)	5.4	4.4
τ_s(10^{-11} sec)	0.149	0.103
	2.5[a]	1.03[a]
τ_0(10^{-11} sec)	2.5	1.036
	0.149[a]	0.103[a]
Δ or D	0.54	2.84
	0.54[a]	2.84[a]
Ω_L(GHz)	6.4	5.6
Ω_T(GHz)	0.81	0.32
Ω(GHz)	6.5	5.64

[a] Values for the Volterra model.

The physical constants needed for the computation are given in Table II. The adiabatic sound speeds v_0 are obtained from ultrasonic data,[5,29] while the high-frequency sound speeds v_∞ are derived from the observed[3] Brillouin frequency shift assuming $\omega_B=v_\infty q$. The thermal-relaxation times have been deduced from an analysis of the width of Brillouin components.[30] In determining the shear- and orientation-relaxation times, we estimate $\tau_s=\eta/G_s$ by using the experimental value of η and an approximate G_s taken to be $\frac{3}{4}$ of the bulk-modulus value estimated by Stegeman.[3] According to the Frenkel model, Δ is the integrated intensity ratio which is known experimentally. We then use (45) to obtain τ_0 after assuming that the observed diffuse linewidth quoted in Ref. 3 is roughly Γ_{sc}.

The I_H^V spectra of quinoline and nitrobenzene are shown in Figs. 2 and 3. Since the experimental spectral distributions in Ref. 3 are traces for which the base lines are not shown, in comparing theoretical spectra with these data it was necessary to establish two reference intensities. We have, therefore, matched the theoretical and observed intensities at the position of maximum intensity and at the half-width at half-maximum. This procedure does not involve fitting another parameter in the Frenkel model to the data. The theoretical spectra, which are obtained using the full expressions (35)–(37), have been convolved with a Lorentzian resolution function having the same width as the experimental resolution spectrum. For quinoline and nitrobenzene the half-widths at half-maximum of the resolution function are 0.39 and 0.37 GHz, respectively.[3] The doublet position in each case is found to be very nearly the expected value, $\Omega_T(1+\Delta)^{1/2}$. In fact the calculations shown in Figs. 2 and 3 are in essentially perfect agreement with the experimental traces.[3] For this reason there is no need to show

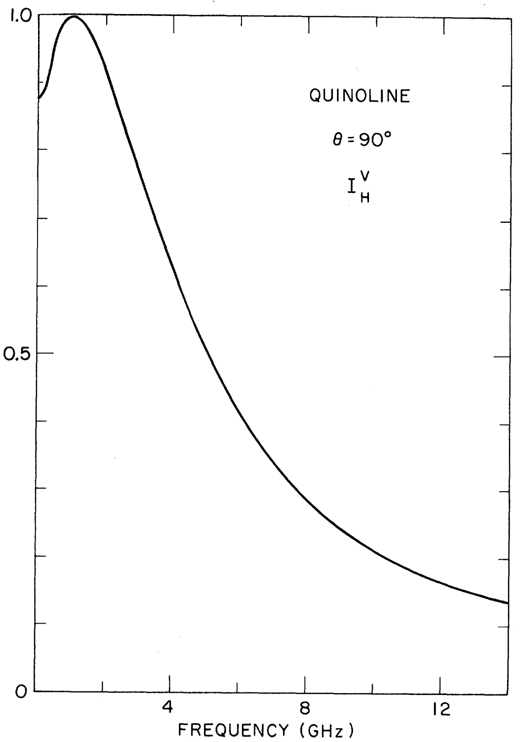


FIG. 2. Spectral distribution $I_H^V(\frac{1}{2}\pi, \omega)$ in arbitrary units for quinoline at 22.3 °C. The theoretical result has been convolved with a Lorentzian resolution function of half-width at half-maximum equal to 0.39 GHz.

the data explicitly.

