

Thermodynamic description of depolarized light scattering from viscoelastic liquids

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A thermodynamic calculation of the depolarized scattering spectrum of a viscoelastic liquid is presented. We introduce the stress tensor and the polarizability density as additional state variables. By using extended irreversible thermodynamics, we derive time evolution equations for all the independent variables. The temperature dependence of the spectrum is calculated and we show that it reproduces the general observed features of the spectrum. We also show that from our description we recover, as special cases, the results of other phenomenological approaches that are in good agreement with experiment and microscopic theories. The implications and limitations of our approach are discussed.

I. INTRODUCTION

The first theoretical prediction on the fine structure of the vertical-horizontal ($V-H$) light-scattering spectra from liquids was given by Leontovich¹ almost half a century ago and 30 years before the first experimental observation was made.² Since then, and owing to the availability of new experimental techniques, such as dielectric relaxation or photon correlation spectroscopy, the subject has given rise to numerous experimental and theoretical investigations on a variety of relaxation phenomena in liquids and complex materials.

Experimentally it is well established that the depolarized ($V-H$) spectrum of viscoelastic liquids essentially consists of a pronounced doublet, symmetrically displaced with respect to the incident frequency and with a breadth substantially larger than the peak separation.³⁻⁶ However, the shape of this spectrum is strongly dependent on the temperature and on the values of relevant parameters such as the rate of molecular reorientation (Γ), the zero-frequency kinematic shear viscosity (ν_s) and the amplitude of the scattering vector (q). For instance, it is known that the depolarized spectrum of viscoelastic liquids displays a fine structure with a dip at the center, for high temperatures such that $\Gamma \gg q^2 \nu_s$. But when the temperature is lowered so that $\Gamma \approx q^2 \nu_s$, this central dip disappears with a narrowing of the entire spectrum, which is not describable as a superposition of several Lorentzian functions. Moreover, at low temperatures where $\Gamma \ll q^2 \nu_s$, the spectrum shows two weak shifted sidebands and an intense, although very narrow, central component.

On the other hand, from the theoretical point of view it was soon realized that these experimental results could

not be accounted for in terms of the classical hydrodynamical theory of simple liquids.⁷ So new macroscopic and microscopic theories were developed for this purpose. Actually, the observed spectral features of depolarized scattering in liquids have been, essentially, analyzed by using statistical mechanical formalisms of the Mori-Zwanzig⁸⁻¹⁰ type or by adopting phenomenological points of view based on irreversible thermodynamics.¹¹⁻¹⁴ Within this latter class of theories the basic idea has been to consider that the systems are so highly dispersive, that additional state variables should be introduced to characterize the relaxation processes occurring in systems like a viscoelastic liquid. Linear irreversible thermodynamics (LIT) is subsequently used to calculate the depolarized spectrum and it has been found that these approaches have been successful in describing correctly the general features of the observed spectra. In particular, using this type of approach, Quentrec *et al.*,¹³⁻¹⁶ for instance, have repeatedly emphasized the importance of local order in describing the hydrodynamics of a liquid when the correlation length and the lifetime of this order are not negligible with respect to a characteristic length and time of the corresponding experiment. Since there is, indeed, experimental and molecular dynamics evidence showing the existence of local order in different kinds of fluids,¹⁴⁻¹⁷ it is reasonable to expect that in order to describe the scattering or transport properties of complex fluids such as viscoelastic liquids, polymeric solutions, or polyatomic fluids, it may be, in fact, convenient to introduce new state variables in addition to the usual hydrodynamic densities. It is in connection with this idea where the motivation for this paper lies. Our main objective is to use extended irreversible thermodynamics (EIT), a recent theory developed precisely with the idea of ex-

tending LIT to regimes where the inclusion of additional state variables is necessary or convenient,^{18–23} to calculate the V - H spectrum of a viscoelastic liquid composed of nonspherical molecules. In particular, we discuss how a phenomenological analysis recently proposed by Wang²⁰ to describe the effect of shear wave coupling on the V - H scattering of a viscoelastic liquid can be derived from our thermodynamic scheme as a special case. In this way we provide a thermodynamic basis for a phenomenological theory that is in good agreement with experiment and other microscopic theories, but, in addition, our treatment allows us to derive the analytic temperature dependence of the phenomenological coefficients involved in our development and, therefore, of the depolarized spectrum. It should be pointed out, though, that Wang has also lucidly performed a microscopic analysis of this problem. We shall mainly refer to his phenomenological approach.

To this end we have organized the paper as follows. In Sec. II the extended thermodynamics for an arbitrary viscoelastic fluid composed of nonspherical molecules is set up and developed to the stage of deriving a complete set of time-evolution equations for all the independent state variables of the system. These equations contain unknown phenomenological coefficients, the usual transport coefficients among them, that can only be determined by comparison either with experiment or with a microscopic model. These evolution equations also show the possible couplings that, consistent with the theory, may arise among the state variables and with the macroscopic flow. In Sec. III the linearized hydrodynamic model to be used is defined and the computation of the depolarization spectrum is carried out. We then derive, for particular choices of the phenomenological coefficients in our result, the spectra for viscous and viscoelastic liquids that Wang has proposed by using a phenomenological, although not thermodynamic, approach. The explicit temperature dependence of this spectrum is also obtained and its limits of validity are also discussed. Finally, in Sec. IV we give some concluding remarks on the scope and validity of our approach.

II. EXTENDED THERMODYNAMICS DESCRIPTION

The foundations and methodology of EIT, considered as an extension of LIT, have been discussed^{18,19} in detail and applied^{21–25} to a variety of physical systems in the last few years. In this section we briefly describe the main features of this theory and we use it to describe a viscoelastic liquid composed of nonspherical molecules in a nonequilibrium thermodynamic state beyond Onsager's linear regime. As already mentioned in the Introduction, an appropriate hydrodynamics for such a system should include other variables in addition to the usual hydrodynamic conserved internal energy $e(\mathbf{r}, t)$ and mass densities $\rho(\mathbf{r}, t)$. With this motivation, and according to the usual procedure of EIT,¹⁸ we choose a stress tensor $\underline{\tau}(\mathbf{r}, t)$, which includes both elastic and viscous effects beyond the Newtonian limit, as a first additional variable. A further motivation for choosing $\underline{\tau}$ as a state variable,

lies in the fact that the vast amount of information regarding rheological equations of state (constitutive relations)²⁶ is precisely expressed in terms of $\underline{\tau}$. So, it seems natural that the hydrodynamic equations we are seeking should include it. On the other hand, since it is well established that the depolarized spectrum arises from polarizability fluctuations,²⁷ we also choose the polarizability anisotropy density $\underline{\alpha}(\mathbf{r}, t)$ as a second nonconserved thermodynamic state variable. It should be mentioned, though, that EIT does not provide for a general criteria to choose, in a unique way, the number and nature of the fast variables. Although in our case their choice may be more or less reasonable, in general, the nonconserved variables have different physical interpretations.

