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# Depolarized Light Scattering from Liquids: Rotations, Collisions, and Hydrodynamics

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VH depolarized light scattering from liquids composed of symmetric top molecules is discussed. The dielectric fluctuations which give rise to the spectrum form an orientational and collisional (or intermolecular) contribution, and cross-correlation between the two can occur. The problem of disentangling the orientational from the collisional effects is shown to be possible, at least within the context of a generalized hydrodynamic model, because of the coupling of rotations and intermolecular interactions to hydrodynamic shear modes. A simple generalized hydrodynamic model is proposed which is successful in describing the observed spctra with an appropriate number of theoretical transport coefficients treated as adjustable parameters. Though this model is quite successful, and though the coefficients can all be described in physically meaningful and mathematically precise molecular terms, it must still be taken as a phenomenological theory until the fitted values of the coefficients can be compared with values calculated from the molecular expressions.

**KEY WORDS:** Light scattering; collision induced scattering; depolarized scattering; relaxation in liquids; hydrodynamic modes; molecular rotations.

## 1. INTRODUCTION

A strength of dynamic light scattering as a tool for studying molecular motions in liquids is that nearly all time-dependent processes contribute to the spectra; however, as a consqequence, it is sometimes difficult to disentangle one effect from another. Depolarized light scattering spectra from liquids composed of nonspherical molecules arise from fluctuations in the traceless dielectric tensor $\varepsilon(\mathbf{k}, t)$. The elements of this tensor are dependent both upon the collective orientation of the anisotropic molecular polarizabilities $\mathbf{D}(\mathbf{k}, t)$ and upon intermolecular or collision-induced

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changes in polarizability $\mathbf{\Phi}(\mathbf{k}, t)$. Thus, it should be possible to obtain information about both these processes from light scattering. Because of cross-correlations, however, it is not simple to disentangle the contributions of each of these processes to the light scattering process. One objective of this article is to disentangle the orientational from the collision-induced processes. Curiously, it is because of the incorporation of still other dynamical processes that the already complicated spectrum arising from orientational and collision-induced polarizability fluctuations can be partially disentangled. In particular, it is the contributions due to standard hydrodynamic modes that give rise to additional spectral structure that can be useful in separating the orientational and collision-induced effects. Here I am also interested in studying the hydrodynamic modes themselves, particularly at high viscosity, where the fluid becomes viscoelastic and approaches the glass transition.

This issue is dedicated to Howard Reiss. Though Howard has contributed brilliantly to many areas of science, he has not worked on the topic of this paper. However, even here this influence has been felt, because some of the fundamental studies(1) on collision-induced light scattering were sponsored by Howard when he served as director of the North American Science Center.

## 2. SIMPLIFIED DEPOLARIZED LS SPECTRA

The VH depolarized light scattering spectrum from liquids composed of nonspherical molecules appear quite different at low and at high viscosity $\eta_s$. At low $\eta_s$ one observes a central "sharp" feature which is reasonably Lorentzian for a few linewidths, but in addition there is a dip (the Rytov dip) in the center of this line.(2,3) The half-width $\Delta\omega_s$ of the sharp line is roughly proportional to $\eta_s^{-1}$ and is independent of $k$, while the half-width of the dip is approximately

$$\Delta\omega_d \cong k^2\eta_s/\rho \tag{1}$$

here

$$k = (4\pi n/\lambda_0) \sin \theta/2 \tag{2}$$

$\rho$ is the mass density, $\lambda_0$ is the laser wavelength, $n$ is the refractive index of the liquid, and $\theta$ is the scattering angle. The sharp line is usually associated with molecular reoriention $\mathbf{D}$ and is essentially independent of $\mathbf{k}$. The strong dependence of the dip upon $\mathbf{k}$ is a signature of hydrodyanamic modes and is an important fingerprint which can be used to help disentangle the mechanisms given rise to light scattering. The sharp line might typically have a half-width of several GHz. One also observes a "broad" central feature with a half-width $\Delta\omega_b$ which is 5–20 times greater than that of the "sharp" line and is independent of $k$.(3) There are also other "background" contributions out to 100 cm$^{-1}$ or more.(4)

At high viscosity the spectrum is quite different.(3,5) The sharp central feature associated with reorientation is still independent of $k$ and very "sharp," the proportionality of $\Delta\omega_s$ on $\eta_s^{-1}$ having been roughly retained throughout the whole range of viscosities. There is no central dip, but there are symmetrically located, weak side peaks (shear waves) shifted from the center by a frequency which is proportional to $k$:

$$\delta\omega_{\mathrm{sh}} = kv \tag{3}$$

The width $\Delta\omega_{\mathrm{sh}}$ of the side peaks appears to be described by

$$\Delta\omega_{\mathrm{sh}} = F + Gk^2 \tag{4}$$

where $F$ appears to be proportional to $\eta_s^{-1}$, and $G$ and $v$ are more or less independent of $\eta_s$.(3) In all the relevant experiments the viscosity is increased by lowering the temperature at constant pressure, and some $T$ dependence is noted in $v$. Most of the measurements are made with an interferometer, but the sharp central line can become so narrow that it must be studied with a correlator.(6,7) The $F$ term in Eq. (4) becomes vanishingly small at very high $\eta_s$.(3,5) At $\theta = 90°$, $Gk^2$ is usually of the order of 1 GHz, the shear wave shift $\delta\omega_{\mathrm{sh}}$ several GHz. Both the central line and the side peaks appear to be quite Lorentzian. There may be additional broad central features in the high-$\eta_s$ spectrum, but these have not been well studied.(3)

The "simplified spectra" discussed above can be described in terms of relatively few "adjustable parameters." One is never interested in the absolute integrated intensity of the spectrum. At low $\eta_s$, therefore, one needs the half-width $\Delta\omega_s$ of the sharp central line, the half-width $\Delta\omega_b$ of the broad line, the ratio of the relative integrated intensity of the broad to that of the central line, and the depth of the Rytov dip relative to the peak height of the central line. Although for diatomics the relative integrated intensities of the broad to that of the central line is apparently quite small,(8,9) for larger molecules, such as triplenyl phosphite, it may be of the order of one.(3) The width of the Rytov dip, as given in Eq. (1), is dependent on independently measured quantities and is therefore not an adjustable parameter. At low $\eta_s$ one thus has the four adjustable parameters $\Delta\omega_s$, $\Delta\omega_b$, the dip depth, and the relative intensities. At high $\eta_s$ one has the relative integrand intensity of the two side peaks to that of the central line, the width $\Delta\omega_s$ of the sharp line, and the three parameters

$\{F, G, v\}$ which describe the side peaks. At high $\eta_s$ one thus has the five adjustable parameters $\Delta\omega_s$, $F$, $G$, $v$, and the relative intensity; at very high $\eta_s$, the parameter $F$ is negligible.