In the case of I_H^H, both theoretical and experimental results are given in Figs. 4 and 5. The normalization procedure is the same. The experimental points are obtained from the traces given in Stegeman's thesis, and the size of the points indicates our estimate of the uncertainty in reading the traces and also in the fluctuations of the data themselves. As a result of the coupling with longitudinal waves in $\tilde{\sigma}_{zz}$, a shoulder now appears at approximately the frequency Ω_L. The sharpness of the structure is quite sensitive to the resolution function. For comparison we have included the results obtained from the Volterra model. Since Volterra does not consider dispersion in the sound speed we have modified his expressions by shifting the shoulder position to Ω_L. The physical constants for the Volterra model are also given in Table II. These values lead to spectra of I_H^V which are indistinguishable from those shown in Figs. 2 and 3.

VI. DISCUSSION

We have presented a calculation of the frequency spectra of light scattered under various polarization conditions by liquids composed of optically anisotropic molecules. There are two fundamental assumptions underlying our analysis. The first is that the behavior of anisotropic fluctuations in the dielectric constant can be described by an effective stress tensor. The stress tensor represents the usual elastic (Newtonian) stress as well as local stresses arising from molecular reorientations. The second assumption concerns the use of viscoelastic equations to evaluate the temporal evolution of thermal fluctuations. These equations are derived with the aid of phenomenological analogous electric circuits which simulate the effects of shear, orientation, and thermal relaxations.

In the absence of optical rotations, the dielectric tensor is symmetric and it seems reasonable that its spatial Fourier transform is Hermitian. In relating the anisotropic fluctuations to the effective stress tensor, we have assumed that $\sigma_{\alpha\beta}(\vec{q}, t)$ is also Hermitian. As mentioned in Sec. III, this assumption does not necessarily imply that the stress tensor is symmetric, but the symmetric and antisymmetric components must satisfy (20). Our analysis of depolarized light scattering was based on the assumption that $\sigma_{\alpha\beta}(\vec{q}, t)$ has five independent components. This is true if $\sigma_{\alpha\beta}$ is either Hermitian or symmetric. Since our calculations proceed in the same way under either condition, our assumption

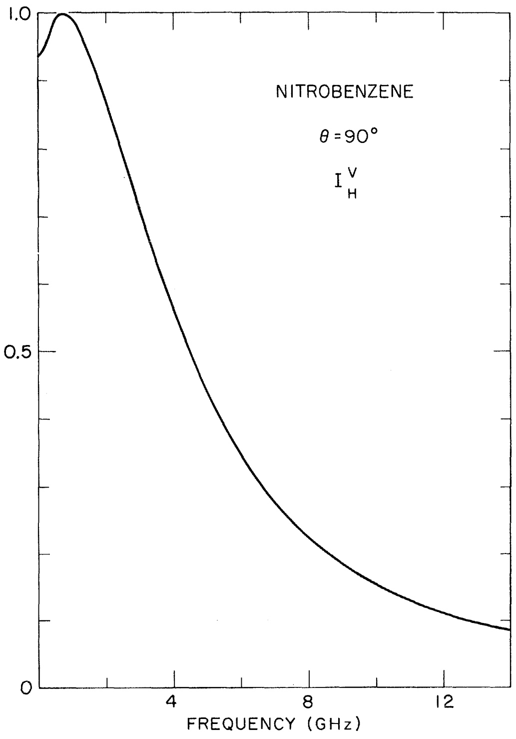


FIG. 3. Spectral distribution $I_H^V(\frac{1}{2}\pi, \omega)$ in arbitrary units for nitrobenzene at 20 °C, convolved with a Lorentzian resolution function of half-width at half-maximum equal to 0.37 GHz.