$\underline{\tau}$ is defined in terms of the pressure tensor $\underline{\Pi}$ through

$$\underline{\Pi} = p\underline{I} + \underline{\tau}, \quad (2.1)$$

where p is the hydrostatic pressure and \underline{I} the unit tensor. Hence, the space of thermodynamic state variables is composed of the set of conserved densities $C \equiv \{e, v\}$ (where the specific volume v is defined as the inverse of the mass density $v \equiv \rho^{-1}$), and the set of fast or nonconserved variables $R \equiv \{\underline{\tau}, \underline{\alpha}\}$. The primary purpose of EIT is to provide for a closed set of differential equations governing the time evolution of all the independent state variables in $G = C \cup R$. The behavior of the conserved ones is given by the familiar conservation laws, but the dynamics of the chosen nonconserved variables should be derived self-consistently from the theory itself. In general, these latter equations will be a coupled set of nonlinear relaxation equations defined in terms of unknown phenomenological coefficients arising from the different stages in the implementation of the theory. The essential point to stress, however, is that these equations describe the way in which the nonconserved variables fade away in the system and how their dynamics affects the behavior of the other variables. They play the role of generalized constitutive relations that allow to obtain a closed set of hydrodynamic equations for the conserved variables. For the system in consideration the conservation equations read

$$\frac{dv}{dt} = v \operatorname{div} \mathbf{u}, \quad (2.2a)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\operatorname{grad} p - \operatorname{div} \underline{\tau}, \quad (2.2b)$$

$$\rho \frac{de}{dt} = -p \operatorname{div} \mathbf{u} - \underline{\tau} : \underline{L}, \quad (2.2c)$$

where \mathbf{u} is the hydrodynamic flow velocity, the tensor \underline{L} stands for the velocity gradient, $\underline{L} = \operatorname{grad} \mathbf{u}$, and $d/dt = \partial/\partial t + \mathbf{u} \cdot \nabla$ is the usual material time-derivative operator. The symbol $:$ denotes the double contraction of the corresponding tensors.

In order to derive time-evolution equations for the R variables, EIT first postulates the existence of a sufficiently continuous and differentiable function η defined over G :

$$\eta = \eta(e, v; \underline{\tau}, \underline{\alpha}). \quad (2.3)$$

Although this function cannot be *a priori* identified with a physical nonequilibrium entropy of the system, in a strictly formal sense it generates a differential form which generalizes the Gibbs relation of local equilibrium thermodynamics. This idea has been frequently used in other formulations of nonequilibrium thermodynamics.²⁸ In fact, if we now carry out the standard manipulations of EIT,^{18–23} from Eq. (2.3) and to lowest order in the nonconserved variables we arrive at

$$T \frac{d}{dt} \eta = \frac{de}{dt} + p \frac{dv}{dt} + v \underline{\beta}_1 : \frac{d}{dt} \underline{\tau} + v \underline{\beta}_2 : \frac{d}{dt} \underline{\alpha} - \underline{\tau} : \underline{L} . \quad (2.4)$$

Here the second-rank tensors $\underline{\beta}_i$, $i = 1, 2$, are given by

$$\underline{\beta}_i = \beta_{i0} \underline{\tau} + \beta_{i1} \underline{\alpha} , \quad (2.5)$$

where the phenomenological coefficients are, in general, functions of all the scalar invariants in G . Consistently with the order involved in writing Eq. (2.4), they are functions of the local equilibrium variables e and v only. Also, to this order of approximation the coefficients T and p are identified with the local equilibrium temperature and pressure, respectively. The idea of order used here should be understood as follows: the first powers of the nonconserved variables measure first-order deviations with respect to local equilibrium and so on. Thus, a Taylor series expansion of *all* the quantities appearing in the theory around the local equilibrium state allows for the consecutive inclusion of deviations from the latter up to any desired order. In this sense the results of EIT should reduce to those of LIT when the system reaches local equilibrium.

We now introduce the assumption that η obeys a balance equation, namely,

$$\rho \frac{d}{dt} \eta + \text{div} \mathbf{J}_\eta = \sigma_\eta , \quad (2.6)$$

where \mathbf{J}_η and σ_η denote, respectively, the generalized flux and source terms associated with η . As the tensors $\underline{\beta}_i$, \mathbf{J}_η , and σ_η should be constructed as the most general vector and scalar in G up to the required order. Thus, consistency with Eq. (2.4) requires that

$$\mathbf{J}_\eta = \mathbf{0} , \quad (2.7)$$

$$\sigma_\eta = \underline{X}_1 : \underline{\tau} + \underline{X}_2 : \underline{\alpha} , \quad (2.8)$$

where, by the assumptions of the theory, one has, to lowest order in the R variables ($i = 1, 2$),

$$\begin{aligned} \underline{X}_i = & \mu_{i0} \underline{\tau} + \mu_{i1} \underline{\alpha} + \mu_{i2} \underline{L} + \mu_{i3} \underline{\tau} : \underline{L} \\ & + \mu_{i4} \underline{\alpha} : \underline{L} + \mu_{i5} \underline{L} : \underline{L} . \end{aligned} \quad (2.9)$$

As usual the multidot between two tensors denotes their scalar product. Again, it is worth stressing that the phenomenological coefficients μ_{ij} , as well as the previous β_{ij} , are unknown and can only be determined either from experiment or from a microscopic theory. Moreover, for simplicity in our development we shall assume from now on that *all* these phenomenological coefficients are constant parameters.