Fitting the spectra with four or five adjustable parameters is a first step, developing a theoretical basis for these fits is a more complicated one. Besides giving the observed spectral shapes, the theory, even at the phenomenological level, must (1) have the correct $k$ dependence, (2) involve the independently measured zero-frequency viscosity $\eta_s$, and (3) be consistent with observed VV and HH spectra. I shall not go into this last point; it has been studied to some extent,$^{(3)}$ but here I merely note that such consistency not only places requirements on a theory, it also makes it possible to introduce more than four or five adjustable parameters in a meaningfull manner.

## 3. THE "SIMPLE" TWO-EXPONENTIAL PROBLEM

The VH depolarized light scattering spectrum is proportional to the Laplace transform of the autocorrelation function $\langle \varepsilon(\mathbf{k}, t)\, \varepsilon(-\mathbf{k}, 0)\rangle$, where $\varepsilon(\mathbf{k}, t)$ is the normalized traceless dielectric tensor and $\langle \cdot \rangle$ indicates an equilibrium ensemble average.$^{(2)}$ At low $\eta_s$ and low resolution (so that the Rytov dip is not observed), the sharp and broad lines of the VH depolarized light scattering spectrum correspond to a $\langle \varepsilon(\mathbf{k}, t)\, \varepsilon(-\mathbf{k}, 0)\rangle$, which is the sum of two exponentials. My first objective is to interpret this two-exponential correlation function. To do this I write $\varepsilon(\mathbf{k}, t)$ as$^{(3,10,11)}$

$$\varepsilon(\mathbf{k}, t) = [1 - I(\mathbf{k})^2]^{1/2}\, \mathbf{D}(\mathbf{k}, t) + I(\mathbf{k})\, \Phi(\mathbf{k}, t) \tag{5}$$

where $\mathbf{D}$ is a normalized second-rank orientational tensor and $\Phi$ is an appropriate normalized second-rank tensor describing the intermolecular contributions to $\varepsilon(\mathbf{k}, t)$. By normalized I mean that $\langle |\varepsilon|^2\rangle = \langle |\mathbf{D}|^2\rangle = \langle |\Phi|^2\rangle = 1$. I call $\mathbf{D}$ and $\Phi$ "primary" variables."$^{(12)}$

It is tempting to associate the sharp spectral line with the slow relaxation of the orientational coordinate, i.e., with the correlation function $\langle \mathbf{D}(\mathbf{k}, t)\, \mathbf{D}(-\mathbf{k}, 0)\rangle$, and the broad one with the rapid relaxation of the intermolecular contributions, i.e., with $\langle \Phi(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0)\rangle$. Actually, this may not be too bad an approach, but even though at $t = 0$ the orientational and intermolecular processes are orthogonal, i.e.,

$$\langle \mathbf{D}(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0)\rangle = 0 \tag{6}$$

there may be significant time-dependent cross-correlations $\langle \mathbf{D}(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0)\rangle$ between the two contributions.$^{(13)}$ A glance at Eq. (5) indicates that such cross-correlations enter into the expression for

$\langle \varepsilon(\mathbf{k}, t)\, \varepsilon(-\mathbf{k}, 0) \rangle$, which in turn determines the scattering spectrum. Thus, even in the simple two-Lorentzian spectrum one runs into the problem of disentangling the relaxation of $\mathbf{D}(\mathbf{k}, t)$ from that of $\Phi(-\mathbf{k}, t)$.(11)

Of course, it is also possible that both Lorentizians can be associated with the rotational relaxation $\langle \mathbf{D}(\mathbf{k}, t)\, \mathbf{D}(-\mathbf{k}, 0) \rangle$, that the cross-correlations $\langle \mathbf{D}(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0) \rangle$ are negligible, and that the intermolecular correlations $\langle \Phi(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0) \rangle$ are so small or relax so rapidly that they contribute negligibly to the low-frequency light scattering spectrum. At least for some liquids, I do not believe this to be the case, because the ratio of the integrated intensity of the broad to that of the sharp line can be of order one,(3) and such a large "broad" contribution would imply a much larger deviation from simple exponential behavior then expected for rotational relaxation $\langle \mathbf{D}(\mathbf{k}, t)\, \mathbf{D}(-\mathbf{k}, 0) \rangle$. It is true, however, that at very high viscosities such nonexponential rotational phenomena do exist, particularly the observed(14) bifurcation of the rotational relaxation into slow $\alpha$ and faster $\beta$ processes, with each being well described by a Williams–Watts function $\exp(-t/\tau)^{\nu}$, where $0 < \nu \leqslant 1$; but even at low viscosities, in depolarized light scattering one observes the two-Lorentzian, low-frequency character of the spectrum.(3) Furthermore, one knows something about the collision-induced light scattering spectrum from studies of spherical-top molecules in which rotational relaxation plays no role(15); from these studies, augmented by calculations for nonspherical molecules, it can be concluded that a significant collision-induced contribution at moderately low frequencies (several $\mathrm{cm}^{-1}$) can be expected.(4) Consequently, *I assume that both $D(\mathbf{k}, t)$ and $\Phi(\mathbf{k}, t)$ contribute significantly to the "two-Lorentzian" depolarized light scattering spectrum.*

## 4. TWO-EXPONENTIAL DYNAMICS

If the orientational relaxation were described by a single exponential, the corresponding equation of motion would be

$$\frac{d\langle \mathbf{D}(\mathbf{k}, t)\, \mathbf{D}(-\mathbf{k}, 0) \rangle}{dt} = -M_{DD}(\mathbf{k}) \langle \mathbf{D}(\mathbf{k}, t)\, \mathbf{D}(-\mathbf{k}, 0) \rangle \tag{7}$$

where $M_{DD}(\mathbf{k})$ is a transport coefficient (relaxation frequency). Similarly, for the intermolecular quantity $\Phi$ we have

$$\frac{d\langle \Phi(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0) \rangle}{dt} = -M_{\Phi\Phi}(\mathbf{k}) \langle \Phi(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0) \rangle \tag{8}$$