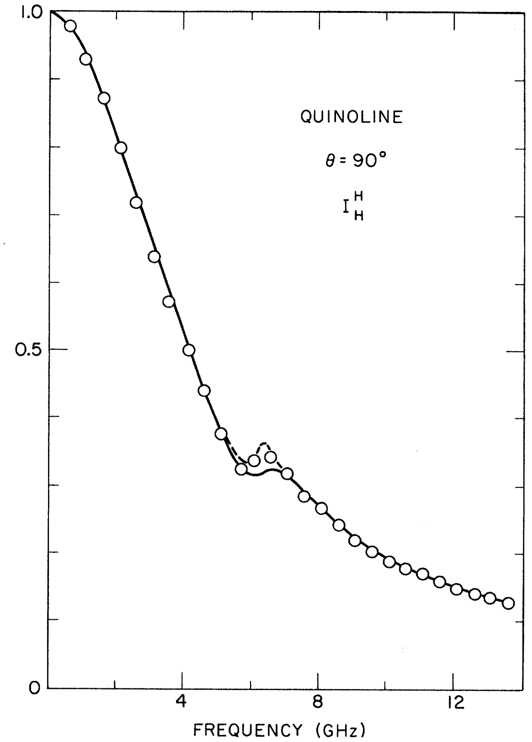


FIG. 4. Spectral distribution $I_H^H(\frac{1}{2}\pi, \omega)$ in arbitrary units for quinoline at 22.3 °C. The results of Frenkel model (solid curve) and of Volterra model (dashed curve) have been convolved with the same Lorentzian resolution as in Fig. 2. The circles represent the experimental data of Stegeman and Stoicheff and their size indicates the uncertainty in reading the measured traces as well as the fluctuations in the data.

of (19) is not essential. The alternative is to take $\sigma_{\alpha\beta}$ to be symmetric. So far as the Frenkel model is concerned, we see from (9) that $\sigma_{\alpha\beta}(\vec{q}, t)$ will be symmetric if the initial conditions are symmetric.

Ailawadi, Berne, and Forster[8] have discussed depolarized light scattering using a stress tensor which has an antisymmetric component. This component is a direct consequence of angular momentum fluctuations. Andersen and Pecora[9] have also considered an antisymmetric part of the stress tensor, and they showed that the results of Leontovich and of Volterra can be obtained from a purely symmetric stress tensor. In an approach such as Leontovich, Volterra, or the present analysis, a phenomenological equation is used to calculate $\sigma_{\alpha\beta}$, and molecular reorientations are considered implicitly through an additional relaxation mechanism.[31] Since $\delta\epsilon_{\alpha\beta}$ is symmetric, the question of the antisymmetric component does not come up during the calculations. On the other hand, in a molecular approach where one considers rotational variables, this component occurs explicitly in the coupled equations.[8,9] The importance of the antisymmetric component in studying depolarized light scattering, however, is still not fully understood.

Although our analysis of depolarized scattering is similar in spirit to the work of Volterra, we have reached different conclusions regarding the effects of reorientations and shear fluctuations in the depolarized spectra. The difference arises from the assumption of the relative magnitudes of τ_0 and τ_s, the reorientation and shear-relaxation times. Our results have been obtained under condition (33), whereas Volterra assumed $\tau_s \gg \tau_0$. Thus we arrive at the interpretation that the sharp component and broad background are governed predominantly by reorientation and shear effects, respectively. This interpretation of the sharp component is in agreement with the work of Ben-Ruven and Gershon, and Keyes and Kivelson. In Volterra's work the interpretation of the sharp component and broad background would be the reverse of our result. Even though it is difficult to make a general statement, we believe that (33) is valid for many liquids in view of the fact that reorientation times are often of the order 10^{-11} sec and shear-relaxation times, at least in simple liquids, can be as small as 10^{-13} sec. Pinnow, Candau, and Litovitz have found that τ_0 can