If we now substitute Eqs. (2.2a) and (2.2c) into Eq. (2.4)

and if the resulting equation together with Eq. (2.7) is then inserted in Eq. (2.6), we get an explicit expression for σ_η . But this quantity may be also obtained in a different way, namely, by substitution of Eq. (2.9) into (2.8). Thus, by equating these expressions for σ_η and after performing tedious but straightforward calculations, we arrive at the sought time-evolution equations for the nonconserved variables:

$$\tau_1 \frac{d}{dt} \underline{\tau} = -\underline{\tau} + a_1 \underline{\alpha} + a_2 \underline{L} + a_3 \underline{\tau} : \underline{L} + a_4 \underline{\alpha} : \underline{L} + a_5 \underline{L} : \underline{L} , \quad (2.10a)$$

$$\tau_2 \frac{d}{dt} \underline{\alpha} = -\underline{\alpha} + b_1 \underline{\tau} + b_2 \underline{L} + b_3 \underline{\tau} : \underline{L} + b_4 \underline{\alpha} : \underline{L} + b_5 \underline{L} : \underline{L} . \quad (2.10b)$$

It is worth emphasizing several important features of these equations. First note that several possible couplings arise among the nonconserved variables $\underline{\tau}, \underline{\alpha}$ themselves and with the macroscopic flow through \underline{L} . But these couplings are not introduced *ad hoc*, they result as a consequence of the postulates of the theory to the approximation to which it has been developed. Second, the coupling constants a_i, b_i are functions of the phenomenological coefficients β_{ij}, μ_{ij} and of the temperature T . However, in order to avoid lengthy expressions in the main text and since the explicit form of a_i, b_i is unnecessary to exhibit the structure of the time-evolution equations, their explicit definitions are given in Appendix A. The essential point to be stressed, though, is that these quantities depend on the temperature T . This fact will allow us to derive the explicit temperature dependence of several physical properties that can be calculated on the basis of Eq. (2.10). This will be developed in the following sections. Third, it is important to mention that Eqs. (2.10) are indeed relaxation equations if it is possible to show that the “relaxation times” τ_1, τ_2 , defined by Eqs. (A2), are positive definite quantities. Actually, as mentioned before, the explicit determination of the phenomenological coefficients is beyond EIT. This can only be accomplished by restoring to microscopic formulations or to experiment. For other systems such as fluids with internal degrees of freedom, where kinetic descriptions are available, the explicit form and sign of the phenomenological coefficients can be established.²³ For the systems we are dealing with we are not aware of microscopic time-evolution equations for the variables we have chosen, for which the same comparison can be done. However, it is reasonable to expect that Eqs. (2.10) should be relaxation equations, if the nonequilibrium states under consideration are not too far from equilibrium, since in this case they ought to be thermodynamically stable. So, we shall view Eqs. (2.10) as a coupled set of relaxation equations with constant coefficients.

III. THE HYDRODYNAMIC MODEL

In order to derive a closed set of linearized hydrodynamic equations for the conserved variables only, we first linearize both the conservation equations (2.2) and

the relaxation equations (2.10), selecting as a reference a total equilibrium state defined by the values ρ_0 , e_0 , $\mathbf{u}_0 = \mathbf{0}$, $\underline{\tau} = 0$, and $\underline{\alpha} = 0$. Thus, if the deviations from this reference state are denoted by δ , we have that

$$\begin{aligned} \rho(\mathbf{r}, t) &= \rho_0 + \delta\rho(\mathbf{r}, t), \quad e(\mathbf{r}, t) = e_0 + \delta e(\mathbf{r}, t), \\ \mathbf{u}(\mathbf{r}, t) &= \delta\mathbf{u}(\mathbf{r}, t), \quad \underline{\tau}(\mathbf{r}, t) = \delta\underline{\tau}(\mathbf{r}, t), \\ \underline{\alpha}(\mathbf{r}, t) &= \delta\underline{\alpha}(\mathbf{r}, t). \end{aligned} \quad (3.1)$$

It should be remarked that this linearization does not imply that the system is in the linear regime of LIT, since the deviations in the nonconserved variables, however small, do not vanish and their presence invalidates the local equilibrium assumption.²²

By substituting Eqs. (3.1) into Eqs. (2.2) and (2.10), neglecting nonlinear deviations, taking the Fourier-Laplace transforms of the resulting equations with respect to \mathbf{r} and t , and expressing e as a function of T and p in terms of ρ , T through the relations

$$e = c_V T, \quad (3.2)$$

$$p = c_T^2(\rho + \alpha\rho_0 T), \quad (3.3)$$

we arrive at the following set of linearized hydrodynamic equations:

$$z\delta\tilde{\rho}(\mathbf{q}, z) = \delta\hat{\rho}(\mathbf{q}) - i\rho_0\mathbf{q} \cdot \underline{\mu}(\mathbf{q}, z), \quad (3.4a)$$

$$z\delta\tilde{T}(\mathbf{q}, z) = \delta\hat{T}(\mathbf{q}) + i\frac{1-\gamma}{\alpha}\mathbf{q} \cdot \underline{\mu}(\mathbf{q}, z), \quad (3.4b)$$

$$\begin{aligned} z\underline{\mu}(\mathbf{q}, z) &= \underline{\mu}(\mathbf{q}) - iC_T^2\rho_0^{-1}\mathbf{q}\delta\tilde{\rho}(\mathbf{q}, z) \\ &\quad - ic_T^2\alpha\mathbf{q}\delta\tilde{T}(\mathbf{q}, z) - i\rho_0^{-1}\mathbf{q} \cdot \underline{\tau}(\mathbf{q}, z), \end{aligned} \quad (3.4c)$$

$$\begin{aligned} I_{VH}(\mathbf{q}, \omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \left\{ \langle \alpha_{yz}(\mathbf{q}, t) \alpha_{yz}^*(\mathbf{q}) \rangle \cos^2 \frac{\theta}{2} + \langle \alpha_{yx}(\mathbf{q}, t) \alpha_{yx}^*(\mathbf{q}) \rangle \sin^2 \frac{\theta}{2} \right\} \\ &\equiv I_{yz}(\mathbf{q}, \omega) \cos^2 \frac{\theta}{2} + I_{yx}(\mathbf{q}, \omega) \sin^2 \frac{\theta}{2}. \end{aligned} \quad (3.8)$$