But if there is "dynamic coupling" between $\mathbf{D}$ and $\Phi$, these equations must be generalized to

$$\frac{d\mathbf{G}(t)}{dt} = -\mathbf{M} \cdot \mathbf{G}(t) \tag{9}$$

where **G** is the matrix

$$G_{AB}(t) = \langle A(\mathbf{k}, t)\, B(-\mathbf{k}, 0) \rangle \tag{10}$$

with $\{A, B\} = \{\mathbf{D}, \Phi\}$, and **M** is the transport matrix with elements $M_{AB}$. If the dynamical variables **A** and **B** are normalized, i.e., $\langle |A|^2 \rangle = 1$, then $M_{AB} = M_{BA}$. One can also show that

$$0 \leqslant R_0 \equiv M_{D\Phi} M_{\Phi D} / M_{DD} M_{\Phi\Phi} \leqslant 1 \tag{11}$$

The two-Lorentizian spectrum yields only the three experimentally determined parameters $\{\Delta\omega_s, \Delta\omega_b, \text{relative intensity}\}$, while the simple theory I have described contains four theoretical coefficients: the dynamical coefficients $M_{DD}$, $M_{\Phi\Phi}$, $M_{D\Phi} = M_{\Phi D}$, and the primary coupling coefficient $I$ introduced in Eq. (5). *The disentanglement problem is equivalent to that of fixing four "adjustable theoretical" parameters in terms of three experimentally determined ones.*

Many of the dynamical coefficients **M**, as we shall see, depend upon temporal integrations over time-dependent correlation functions; the $I(k)$ parameter is a thermodynamic or static coefficient. I expect the *thermodynamic coefficients to be relatively insensitive to temperature ($T$), but the dynamical coefficients often have an Arrhenius temperature dependence.* Because it is a ratio of dynamical coefficients, there is reason to expect the $R_0$ defined in Eq. (11) to be only mildly dependent upon $T$ or $\eta_s$.(16,17)

The solutions to Eq. (9) have the form

$$G_{AB}(t) = c_{AB} \exp(-\lambda_1 t) + (1 - c_{AB}^2)^{1/2} \exp(-\lambda_2 t) \tag{12}$$

We take $\lambda_1 < \lambda_2$. Thus, in addition to the existence in $\langle \varepsilon(\mathbf{k}, t)\, \varepsilon(-\mathbf{k}, 0) \rangle$ of the cross-correlation function $\langle \mathbf{D}(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0) \rangle$, we find that the orientational $\langle \mathbf{D}(\mathbf{k}, t)\, \mathbf{D}(-\mathbf{k}, 0) \rangle$ decays not as a simple exponential $\exp(-\lambda_1 t)$, but as the sum of two exponentials.(3,10) The same is true of $\langle \Phi(\mathbf{k}, t)\, \Phi(-\mathbf{k}, 0) \rangle$ and of the cross-correlations. In "favorable" situations, however, we expect $c_{DD} \gg c_{\Phi\Phi}$, and all cross-correlations to be insignificant; in this case we could interpret the half-width $\Delta\omega_s = \lambda_1$ of the sharp spectral line as the rotational relaxation frequency and the half-width $\Delta\omega_b = \lambda_2$ of the broad spectral line as the intermolecular relaxation frequency. This "favorable" situation should occur if there is a great separation of time scales, i.e., if $\lambda_1 \ll \lambda_2$; actually, however, this does not always seem to be the case.(3,18,10)

## 5. "SLOW" DYNAMICS

Equation (5) is an "exact" expression provided the intermolecular variable $\Phi(\mathbf{k}, t)$ is properly identified and provided internal motions of the molecules are neglected. But the equations of motion (9) can be correct only at long times. Equivalently, this means that the simple two-Lorentzian character of the low-resolution spectrum must be compromised at high frequency, i.e., in the spectral wings. If we focus on the low-frequency spectrum and long-time behavior, we are then interested only in "slow" variables, variables which "principally" relax slowly. Thus, if a variable such as the dielectric fluctuation $\varepsilon(t)$ has

$$\langle \varepsilon(t)\, \varepsilon(0) \rangle = b_1 \exp(-\lambda_1 t) + b_2 \exp(-\lambda_2 t) + b_3 \exp(-\lambda_3 t) \tag{13}$$

where $\lambda_1 < \lambda_2 \ll \lambda_3$, it is "slow" provided $|b_2|$, $|b_2| \gg |b_3|$. Whether or not $b_3$ is small, if we focus on the low-frequency spectrum, we can usually neglect the $b_3 \exp(-\lambda_3 t)$ term and renormalize the $\langle \varepsilon(t)\, \varepsilon(0) \rangle$. Thus, even though $\langle \varepsilon(t)\, \varepsilon(0) \rangle$ might correctly give rise to a three-Lorentzian spectrum, if we focus on the low-frequency range, we will see only two Lorentzians. The relevant "slow" part of $\varepsilon(\mathbf{k}, t)$ can then be indicated by $\tilde{\varepsilon}(\mathbf{k}, t)$, and the relevant form of Eq. (5) should be

$$\tilde{\varepsilon} = (1 - \tilde{I}^2)^{1/2} \tilde{D} + \tilde{I} \tilde{\Phi} \tag{5a}$$

where the tilde indicates that the "fast" parts have been projected out and only the slow" parts retained. The fluctuations giving rise to the low-frequency spectrum are then $\langle \tilde{\varepsilon}(t)\, \tilde{\varepsilon}(0) \rangle$. This procedure is equivalent to restricting our interest to the sharp spectral feature plus the broader superimposed line, but ignoring the very broad spectral background.