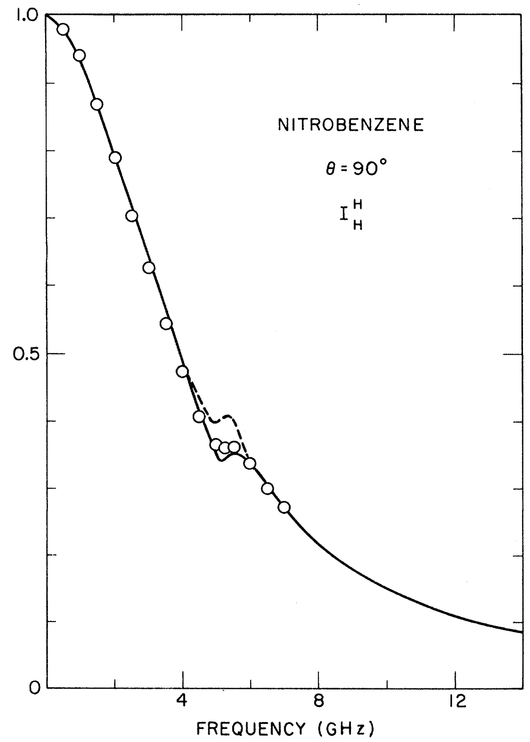


FIG. 5. Spectral distribution $I_H^H(\frac{1}{2}\pi, \omega)$ in arbitrary units for nitrobenzene at 20 °C. The notations are the same as in Fig. 4.

be larger than or comparable to τ_s, depending on whether reorientations occur in small steps or large jumps.[32]

The existence and origin of the narrow doublet in the depolarized spectra have been a subject of considerable theoretical analysis. There is general agreement that it arises from the coupling between reorientational motions and shear modes. Although the initial interpretation[2,3,7] has emphasized the connection with shear-wave propagation, more recent study suggests that the coupling should be related to dissipative motions instead of wavelike excitations.[12] Our spectral decomposition of I_H^V supports this conclusion. From (44) we have seen that the origin of the apparently resonant behavior does not depend on the existence of propagating waves. Specifically, the doublet behavior is found to be simply a consequence of the last term in (44) being negative in the vicinity of the origin. It is also interesting that the observed peak in I_H^H in the vicinity of the Brillouin frequency has an entirely different structure, as shown by (47) or (49).

We have obtained numerical results from the Frenkel model which can be compared with experiment. Figures 2–5 show excellent agreement between the calculated spectra and the measurements. We have also repeated the calculations using Volterra's model. The values of τ_0 and τ_s are obtained by reversing the assignment for the Frenkel model (cf. Table II). We then found that Volterra's model gave results which are indistinguishable from those in Figs. 2 and 3, and there is only a slight difference in I_H^H. We can therefore conclude that, aside from the interpretation of the physical mechanisms underlying the sharp-component width, the two models are essentially equivalent. If we compute the shear modulus from $\eta\Gamma_s$, assuming Γ_s is proportional to Γ_{sc}, then we would obtain a value which is smaller than the bulk modulus by at least an order of magnitude. This observation would indicate that the sharp component has little direct connection with shear modes.[33]

ACKNOWLEDGMENT

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[22] We ignore the possibility of optical rotation.

[23] There are several misprints in the general intensity expression given by Volterra in Ref. 7. His Eq. (10) should read

$$
\begin{aligned}
I_\Omega \propto {} & A^2(u)_\Omega (\vec{p}\cdot\vec{p}\,')^2 + AB(uZ)_\Omega \vec{p}\cdot\vec{p}\,' (\tfrac{3}{2}p_z p_z' - \tfrac{1}{2}\vec{p}\cdot\vec{p}\,') \\
& + B^2(Z)_\Omega (\tfrac{3}{2}p_z p_z' - \tfrac{1}{2}\vec{p}\cdot\vec{p}\,')^2 + B^2(\zeta_{xz})_\Omega (p_x p_z' + p_z p_x')^2 \\
& + B^2(\zeta_{yz})_\Omega (p_y p_z' + p_z p_y')^2 + B^2(\zeta_{xy})_\Omega (p_x p_y' + p_y p_x')^2 \\
& + B^2(X)_\Omega (p_x p_x' + p_y p_y')^2 .
\end{aligned}
$$

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Two-Photon Decay Rate of the 2^1S_0 Metastable State of Helium[†]

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Two alternative expressions for the two-photon decay rate of the $2\,^1S_0$ metastable state of helium are evaluated by performing the summations over intermediate $^1P_1$ states. The values obtained from the "length" and "velocity" expressions for the decay rate are 50.85 sec^{-1} and 50.89 sec^{-1}, respectively, in good agreement with a recent experimental value and with previous calculations done by different methods. Incidental results are given for the photoionization cross sections of the $1\,^1S_0$ and $2\,^1S_0$ states of helium in the energy region 0–0.2 Ry.