This expression corresponds to a geometry such that the scattering plane, which contains the incident (\mathbf{k}_i) and scattering (\mathbf{k}_s) wave vectors, is the xz plane. The polarization of the incident light is along the y axis and the scattering vector $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_i$ is directed along the z axis. As usual, θ is the scattering angle, the angular brackets denote an equilibrium ensemble average and the asterisk stands for the complex conjugate. Moreover, for the purpose of a later comparison of our results with those of Wang,²⁰ we further assume that the liquid is flowing with a velocity \mathbf{u}_y along y under the effect of a velocity gradient along z , that is, $L_{yz} = \partial u_y / \partial z$. With these assumptions our hydrodynamic model simplifies and the conservation equations (3.4) reduce to

$$z\delta\tilde{\rho}(\mathbf{q}, z) = \delta\hat{\rho}(\mathbf{q}), \quad (3.9a)$$

$$z\delta\tilde{T}(\mathbf{q}, z) = \delta\hat{T}(\mathbf{q}), \quad (3.9b)$$

$$\begin{aligned} \tilde{\underline{\tau}}(\mathbf{q}, z)(z\tau_1 + 1) &= \tau_1\hat{\underline{\tau}}(\mathbf{q}) + a_1\tilde{\underline{\alpha}}(\mathbf{q}, z) \\ &\quad - ia_2\mathbf{q}\tilde{\underline{\mu}}(\mathbf{q}, z), \end{aligned} \quad (3.5a)$$

$$\begin{aligned} \tilde{\underline{\alpha}}(\mathbf{q}, z)(z + \tau_2^{-1}) &= \hat{\underline{\alpha}}(\mathbf{q}) + b_1\tilde{\underline{\tau}}(\mathbf{q}, z) \\ &\quad - ib_2\mathbf{q}\tilde{\underline{\mu}}(\mathbf{q}, z). \end{aligned} \quad (3.5b)$$

The tilde and the caret denote, respectively, the Fourier and Laplace transforms; α and γ represent the isobaric expansion coefficient and the ratio of specific heats, i.e.,

$$\alpha \equiv -\rho_0^{-1} \left[\frac{\partial \rho_0}{\partial T_0} \right]_p, \quad \gamma \equiv \frac{c_p}{c_V}, \quad (3.6)$$

whereas c_T^2 stands for

$$c_T^2 \equiv \gamma \left[\frac{\partial p}{\partial \rho_0} \right]_{T_0}. \quad (3.7)$$

Equations (3.4) and (3.5) represent a rather general closed set of hydrodynamic equations which involve several phenomenological coefficients (τ_i, a_i, b_i) that are, so far, unspecified. In the following subsections we shall now use this model to calculate the depolarized light-scattering properties of our system.

A. Depolarized spectrum

It is well known that this spectrum arises from the temporal and spatial fluctuations of the polarizability anisotropy density. More specifically, its spectral density is proportional to the Fourier transform of two anisotropic polarizability time-correlation functions, namely,^{8,27}

$$\begin{aligned} \tilde{u}_y(\mathbf{q}, z) &= -ic_T^2\rho_0^{-1}qz^{-2}\delta\hat{\rho}(\mathbf{q}) - ic_T^2\alpha qz^{-2}\delta\hat{T}(\mathbf{q}) \\ &\quad - i\rho_0^{-1}qz^{-1}\tilde{\tau}_{zy}(\mathbf{q}, z), \end{aligned} \quad (3.9c)$$

whereas for the zy component the relaxation equations read

$$\tilde{\tau}_{zy}(\mathbf{q}, z)(z\tau_1 + 1) = \tau_1\hat{\tau}_{zy}(\mathbf{q}) + a_1\tilde{\alpha}_{zy}(\mathbf{q}, z) - ia_2q\tilde{u}_y(\mathbf{q}, z), \quad (3.10a)$$

$$\tilde{\alpha}_{zy}(\mathbf{q}, z)(z + \tau_2^{-1}) = \hat{\alpha}_{zy}(\mathbf{q}) + b_1\tilde{\tau}_{zy}(\mathbf{q}, z) - ib_2q\tilde{u}_y(\mathbf{q}, z), \quad (3.10b)$$

and for the yx component they are given by

$$\tilde{\tau}_{yx}(\mathbf{q}, z)(z\tau_1 + 1) = \tau_1\hat{\tau}_{yx}(\mathbf{q}) + a_1\tilde{\alpha}_{yx}(\mathbf{q}, z), \quad (3.11a)$$

$$\tilde{\alpha}_{yx}(\mathbf{q}, z)(z + \tau_2^{-1}) = \hat{\alpha}_{yx}(\mathbf{q}) + b_1\tilde{\tau}_{yx}(\mathbf{q}, z). \quad (3.11b)$$

From this set of equations we can now calculate the polarizability correlation functions involved in Eq. (3.8). By eliminating $\tilde{\tau}_{zy}(\mathbf{q}, z)$ from Eqs. (3.9) and (3.10) we obtain an expression for $\tilde{\alpha}_{zy}(\mathbf{q}, z)$ in terms of the initial values $\delta\hat{\rho}(\mathbf{q}), \delta\hat{T}(\mathbf{q}), \hat{\alpha}_{zy}(\mathbf{q}), \hat{\tau}_{zy}(\mathbf{q})$. If this resulting equation is

$$\langle \tilde{\alpha}_{zy}(\mathbf{q}, z) \hat{\alpha}_{zy}^*(\mathbf{q}) \rangle = \chi \frac{z\tau_1 + 1 + a_2\rho_0^{-1}q^2z^{-1}}{(z + \tau_2^{-1})(z\tau_1 + 1 + a_2\rho_0^{-1}q^2z^{-1}) + a_1(b_2\rho_0^{-1}q^2z^{-1} - b_1)} \quad (3.12a)$$

with

$$\chi \equiv \langle |\hat{\alpha}_{zy}(\mathbf{q})|^2 \rangle = \langle |\hat{\alpha}_{yx}(\mathbf{q})|^2 \rangle, \quad (3.12b)$$

due to the isotropy of the fluid. In a similar way, from Eqs. (3.11) we get

$$\langle \tilde{\alpha}_{yx}(\mathbf{q}, z) \hat{\alpha}_{yx}^*(\mathbf{q}) \rangle = \chi \frac{z\tau_1 + 1}{(z\tau_1 + 1)(z + \tau_2^{-1}) - a_1b_1}. \quad (3.13)$$