It is generally thought that the variable **D** is a "slow" one, that only a very small portion relaxes within 1 psec or so.(3, 10) Thus, we can continue to use **D** rather than $\tilde{\mathbf{D}}$. This is good, because we know how to identify **D**. The same is not true of $\Phi$; it undoubtedly has significant "fast" as well as "slow" components,(4) and we are interested only in the "slow" components. Thus, Eq. (5a) should be rewritten as

$$\tilde{\varepsilon}(t) = (1 - \tilde{I}^2)^{1/2}\, \mathbf{D}(t) + \tilde{I} \tilde{\Phi}(t) \tag{5b}$$

Equation (9) is then appropriate only for the "slow" parts of the intermolecular variable $\Phi$, i.e., $\Phi$ should be replaced by $\tilde{\Phi}$; thus, below [Eq. (10)] we should have $\{A, B\} = \{\mathbf{D}, \tilde{\Phi}\}$. Unfortunately, though we have a pretty good idea of how to identify the intermolecular variable $\Phi$, we do not know how to identify its "slow" part $\tilde{\Phi}$; *this is a major part of the disentanglement problem.*

Note that whether or not we can identify $\tilde{\Phi}$ properly, if at low frequencies we observe a two-Lorentizian spectrum, Eqs. (5b) and (9) hold, and we are left with the four "theoretical adjustable" and three experimentally determined parameters discussed above. This brings out another important point: In using phenomological equations of motion such as those in Eq. (9), with adjustable transport coefficients, *we do not automatically identify the correct slow variable* $\tilde{\Phi}$ *even if good fits are obtained.* Only by calculating the transport coefficients $M_{AB}$ and the thermodynamic coupling $\tilde{I}$ by means of theory or molecular dynamics simulations can one check whether the fitted values correspond to a particular choice of $\tilde{\Phi}$. To do this, we need molecular expressions for $M_{AB}$; we obtain these in the next section.

Instead of choosing **D** and $\tilde{\Phi}$ as the slow primary variables, one might choose the "slow" dielectric tensor $\tilde{\varepsilon}$ directly, together with a secondary "slow" variable $\phi$. Then, of course, there are no cross-correlations in the expression that determines the spectrum, no $\tilde{I}$ coupling coefficient, only $\langle \tilde{\varepsilon}(\mathbf{k}, t)\, \tilde{\varepsilon}(-\mathbf{k}, 0) \rangle$. This is an apparent simplification, but since we do not know how to specify $\tilde{\varepsilon}$ microscopically any more than we do $\tilde{\Phi}$ and $\phi$, the simplification may be more apparent then real. Furthermore, by choosing $\tilde{\varepsilon}$, which includes both rotation (**D**) and intermolecular ($\tilde{\Phi}$) contributions, as the primary variable, we stand less chance of developing a successful model than by treating these two motions as independent but coupled processes. However, models formulated in this way can be related to those using **D** and $\tilde{\Phi}$ as primary orthonormal slow variables, by replacing **D** and $\tilde{\Phi}$ in Eq. (9) by the two linearly independent orthonormal combinations $\{\tilde{\varepsilon}, \phi\}$, where $\tilde{\varepsilon}$ is given in Eq. (5b) and

$$\phi = \tilde{I}D - (1 - \tilde{I}^2)^{1/2} \tilde{\Phi} \tag{14}$$

Equation (9) is still the equation of motion, but the slow variables are now $\{\tilde{\varepsilon}, \phi\}$, with $\tilde{\varepsilon}$ as the primary and $\phi$ as a secondary variable.

## 6. MOLECULAR EXPRESSIONS

The orientational variable $\mathbf{D}(\mathbf{k}, t)$ can readily be related to molecular quantities:

$$\mathbf{D}(\mathbf{k}) = \sum_j \mathbf{D}_2(\Omega^j) \exp(ikx^j) \left\{ \sum_{(j,l)} \langle \mathbf{D}_2(\Omega^j)\, \mathbf{D}^2(\Omega^l) \exp[i\mathbf{k}(x^j - x^l)] \rangle \right\}^{-1/2} \tag{15}$$

where $\Omega^j$ are the Eulerian angles describing the orientation of the $j$th molecule, whose center of mass has $x$ coordinate $x^j$, and $\mathbf{D}_2$ is an appropriate second-rank rotational tensor, i.e., a linear combination of Wigner rotational functions.(2) In light scattering, $k$ is quite small, and in liquids far from critical points, the **k** dependence of the denominator in Eq. (15) can be neglected.

The intermolecular quantity $\Phi(\mathbf{k}, t)$ is more difficult to characterize. It certainly contains first-order dipole-induced-dipole (DID) contributions, but may also contain contributions associated with higher DID contributions,(19) distortion of the polarizability tensor, and electronic overlap between molecules.(20) We assume here that $\Phi$ is first-order DID. It then follows that

$$\Phi(\mathbf{k}) = \sum_{jl} u(\mathbf{r}^{rjl})\,\mathbf{D}_2(\Omega^j)\,\mathbf{D}_2(\Omega^l)\exp(i\mathbf{k}\cdot\mathbf{r}^j)$$
$$\times\left\langle\left|\sum_{jl}\mathbf{u}(\mathbf{r}^{jl})\,\mathbf{D}_2(\Omega^j)\,\mathbf{D}_2(\Omega^l)\exp(i\mathbf{k}\cdot\mathbf{r}^j)\right|^2\right\rangle^{-1/2} \tag{16}$$

where $\mathbf{u}(\mathbf{r}^{jl})$ is the dipole–dipole interaction tensor and $\mathbf{r}^{jl}$ is the displacement between the $j$th and $l$th molecules. Thus, if limited to first-order DID, $\Phi$ is easy enough to identify in molecular terms, but the low-frequency LS spectrum depends only on the slow components ($\tilde{\Phi}$) of $\Phi$. And we do not know how to identify $\tilde{\Phi}$. *Various models can be constructed* for $\tilde{\Phi}$; I will discuss some of these below. But, as discussed above, on the basis only of experimental fits of the adjustable parameters, we can eliminate some models, but we cannot readily distinguish among others.

If we choose a model, a procedure equivalent to selecting $\tilde{\Phi}$, we can then in principle calculate the transport coefficients $M_{AB}$. In particular, making use of the Mori formalism,(21) we find that

$$M_{AB} = \int_0^\infty dt\,\langle[\exp(i\mathbf{QL}t)\,\mathbf{Q}\dot{A}][Q\dot{B}]^*\rangle - \langle\dot{A}B\rangle \tag{17}$$

where $\mathbf{L}$ is the Liouville operator and $\mathbf{Q}$ is the Mori–Zwanzig projection operator, which when acting on a function $H$ yields

$$\mathbf{Q}H = H - \langle HA^*\rangle A - \langle HB^*\rangle B \tag{18}$$

So, indeed if we know $A$ and $B$, i.e., if we know $\mathbf{D}$ and $\tilde{\Phi}$, we can calculate the three transport coefficients $M_{AB}$, i.e., $\{M_{DD}, M_{\Phi\Phi}, M_{D\Phi}\}$, as well as the thermodynamic coupling $\tilde{I}$. By calculating these four "theoretial" coefficients with different choices of $\tilde{\Phi}$, and then using these to calculate the three "adjustable" parameters needed to fit the spectra, we should be able to distinguish among models by comparing these calculated "adjustable" parameters with those obtained experimentally. This is, however, difficult to do,(22) and one is usually confronted with four "adjustable theoretical" parameters to fit the three-parameter spectrum; this does not yield definitive results.