I. INTRODUCTION

The radiative lifetime of the $2\,^1S_0$ metastable state of helium is of fundamental interest because single-photon decay to the $1\,^1S_0$ ground state is strictly forbidden by the selection rule $J=0 \nrightarrow J=0$. This selection rule is violated only by the presence of nuclear spin. Breit and Teller[1] pointed out that the $2\,^1S_0$ state of helium should decay predominantly by two-photon electric-dipole emission. This decay process gives rise to a continuous emission spectrum, since the only restriction on the photon energies is that their sum equal the energy difference between the $2\,^1S_0$ and $1\,^1S_0$ states.

The two-photon decay of the $2\,^1S_0$ state proceeds through virtual transitions to intermediate $^1P_1$ states. In order to evaluate directly the expression for the decay rate, an infinite summation over the intermediate $^1P_1$ states (which includes integrations over the continua) has to be performed for each pair of photon energies. Dalgarno[2] first attempted a direct evaluation of the expression for the two-photon decay rate of the $2\,^1S_0$ state by explicitly carrying out the summations over the intermediate states. In subsequent calculations, Dalgarno and Victor[3,4] avoided doing the infinite summations over intermediate states by carrying out variational calculations for the complete perturbed wave function for each pair of photon energies. In a recent calculation of the two-photon decay rates of the $2\,^1S_0$ and $2\,^3S_1$ states of heliumlike ions, Drake, Victor, and Dalgarno[5] conveniently performed the summations over intermediate states by replacing the sets of true excited-state wave functions by discrete sets of variationally determined functions.

In the calculation of the two-photon decay rate described in this paper, the summations over the intermediate $^1P_1$ states are explicitly performed. Use is made of the oscillator strengths recently obtained by Schiff, Pekeris, and Accad[6] for the electric-dipole transitions from the $1\,^1S_0$ and $2\,^1S_0$ states to the lowest four discrete $^1P_1$ states. An expansion into a complete discrete basis set (a modification of the close-coupling method used to describe electron scattering by hydrogenlike ions) has been carried out for the $^1P_1$ continuum wave functions. These wave functions have been applied with success in an evaluation of the photoionization cross sections of the $1\,^1S_0$ and $2\,^1S_0$ states of helium.[7]

Pearl[8] has reported an experimental value of $(38\pm 8)\times 10^{-3}$ sec for the radiative lifetime τ of the $2\,^1S_0$ metastable state of helium. However, a more recent series of measurements made by Van Dyck and co-workers[9,10] has yielded the result $\tau=(20\pm 1)\times 10^{-3}$ sec, which is in good agreement with the theoretical value of $\tau = 19.5\times 10^{-3}$ sec calculated by Drake, Victor, and Dalgarno.[5]

II. THEORY OF TWO-PHOTON EMISSION

The probability for the simultaneous electric-dipole emission of two photons with one photon in the frequency range from ν_1 to $\nu_1 + d\nu_1$ is given (in sec^{-1}) by[1]

$$A(\nu_1)\,d\nu_1 = \frac{2^{10}\pi^6 e^4}{h^2 c^6}\,\nu_1^3\nu_2^3\,d\nu_1$$

$$\times \Bigg\langle \Bigg| \sum_{n'} \Bigg[\frac{\langle 1\,^1S|\vec{R}\cdot\vec{\epsilon}_1|n'\rangle\langle n'|\vec{R}\cdot\vec{\epsilon}_2|2\,^1S\rangle}{\nu_{n'2}+\nu_2}$$