This, if we now set $z = i\omega$, from Eqs. (3.12), (3.14), and (3.8) we finally have that

$$I_{VH}(\mathbf{q}, \omega) \sim \text{Re} \left[\frac{1 + z\tau_1}{(1 + z\tau_1)(\tau_2^{-1} + z) - a_1b_1} + \frac{1 + z\tau_1 + a_2\rho_0^{-1}q^2z^{-1}}{(\tau_2^{-1} + z)(1 + z\tau_1 + a_2\rho_0^{-1}q^2z^{-1}) + a_1(b_2\rho_0^{-1}q^2z^{-1} - b_1)} \right]_{z=i\omega}. \quad (3.14)$$

To avoid writing complicated expressions in the main text, in Appendix B we give the explicit form of $I_{VH}(\mathbf{q}, \omega)$ in full detail.

B. Viscous fluid limit

The spectra given by Eq. (3.14), being a result of a thermodynamic theory, involves phenomenological coefficients which are, so far, completely unspecified. We shall now show that for particular choices of these coefficients we may recover, as special cases, several results obtained by using different approaches. To this end let us first set $\tau_1 \rightarrow 0$ in the relaxation equations (3.10). This eliminates the relaxation in the stress tensor and corresponds to a limit where the fluid is essentially Newtonian. More explicitly, if, in addition, we set $b_1 = 0$ and make the identifications

$$\tau_2^{-1} \equiv \Gamma, \quad a_2 \equiv \eta_s, \quad a_1 \equiv \mu, \quad b_2 \equiv \mu', \quad (3.15)$$

the relaxation equations (3.10) reduce to

$$\tilde{\tau}_{zy}(\mathbf{q}, z) = \mu \tilde{\alpha}_{zy}(\mathbf{q}, z) - i\eta_s q \tilde{u}_y(\mathbf{q}, z), \quad (3.16a)$$

$$\tilde{\alpha}_{zy}(\mathbf{q}, z)(z + \Gamma) = \hat{\alpha}_{zy}(\mathbf{q}) - i\mu' q \tilde{u}_y(\mathbf{q}, z). \quad (3.16b)$$

These equations are precisely the Fourier-Laplace transforms of Eqs. (A1) and (A2) in Ref. 20. Equation (3.16a) describes a viscous fluid whose shear stress component τ_{zy} is related, as usual, to the zy component of the velocity gradient through the shear viscosity η_s . Also, from these equations follows that Γ may be interpreted as the time rate of molecular orientation. Note, however, that these and the remaining coupling constants μ, μ' arise as a consequence of the postulates of the thermodynamic

then multiplied by $\hat{\alpha}_{xy}^*(\mathbf{q})$ and averaged over an equilibrium ensemble, owing to the fact that ρ, T, α_{zy} , and τ_{zy} have been chosen as (statistically) *independent* state variables, we arrive at the result

theory itself and have not been introduced *ad hoc*. Moreover, according to our previous results, these coupling coefficients are functions of temperature and their explicit form is given in Appendix A, a fact that will be used later on.

If this particular choice of phenomenological coefficients is also used in Eqs. (3.11), then our V - H spectrum, as given by Eqs. (3.14) or (B1), reduces to the result obtained by Wang in Appendix A of Ref. 20, namely,

$$I_{VH}(\mathbf{q}, \omega) = \frac{\chi}{\Pi} \left[\frac{\Gamma}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{\eta\omega_s^2 + \Gamma\omega^2}{(\omega^2 - \omega_s^2)^2 + \omega^2\Gamma_s^2} \cos^2 \frac{\theta}{2} \right]. \quad (3.17)$$

Here, following Wang's notation to facilitate the comparison, we have used the abbreviations

$$\eta \equiv \eta_s q^2 \rho_0^{-1}, \quad \Gamma_s \equiv \Gamma + \eta, \quad (3.18)$$

$$\omega_s^2 \equiv \eta\Gamma + \delta, \quad \delta \equiv q^2 \mu \mu' \rho_0^{-1},$$

to denote certain combinations of phenomenological coefficients. However, the physical interpretation of these quantities is obtained in Ref. 20 from a microscopic theory. χ is defined by Eq. (3.12a). Equation (3.17) is the form of the V - H spectrum commonly used to analyze and successfully compare with experiment the depolarized Rayleigh scattering data of many viscous liquids.^{29,30} Note that the second term in (3.17) shows that the spectrum is not composed of a single Lorentzian, except in the limit $\Gamma \gg \eta q^2 \rho_0^{-1}$. Furthermore, Eq. (3.17) is precisely of the same form as the spectrum obtained from the

microscopic theory of Andersen and Pecora.⁸ It is worth stressing that in spite of the many phenomenological coefficients introduced at the different stages in our development, only a few combinations of them are the relevant ones to describe the spectra. Therefore, the introduction of a host of parameters in the phenomenological theories does not necessarily make the comparison with experiment more difficult. Since Wang has discussed and compared Eq. (3.17) with experiment and with other theories such as Pecora's, we may say that the results of EIT for the depolarized spectrum of a viscous liquid are also in good agreement with experiment and with microscopic approaches. Let us now turn our attention to viscoelasticity.

C. Linear viscoelastic liquids

Let us now consider explicitly the relaxation in the stress tensor by assuming $\tau_1 \neq 0$. If, as before, we keep the identifications (3.15) but now we set $a_2 = G(0)$, where $G(0)$ stands for the static relaxation modulus of the fluid, Eqs. (3.10) become

$$\tau_1 \frac{\partial}{\partial t} \tau_{zy} = -\tau_{zy} + \tau_1 G(0) L_{zy} + a_1 \alpha_{zy}, \quad (3.19a)$$

$$\frac{\partial}{\partial t} \alpha_{zy} = -\Gamma \alpha_{zy} + \mu' L_{zy}. \quad (3.19b)$$