One model, not a particularly successful one,(10, 23) takes $\tilde{\Phi}$ to be the "normalized" stress tensor $\sigma$:

$$\tilde{\Phi} \rightarrow \sigma \tag{19}$$

The stress tensor is an intermolecular quantity which can be molecularly well specified, and is often introduced into theories of viscoelasticity as a "slow" variable.(24) If indeed it is a "slow" variable, it may well describe the slow parts of the DID interaction. At low $k$, the normalized stress tensor is defined by the relation(25)

$$\sigma(\mathbf{k}) = \sum_j \exp(ikx^j) \frac{d}{dt} (p_z^j x^j)/\rho k_B T V \mu)^{1/2} \tag{20a}$$

where $x^j$ is the $x$ component of the position of the center of mass of the $j$th particle and $p_z^j$ is its $z$ component of momentum, $\mathbf{k}$ is taken along the $x$ axis, $k_B$ is the Boltzmann constant, $V$ is the sample volume, and $\mu$ is the shear modulus. The scattering plane is the $xy$ plane.(2) See Appendix B for a molecular expression for $\mu$. Equivalently, we can write

$$\sigma(\mathbf{k}) = \sum_j \left[ \dot{x}^j p_z^j + (1/2) \sum_l (x^j - x^l) \dot{p}_z^{jl} \right] \exp(i\mathbf{k}x^j) \tag{20b}$$

where $\dot{p}_z^{jl}$ is the force on the $j$th particle due to the $l$th one.

## 7. HYDRODYNAMIC INTERACTIONS

In the preceding discussion of theory, I ignored the $\mathbf{k}$ dependence observed in the high-resolution, good-quality spectra.(3) I address this problem here.

Conserved variables decay very slowly in the low-$k$ limit, the decay rate vanishing as $k^2$. Since light scattering is carried out at reasonably small $k$, we must consider the possibility that conserved variables, even though they do not enter equations (5), (5a), (5b), can affect the relevant dynamics. In particular, it is found that the transform of the "normalized" transverse momentum density,

$$p(\mathbf{k}) = \sum_j p_z^j \exp(i\mathbf{k}x^j)/(\rho k_B T V)^{1/2} \tag{21}$$

can affect the VH depolarized light scattering spectrum.

At very low $k$, where $p(\mathbf{k}, t)$ is much slower than all other variables, e.g., than $\mathbf{D}$ and $\tilde{\Phi}$, its correlation function $\langle p(\mathbf{k}, t)\, p(-\mathbf{k}, 0) \rangle$ decays as $\exp[-k^2(\eta_s/\rho)t]$. But at somewhat higher $k$, one must incorporate all "slow" modes; in our case, $\mathbf{D}(\mathbf{k}, t)$ and $\tilde{\Phi}(\mathbf{k}, t)$ as well as $p(\mathbf{k}, t)$. The equations of motion are once again given by Eq. (9), but with $\{A, B\} = \{\mathbf{D}, \tilde{\Phi}, p\}$; however, Eq. (5b) still does not contain $p$. Thus, $p$ is called a "secondary" variable, one which does not enter into the expression for $\tilde{\varepsilon}$ but does affect its dynamics.(12)

The fact that the observed spectra have features with very strong $k$ dependences indicates that the coupling of $\tilde{\varepsilon}$, i.e., of either $\mathbf{D}$ or $\tilde{\Phi}$ or both to $p$, is significant. There are numerous consequences resulting from the introduction of $p(\mathbf{k}, t)$ into the problem:

1. The transport matrix $\mathbf{M}$ in Eq. (9) is now a three by three matrix with six independent elements.

2. Though the $k$ dependence was negligible in the $\{\mathbf{D}, \tilde{\Phi}\}$ problem, the conserved quantity $\mathbf{p}$ introduces a distinctive $k$ signature, i.e.,

$$\begin{aligned} M_{pp} &= k^2 m_{pp} \\ M_{p\Phi} &= ikm_{p\Phi} \\ M_{pD} &= ikm_{pD} \end{aligned} \tag{22}$$

with relatively little $k$ dependence in

$$\tilde{I},\ M_{DD},\ M_{\Phi\Phi},\ M_{D\Phi},\ m_{pp},\ m_{p\Phi},\ m_{pD} \tag{23}$$

3. The viscosity $\eta_s$ is introduced quite naturally by the requirement that

$$\lim_{k \to 0} \langle p(\mathbf{k}, t)\, p(-\mathbf{k}, 0)\rangle \to \exp[-\mathbf{k}^2(\eta_s/\rho)t] \tag{24}$$

This requirement *reduces the number of independent $M_{AB}$ from six to five.* It is interesting to note that in the low-$k$ limit

$$\dot{p}(\mathbf{k}, t) = i\mathbf{k}\mu^{1/2}\boldsymbol{\sigma}(\mathbf{k}, t) \tag{25}$$

It is sometimes useful to break $\sigma$ into its normalized symmetric ($\sigma^{\mathrm{s}}$) and antisymmetric ($\sigma^{\mathrm{a}}$) parts(10):

$$\sigma = \sigma^{\mathrm{s}}(\mu^{\mathrm{s}}/\mu)^{1/2} + \sigma^{\mathrm{a}}(\mu^{\mathrm{a}}/\mu)^{1/2} \tag{26}$$

See Appendix B for molecular expressions for all these quantities. It can be shown that(25)

$$\langle D(\mathbf{k}, 0)\, \sigma(-\mathbf{k}, 0)\rangle = 0 \tag{27}$$

and also that(3,10)

$$\langle \mathbf{D}(\mathbf{k}, 0)\, \sigma^{\mathrm{s}}(-\mathbf{k}, 0)\rangle = \langle \mathbf{D}(\mathbf{k}, 0)\, \sigma^{\mathrm{a}}(-\mathbf{k}, 0)\rangle = 0 \tag{28}$$

$$\langle \sigma^{\mathrm{s}}(\mathbf{k}, 0)\, \sigma^{\mathrm{a}}(-\mathbf{k}, 0)\rangle = 0 \tag{29}$$