It can be easily seen that these equations correspond to the viscoelastic model proposed by Wang: Eq. (3.19b) is identical to Eq. (A2) in Ref. 20, and (3.19a), as we shall see below, essentially corresponds to Eq. (A6), namely,

$$\tau_{zy} = \int_0^t G(t-t') L_{zy}(t') dt' + a_1 \alpha_{zy}. \quad (3.20)$$

Here $G(t)$ is the relaxation shear modulus and is only a function of time. Note that if in this last equation we neglect the coupling between τ_{zy} and α_{zy} and assume that the modulus $G(t)$ is of the Maxwell-type (linear viscoelasticity),²⁶

$$G(t) = G(0) \exp(-t\tau_1^{-1}). \quad (3.21)$$

Equation (3.20) may be rewritten in differential form as

$$\tau_1 \frac{\partial}{\partial t} \tau_{zy} = -\tau_{zy} + \tau_1 G(0) L_{zy}. \quad (3.22)$$

Clearly, if following Wang we now couple this viscoelastic model with α_{zy} , we get the EIT result given by Eq. (3.19a). This then shows that the phenomenological models proposed by Wang, both for Newtonian and viscoelastic (Maxwell) fluids, may be consistently derived from our version of extended irreversible thermodynamics. However, although the models are formally the same, from our thermodynamic description we may obtain in addition the (analytic) temperature dependence of the phenomenological coefficients in Eqs. (3.19), up to the order of approximation considered, and, therefore, of properties derived from them, such as the V - H spectrum. Indeed, if we solve Eqs. (3.19) for α_{zy} , taking into account Eqs. (3.9), a similar procedure to the one leading to Eq. (3.12) yields

$$\langle \bar{\alpha}_{zy}(\mathbf{q}, z) \hat{\alpha}_{zy}^*(\mathbf{q}) \rangle = \chi \frac{z + q^2 \rho_0^{-1} \hat{G}(z)}{(z + \Gamma)[z + q^2 \rho_0^{-1} \hat{G}(z)] + \delta}, \quad (3.23a)$$

with χ and δ given, respectively, by Eqs. (3.12a) and (3.18), and where $\hat{G}(z)$ denotes the Laplace transform of the shear modulus $G(t)$. Similarly, by setting $b_1 = 0$ in Eqs. (3.11), we also arrive at

$$\langle \bar{\alpha}_{yx}(\mathbf{q}, z) \hat{\alpha}_{yx}^*(\mathbf{q}) \rangle = \chi \frac{1}{z + \tau_2^{-1}}. \quad (3.23b)$$

To exhibit the effects of temperature on the spectrum we follow Wang and assume that for viscoelastic liquids where $\tau_1^{-1} \gg 1$, $G(t)$ may be approximated by

$$G(t) = G(0) + 2\eta' \delta(t) \quad (3.24)$$

[see Eq. (A10) in Ref. 20], so that the memory in Eq. (3.20) may be neglected. In this case (3.23a) reduces to

$$\langle \alpha_{yz}(\mathbf{q}, z) \hat{\alpha}_{yz}^*(\mathbf{q}) \rangle = \chi \frac{z^2 + q^2 \eta' \rho_0^{-1} z + q^2 \rho_0^{-1} G(0)}{(z + \Gamma)\{z^2 + q^2 \rho_0^{-1} [G(0) + \eta' z]\} + z\delta} \quad (3.25)$$

and from Eqs. (3.8), (3.23b), and (3.25), using Wang's notation, we also arrive at

$$I_{VH}(\mathbf{q}, \omega) = \frac{\chi}{\pi} \left[\frac{\Gamma}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{\eta \omega_s^2 \omega^2 + \Gamma(\omega^2 - \Omega^2)^2}{\omega^2 [-\omega^2 + (\omega_s^2 + \Omega^2)]^2 + (\omega^2 \Gamma_s - \Gamma \Omega^2)^2} \cos^2 \frac{\theta}{2} \right]. \quad (3.26)$$

Here instead of defining $\eta = \eta_s q^2 \rho_0^{-1}$, as in Eq. (3.18), we have used

$$\eta \equiv q^2 \rho_0^{-1} \eta', \quad \Omega \equiv q^2 \rho_0^{-1} G(0). \quad (3.27)$$

There are four independent parameters in Eq. (3.26), namely, η , Γ , δ , and Ω . However, if we set $\Omega = 0$, then $\eta' \rightarrow \eta$ (Ref. 20) and we are left with three parameters whose temperature dependence follows from Eqs. (3.18),

(A2b) and (A5), i.e.,

$$\Gamma = AT, \quad (3.28a)$$

$$\eta = DT^{-1} + C, \quad (3.28b)$$

$$\delta = T(ET + F). \quad (3.28c)$$

The coefficients in these equations are combinations of phenomenological coefficients and their numerical values

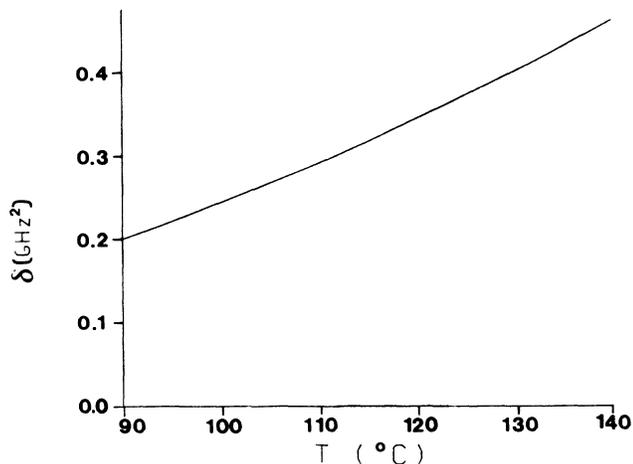


FIG. 1. The dynamic coupling δ vs T as given by Eq. (3.29c).

should be determined from experimental data. Now, for those temperatures for which the V - H spectrum has been measured,⁴ Wang²⁰ has adjusted the values of Γ , η , δ . So, if we choose the values of these quantities at 122 and 101.5 °C for liquid salol, from Eqs. (3.28) we find that

$$\Gamma = 0.33T, \quad (3.29a)$$

$$\eta = 31.25T^{-1} - 0.16, \quad (3.29b)$$

$$\delta = 2.16 \times 10^{-5}T^2 + 2.75 \times 10^{-4}T. \quad (3.29c)$$

Thus, our thermodynamic description allows us to estimate the numerical values of these parameters at any temperature. However, since for salol $\Omega = 0$ above 40 °C, we expect our results to be valid only at high temperatures. In Fig. 1 we have plotted δ as a function of T , as given by Eq. (3.29c). Note that for high temperatures its behavior is similar to the one given in Fig. 4 of Ref. 20. If we now insert Eqs. (3.29) into Eq. (3.26) and plot I_{VH} vs ω for different values of T , we get the qualitative behavior shown in Fig. 2. From this figure it follows that, indeed, as T decreases there is a narrowing of the entire