## 8. OUR MODEL

Our first goal is to seek a molecular expression for the slow intermolecular variable $\tilde{\Phi}$ which yields transport equations which can be used to describe the observed VH spectra. We would, of course, like to find the "correct" form of $\tilde{\Phi}$ so that $\tilde{I}$ and the five independent $M_{AB}$ could be calculated, but since we usually introduce these as adjustable parameters, we cannot check whether we have the "correct" model or form of $\tilde{\Phi}$. Under these conditions we seek a form for $\tilde{\Phi}$ which reduces the number of adjustable parameters while still giving fits to the spectra and still satisfying the various imposed physical conditions such as (24) and the fact that $\tilde{I} \neq 0$. *Our choice* is $\Phi \to \sigma_s$, where $\sigma^s$ is the *symmetric stress tensor* specified in Eq. (26).

As a consequence of Eqs. (17), (25)–(29) it follows that

$$M_{pD} = 0 \tag{30}$$

The low-$k$ requirement on viscosity given in (24) leads to

$$\eta_s/\rho = [\mu^s/(1-R)\, M_{\Phi\Phi}] + m_{pp} \tag{31}$$

where

$$|m_{\Phi p}|^2 = \mu^s/\rho \tag{32}$$

and the dimensionless parameter $R$, defined by Eq. (11), is

$$R_0 = |M_{D\Phi}|^2/M_{DD}M_{\Phi\Phi} \tag{33}$$

With this model, we can fit both the high- and low-viscosity spectra with the five coefficients $\{I, \mu^s, m_{pp}, M_{\Phi\Phi}, M_{DD}\}$. The coefficient $M_{D\Phi}$ is determined by the condition in Eq. (31) and the definition of $R_0$. At low $\eta_s$ this model yields

$$\Delta\omega_s \approx M_{DD}(1-R_0) \tag{34a}$$

$$\Delta\omega_b \approx M_{\Phi\Phi} \tag{34b}$$

$$m_{pp} \approx 0 \tag{34c}$$

and at high $\eta_s$

$$2\Delta\omega_{sh} \approx M_{\Phi\Phi} + k^2 m_{pp} \tag{35a}$$

$$\delta\omega_{sh} \approx k(\mu^s/\rho)^{1/2} \tag{35b}$$

$$\text{fraction of depolarized intensity in shear wave} \approx \tilde{I}^2 \tag{35c}$$

$$\Delta\omega_s \approx M_{DD} \tag{35d}$$

It the five theoretical coefficients are treated as adjustable parameters, we find that at low viscosity, because $m_{pp}$ is insignificant, we have four "adjustable theoretical" and four experimental parameters, while at high viscosity we have five "theoretical adjustable" and five experimental parameters. This in itself is not a very remarkable achievement. However, we are able to obtain:

1. All the correct $k$ dependence as described in Eqs. (1), (3), and (4).
2. The correct viscosity dependence as described in Eq. (1).
3. Simultaneous fulfillment of the requirements in Eqs. (31) and (11).
4. As expected, strong temperature (viscosity) dependences of the dynamical quantities: rotational frequency $M_{DD}$ varying roughly as $\eta_s/T$, and the intermolecular relaxation frequency $M_{\Phi\Phi}$ as $\eta_s^{1/2}$,
$$M_{\Phi\Phi} \gg M_{DD} \tag{36}$$
See ref. 10 and Appendix C.
5. As expected, relatively weak temperature (viscosity) dependences of the thermodynamic quantities $\tilde{I}^2$ and $\mu^s$ or $\delta\omega_s k_{60}/k$. See Appendix C.
6. As predicted, proportionality of the coefficient $F$ defined in Eqs. (4) and (35a) to $M_{\Phi\Phi}$, i.e., to $\eta_s^{-1/2}$. See Appendix C.
7. Monotonic, continuous temperature and $\eta_s$ dependences for all parameters. See refs. 3 and 10.

But there are features of this model which, though not demonstrably wrong, are nonetheless disturbing.

1. The coefficient $m_{pp}$, which corresponds to the coefficient $G$ in Eqs. (4) and (35a), is a dynamic coefficient$^{(10)}$ which might be expected to have a strong $T$ (or $\eta_s$) dependence, but is found to be quite constant for high-$\eta_s$ spectra. On the other hand, at low viscosity, in order to satisfy Eq. (31), one finds $m_{pp} \approx 0$. See Appendix C. This behavior of $m_{pp}$ remains unexplained.

2. For $k = 0$, e.g., for the scattering angle $\theta \approx 0$, even at high viscosity there are no side peaks, and the half-width of the sharp central line is given by Eq. (35d) rather than Eq. (34a). Thus, if $R_0 \approx 0.7$, as it seems to be at high viscosity,$^{(3)}$ then $\Delta\omega_s$ at very small angles ($k = 0$) should be narrower than at large angles. However, measurements at very high $\eta_s$ seem to indicate that $\Delta\omega_s$ is independent of scattering angle $\theta$.$^{(6,7)}$ Though it is possible that the measurements were all made at sufficiently high $k$ for Eq. (35d) to hold, the situation is a bit more complicated when one realizes

that the VH spectrum is actually the superposition of two spectra, $J_{xz}(\omega)$ and $J_{yz}(\omega)$, which are, respectively, the transforms of $\langle \tilde{\varepsilon}_{xz}(\mathbf{k}, t)\tilde{\varepsilon}_{xz}(-\mathbf{k}, 0)\rangle$ and $\langle \tilde{\varepsilon}_{yz}(\mathbf{k}, t)\, \tilde{\varepsilon}_{yz}(-\mathbf{k}, 0)\rangle$; **k** is taken along the $x$ axis, with the scattering plane being the $xy$ plane.(2) It can readily be shown that the VH spectrum $J_{\mathrm{VH}}(\omega)$ is(2)

$$J_{\mathrm{VH}}(\mathbf{k}, \omega) = J_{xz}(\mathbf{k}, \omega) \cos^2 \theta/2 + J_{yz}(\mathbf{k}, \omega) \sin^2 \theta/2 \tag{37}$$

and though $\tilde{\varepsilon}_{xz}$ couples dynamically to the conserved variable $p$, $\tilde{\varepsilon}_{yz}$ does not.(2) Thus, $J_{\mathrm{VH}}(0, \omega) \approx J_{yz}(k, \omega)$. With our model, at $\theta^\circ = 0^\circ$ we expect a single $(xz)$ sharp central line governed by Eq. (34a); at $0 < \theta < 90^\circ$ we expect a strong $(xz)$ line governed by Eq. (35d), and a weaker $(yz)$ line governed by Eq. (34a); at $\theta = 90^\circ$, the $(xz)$ has equal integrated intensity with the $(yz)$ line; at $\theta > 90^\circ$ there is a weak $(xz)$ and a strong $(yz)$ line. It is not yet known for sure whether careful measurements of the central spectral features, over and above the sharpest one, will yield results compatible with the pedictions of the model.