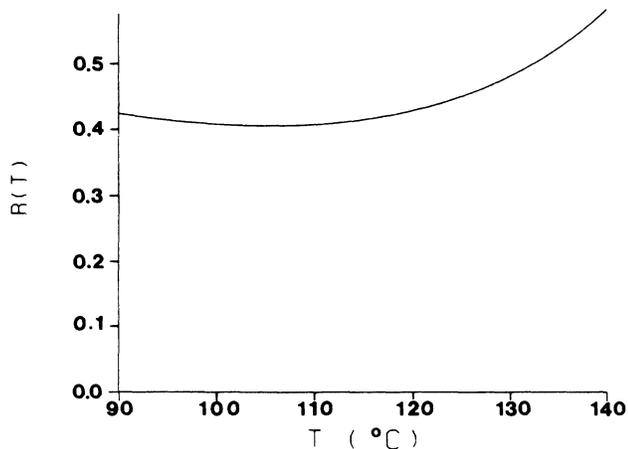


FIG. 2. Evolution of the calculated depolarized spectrum for a continuous range of high temperatures.

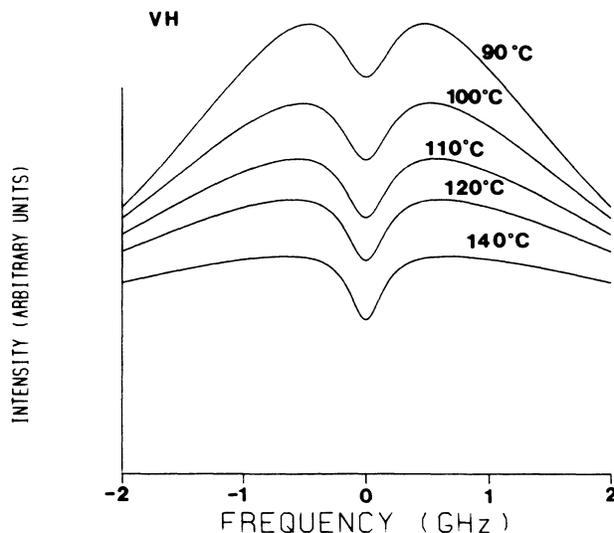


FIG. 3. Variation of R vs T , as defined by Eq. (3.31), for $g = -2.111 \times 10^{-6}$ and $h = 3.294 \times 10^{-4}$.

spectrum, consistently with the experimental observations. However, for the rather small temperature interval considered, it is not clear if the dip also tends to disappear. To show that this is indeed the case, we first recall that the spectral central dip is now understood as due to scattering from the overdamped shear mode, which couples to the polarizability density. So if, following Refs. 8 and 20, we take this into account by changing the damping constant η , Eq. (3.18), of the shear wave to

$$\eta = q^2 \rho_0^{-1} \eta_s (1 - R), \quad (3.30)$$

we expect, according to (3.29b), that as T decreases, η increases and R should decrease. Now the temperature dependence of R may be obtained from Eqs. (3.15) and (A3b) and the measured values of the viscosity of salol.³¹ This leads to

$$R(T) = 1 - T(gT + h) \exp[2.74 - 148(T - 226)^{-1}]. \quad (3.31)$$

If the numerical value of the constants g, h is determined by choosing the values of R at $T = 122$ and 101.5 °C in reference 20, we find the behavior plotted in Fig. 3. So, from Figs. 2 and 3 we see that EIT qualitatively predicts for the spectral dip, the observed tendency.

IV. CONCLUDING REMARKS

To clarify and elaborate on some of the points raised in this paper the following comments may be useful. First, we want to emphasize that the main result of this paper has been to show that EIT is, indeed, an alternative thermodynamic description for the depolarized scattering spectra of viscoelastic liquids, when their nonequilibrium states lie beyond the linear regime of LIT. We have shown that in a consistent way, EIT allows for couplings between relaxation processes for the nonconserved state

variables, whose explicit (analytic) temperature dependence is provided by the theory itself. As a consequence, as shown in Sec. III, the dependence of the V - H spectrum on temperature may be also determined.

Second, we should stress that the time-evolution equations for the (fast) nonconserved variables, Eqs. (2.10) or (3.9), were derived within two approximations: the first one assumes that the phenomenological coefficients $\alpha_{ij}, \beta_{ij}, \mu_{ij}$ appearing in the theory are strictly constants, in spite of the fact that, to lowest order in the fast variables, they ought to be functions of the local equilibrium densities $e(\mathbf{r}, t)$ and $\rho(\mathbf{r}, t)$. The second approximation consists in performing the expansions of these coefficients only up to first order in the sense discussed in Sec. II. This approximation eliminates their possible dependence on higher-order scalar invariants in G , involving terms with powers of order higher than 1 in the nonconserved variables. The removal of the first approximation would lead to relaxation equations with nonconstant coefficients, whereas the elimination of the second one introduces nonlinear terms in the relaxation equations. Thus, EIT is a far more general theory than the approximated scheme presented here; however, its potential use in connection with other problems of depolarized light scattering,³² where the introduction of additional state variables might be necessary, remains to be assessed.

A third and important aspect of the theory dealt with here is the way in which the dispersive character of the medium has been taken into account. Instead of assuming a frequency dependence of the transport coefficients to describe that the dispersive mechanisms vary with frequency, we have introduced additional relaxing state variables (processes) with constant phenomenological coefficients, the usual transport coefficients among them. This point of view is clearly different from the usual ones,¹¹ but as shown here for viscoelastic liquids, and for other systems as well,²³ it is capable of yielding a description in good agreement with experiment and with microscopic theories.

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APPENDIX A

In this appendix we give the explicit definitions of the coefficients τ_i, a_i, b_i appearing in the time-evolution equations (2.10) for the fast variables and for the coefficients A, D, C, E, F in Eqs. (3.28), in terms of the constant phenomenological coefficients $\alpha_{ij}, \beta_{ij}, \mu_{ij}$ and the temperature T , up to first order in the nonconserved variables.