3. At high $T$ (low $\eta_s$), the fits yield values of $R_0$ which are quite small, i.e., $R_0 < 0.1$. This means that the coupling of reorientation **D** to the momentum gradients are very weak, and consequently their orientation due to flow is small, much smaller than expected.(26) However, in a flow birefringence experiment, as in a light scattering experiment, we measure $\tilde{\varepsilon}$ and not **D**, and since $\tilde{\varepsilon}$ may have a large intermolecular component $\tilde{\Phi}$ which couples strongly to momentum gradients, it may be the coupling of $p$ to $\Phi$ rather than to **D** that contributes principally to flow birefringence (and to the Rytov dip as well). This can be checked only by MD simulations from which one can measure the effect of flows on **D** itself, rather than on $\tilde{\varepsilon}$. The existing MD results are encouraging but inconclusive.(22)

## 9. GENERAL DISCUSSION: THREE-VARIABLE MODELS

The analysis given above is based on the use of the three slow variables $\{\mathbf{D}, p, \tilde{\Phi}\}$; the first two are well-specified molecular quantities, the third is not but is chosen to be $\sigma_s$. The thermodynamic coupling parameter $\tilde{I}$ is introduced via Eq. (5b), and six dynamic parameters $M_{DD}$, $M_{D\Phi}$, $M_{\Phi\Phi}$, $ikm_{Dp}$, $ikm_{\Phi p}$, and $k^2 m_{pp}$ are introduced into the equations of motion (9). The explicit $k$ dependence of these dynamic coefficients is the only $k$ dependence considered. Equation (24) not only serves to introduce the viscosity $\eta_s$ into the problem, but it places a restriction on the dynamic coupling parameters, so that *only five of them are linearly independent.* Nevertheless, this leaves us with six "adjustable theoretical" coefficients and only four or five parameters to be fixed by the spectra. So choices of $\tilde{\Phi}$ have been sought which cause some of the coefficients to vanish.

Alternatively, we could use the three slow variables $\{\tilde{\varepsilon}, p, \phi\}$. Here neither $\tilde{\varepsilon}$ nor $\phi$ is a well-specified molecular quantity, but there is no parameter $\tilde{I}$ to worry about. Thus, there are only five "adjustable theoretical" coefficients. But this is still too many. Furthermore, when trying to interpret the results in molecular terms, one is forced to break $\tilde{\varepsilon}$ into orientational (**D**) and intermolecular ($\Phi$) terms, so that one returns to the $\{\mathbf{D}, p, \tilde{\Phi}\}$ representation with the consequent inclusion of the coefficient $\tilde{I}$.

A discussion of various models is given in Appendix A.

## 10. SUMMARY

I summarize by stating that the simplest model for describing the principal features of the VH depolarized light scattering spectrum makes use of three slow variables: **D**, $p$, $\tilde{\Phi}$. With the various imposed constraints, for an arbitrary $\tilde{\Phi}$ we have six linearly independent theoretical coefficients, too many if they are to be obtained from spectral fits. Certain models, i.e., certain choices of $\tilde{\Phi}$, reduce the number of such coefficients. If $\tilde{\Phi}$ is taken to be the symmetric stress tensor $\sigma^s$, one of the theoretical coefficients vanishes, and all principal features of the spectra can still be described, with the number of theoretical parameters equal to the number of experimentally determined ones.

Within the constraints of this model, the parameter $\tilde{I}$ in Eq. (5b) can be determined, *which enables us to disentangle the intermolecular from the orientational relaxations.* This is what we set out to do. But remember that this disentanglement is based upon a specific model, one in which $M_{pD} = 0$. In Appendix C it is shown that for triphenyl phosphate, $\tilde{I}^2$ is about 0.5 at low viscosity and decreases to about 0.1 at high viscosity; a decrease in collision-induced scattering is to be expected with increasing density.(27)

The model used is a phenomenological one in that even though the form of the equations and the vanishing of some parameters is due to the specifics of the model, i.e., the choice of $\tilde{\Phi}$, the theoretical coefficients have been evaluated by fits of spectral data. One must keep in mind that even though the model gives good fits with these empirically adjusted parameters, theoretical parameters calculated with $\tilde{\Phi} = \sigma^s$, if available, might not agree with these fitted values. Since we have molecular expressions for the theoretical coefficients, we could, in principle, try to calculate them, thereby checking the model or theory.(22) A model with the "correct" slow $\tilde{\Phi}$ may not have the simplifying property that $M_{pD} = 0$, so that there may intrinsically be five linearly independent $M_{AB}$ plus $\tilde{I}$ as theoretically adjustable parameters; such *a "correct" theory could be useful if indeed the parameters were calculated by MD simulations, but not if they are treated as adjustable.*

Appendix A discusses and compares the present approach with those of a number of others,$^{(3,10,23,28-36)}$ none of which, I believe, fulfills all the imposed requirements—spectral fits and molecular interpretation—as simply or as well as this one does.

Some experimental results for the $\tilde{\Phi} = \sigma^s$ model are given in Appendix C. In detail the spectral are more complicated than indicated here.$^{(3)}$

## APPENDIX A. OTHER MODELS

A detailed discussion of the models listed below is given in ref. 10.

*All* the "three-variable models" introduce the transverse momentum **p** as a variable, and it is this variable which introduces the significant **k** dependences indicated in Eq. (22) as well as the low-$k$ viscosity condition in (24). All the models found in the literature fit one of the following categories: (a) $\{\mathbf{D}, p, \tilde{\Phi}\}$ with $\tilde{I}=0$, (b) $\{\mathbf{D}, p, \tilde{\Phi}\}$ with $\tilde{I}\neq 0$, (c) $\{\tilde{\varepsilon}, p, \phi\}$.