If we define

$$\lambda \equiv (\beta_{10}\beta_{21} - \beta_{11}\beta_{20})^{-1}, \quad (\text{A1})$$

the relaxation times τ_1 and τ_2 are given by

$$\tau_1^{-1} = T\lambda(\mu_{20}\beta_{20} - \mu_{10}\beta_{21}), \quad (\text{A2a})$$

$$\tau_2^{-1} = T\lambda(\mu_{21}\beta_{20} - \mu_{11}\beta_{21}) \equiv TA. \quad (\text{A2b})$$

The remaining coefficients a_i, b_i in Eqs. (2.10) stand for the following combinations of phenomenological coefficients:

$$a'_1 \equiv a_1\tau_1^{-1} = T\lambda(\mu_{21}\beta_{10} - \mu_{11}\beta_{11}), \quad (\text{A3a})$$

$$a'_2 \equiv a_2\tau_1^{-1} = T\lambda(\mu_{12}\beta_{21} - \mu_{22}\beta_{20}) + \lambda\beta_{21}, \quad (\text{A3b})$$

$$a_3 \equiv T\lambda(\mu_{13}\beta_{21} - \mu_{23}\beta_{20}), \quad (\text{A3c})$$

$$a_4 \equiv T\lambda(\mu_{14}\beta_{21} - \mu_{24}\beta_{20}), \quad (\text{A3d})$$

$$a_5 \equiv T\lambda(\mu_{15}\beta_{21} - \beta_{20}\mu_{25}). \quad (\text{A3e})$$

Similarly,

$$b_1 \equiv T\lambda(\mu_{20}\beta_{10} - \mu_{10}\beta_{11}), \quad (\text{A4a})$$

$$b_2 \equiv T\lambda(\mu_{22}\beta_{10} - \mu_{12}\beta_{11}) - \lambda\beta_{11}, \quad (\text{A4b})$$

$$b_3 \equiv T\lambda(\mu_{23}\beta_{10} - \mu_{13}\beta_{11}), \quad (\text{A4c})$$

$$b_4 \equiv T\lambda(\mu_{24}\beta_{10} - \mu_{14}\beta_{11}), \quad (\text{A4d})$$

$$b_5 \equiv T\lambda(\mu_{25}\beta_{10} - \mu_{15}\beta_{11}). \quad (\text{A4e})$$

While the coefficient A in Eq. (3.28a) is defined by Eq. (A2b), the expressions for the remaining coefficients in Eqs. (3.28) are found from Eqs. (3.15), (3.18), and (A3) with the result

$$D \equiv \beta_{21}(\mu_{20}\beta_{20} - \mu_{10}\beta_{21})^{-1}, \quad (\text{A5a})$$

$$C \equiv (\mu_{12}\beta_{21} - \mu_{22}\beta_{20})(\mu_{20}\beta_{20} - \mu_{10}\beta_{21})^{-1}, \quad (\text{A5b})$$

$$E \equiv \lambda^2(\mu_{20}\beta_{10} - \mu_{11}\beta_{11})(\mu_{22}\beta_{10} - \mu_{12}\beta_{11}), \quad (\text{A5c})$$

$$F \equiv \lambda\beta_{11}(\mu_{11}\beta_{11} - \mu_{20}\beta_{10}). \quad (\text{A5d})$$

APPENDIX B

In this appendix we give the explicit expression for the V - H spectrum corresponding to Eq. (3.14). By setting $z = i\omega$ and taking the real part of Eq. (3.13) we get

$$\text{Re}\langle \tilde{\alpha}_{yx}(\mathbf{q}, \omega) \hat{\alpha}_{yx}^*(\mathbf{q}) \rangle = \chi \frac{H\omega^2 + I}{J\omega^4 + K\omega^2 + M} \quad (\text{B1})$$

with

$$H \equiv \tau_1^2\tau_2^{-1}, \quad (\text{B2})$$

$$I \equiv \tau_2^{-1} - a_1b_1, \quad (\text{B3})$$

$$J \equiv \tau_1^2, \quad (\text{B4})$$

$$K \equiv 1 + 2\tau_1a_1b_1 + \tau_1^2\tau_2^{-2}, \quad (\text{B5})$$

$$M \equiv (\tau_2^{-1} - a_1b_1)^2. \quad (\text{B6})$$

Similarly, from Eq. (3.12a) we find

$$\text{Re}\langle \tilde{\alpha}_{zy}(\mathbf{q}, \omega) \hat{\alpha}_{zy}^*(\mathbf{q}) \rangle = \chi \frac{H\omega^4 + P\omega^2 + Q}{J\omega^6 + S\omega^4 + U\omega^2 + W}, \quad (\text{B7})$$

where

$$P \equiv I - q^2 \rho_0^{-1} (2a_2 \tau_1 \tau_2^{-1} + \tau_1 a_1 b_2), \quad (\text{B8})$$

$$Q \equiv q^4 a_2 \rho_0^{-2} (a_1 b_2 + a_2 \tau_2^{-1}), \quad (\text{B9})$$

$$S \equiv K - 2q^2 \rho_0^{-1} \tau_1 a_2, \quad (\text{B10})$$

$$U \equiv M - 2q^2 \rho_0^{-1} (a_1 b_2 + a_1 a_2 b_1 + a_2 \tau_1 \tau_2^{-2} + a_1 b_2 \tau_1 \tau_2^{-1}) + q^4 \rho_0^{-2} a_2^2, \quad (\text{B11})$$

$$W \equiv q^4 \rho_0^{-2} (a_2 \tau_2^{-1} + a_1 b_2)^2. \quad (\text{B12})$$

Thus, the V - H scattering spectrum is given by

$$I_{VH}(\mathbf{q}, \omega) = \frac{\chi}{\pi} \left[\frac{H\omega^2 + I}{J\omega^4 + K\omega^2 + M} \sin^2 \frac{\theta}{2} + \frac{H\omega^4 + P\omega^2 + Q}{J\omega^6 + S\omega^4 + U\omega^2 + W} \cos^2 \frac{\theta}{2} \right]. \quad (\text{B13})$$

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