All theories with

$$M_{pp} = 0 \tag{A1}$$

and with $M_{\Phi\Phi}$ independent of $k$ lead to

$$G = 0 \tag{A2}$$

in Eq. (4); this is contrary to observation. Theories in this category include those of Volterra$^{(23)}$ (type a) and of Chappell *et al.*$^{(10)}$ (type b), both of which set $\tilde{\Phi} = \sigma$ and, as a consequence, have both $M_{pD} = 0$ and $M_{pp} = 0$. Also in this category is the theory of Romanov and Solovev$^{(28)}$ (type c), in which $M_{\varepsilon\phi} = 0$, and $\sigma = \langle \sigma\tilde{\varepsilon} \rangle \tilde{\varepsilon} + \langle \sigma\phi \rangle \phi$, the latter leading to $M_{pp} = 0$. The only way in which to *guarantee* that $M_{\varepsilon\phi} = 0$ is to set $\tilde{\varepsilon} = \sigma^s$ and $\phi = \sigma^a$.

MacPhail and Kivelson$^{(29)}$ have suggested that even with $M_{pp} = 0$, finite $G$'s could be obtained, provided

$$M_{\Phi\Phi} = f + gk^2 \tag{A3}$$

where $f \gg gk^2$ at low $\eta_s$, but with $f \to 0$ as $\eta_s \to \infty$. The conditions in Eqs. (A1) and (A3) are satisfied by the model of Ailawadi$^{(30,31)}$ (type a), in which $\tilde{\Phi}$ is the spin or intrinsic molecular angular momentum; but because of the spin's odd time-reversal symmetry, the theory does not give good spectral fits. Eq. (A-3) could also be the result of a $k$-expansion of $M_{\phi\phi}$.$^{(29)}$

The theory of Anderson and Pecora$^{(32)}$ (type a) sets $\tilde{\Phi} = \sigma^s$; consequently, $M_{Dp} = 0$ and $M_{pp} = k^2 m_{pp} \neq 0$. This model differs from ours in that it sets $\tilde{I} = 0$, and finite $\tilde{I}$ is needed to obtain good spectral fits.

The theory of Quentrec$^{(33-35)}$ (type a or perhaps type c) sets either $\tilde{\Phi}$ or $\phi$ equal to a mass quadrupole variable. Here, none of the transport coefficients $M_{AB}$ necessarily vanishes. Mathematically, this model is equivalent to the one given here with the same number of adjustable theoretical coefficients. However, if taken as a model of type a, then it has $\tilde{I}=0$, which I believe to be unphysical, and if taken as a model of type c, then $\tilde{\varepsilon}$ is not well specified in molecular terms. (Furthermore, though a mass quadrupole variable is introduced, $\tilde{\Phi}$ or $\phi$ could be any symmetric second-rank tensor with even time-reversal symmetry; however, the mass quadrupole is indeed a sensible choice for an intermolecular "slow" variable).

The theory of Wang$^{(36)}$ (type c) sets $\tilde{\Phi}=\mathbf{q}/\langle\mathbf{q}^2\rangle^{1/2}$, where $\mathbf{q}=\mathbf{p}(k_{\mathrm{B}}T\rho V)^{1/2}$. It assumes that $\langle|q|^2\rangle^{-1}=Z^2k^2$. As a consequence, $M_{\phi\phi}=M_{\varepsilon\phi}=0$. In this model there are only four adjustable theoretical parameters, less than in any other model, but it has some serious difficulties:

1. The low-$k$ viscosity condition (24) cannot be satisfied. The momentum decays dissipatively at high $k$ and exhibits shear waves at low $k$, contrary to observation.
2. The parameter $F$ in Eq. (4) vanishes, contrary to observation, which suggests that the small number of adjustable parameters is in fact too small.
3. Contrary to assumption, though bounded in the solid state, $\langle|q|^2\rangle$ appears to be unbounded in the liquid state. Because of the minimal structural differences observed between liquids and glasses, the existence of a *thermodynamic* correlation length or order parameter which could account for the change in "boundedness" in going continuously from liquid to glass is unexpected.

The more complex four-variable theory introduced by Chappell and Kivelson$^{(3)}$ fits the data, well but introduces additional adjustable theoretical parameters. However, since they obtained simultaneous fits of the VH, HH, and VV spectra, they found enough experimental features to evaluate the parameters.

## APPENDIX B. MOLECULAR EXPRESSIONS FOR THERMODYNAMIC COEFFICIENTS

The shear modulus $\mu$ is

$$\mu=k_{\mathrm{B}}T\left(\frac{N}{V}\right)+\frac{1}{4}\frac{\langle[\sum_{(j,l)}(x^j-x^l)\dot{p}_z^{jl}]^2\rangle}{k_{\mathrm{B}}TV} \tag{B1}$$

The symmetric shear modulus is

$$\mu^{\mathrm{s}}=\frac{k_{\mathrm{B}}TN}{V}+\frac{1}{16}\frac{\langle[\sum_{(j,l)}(x^j-x^l)\,\dot{p}_z^{jl}+(z^j-z^l)\,\dot{p}_x^{jl}]^2\rangle}{k_{\mathrm{B}}TV} \tag{B2}$$

and the antisymmetric shear modulus is

$$\mu^{\mathrm{a}}=\frac{k_{\mathrm{B}}TN}{V}+\frac{1}{16}\frac{\langle[\sum_{(j,l)}(x^j-x^l)\,\dot{p}_z^{jl}+(z^j-z^l)\,\dot{p}_x^{jl}]^2\rangle}{k_{\mathrm{B}}TV} \tag{B3}$$

The thermodynamic coupling parameter $\tilde{I}$, which enters the $\tilde{\Phi}=\sigma^{\mathrm{s}}$ model, is

$$\tilde{I}^2=[1+W^2]^{-1}W^2 \tag{B4}$$

where

$$W=\frac{[(k_{\mathrm{B}}TV)\mu^{\mathrm{s}}]^{-1/2}}{\Delta\alpha}\frac{\langle Y\sigma_0^{\mathrm{s}}\rangle}{\langle\Delta^2\rangle^{1/2}} \tag{B5}$$

$\sigma_0^{\mathrm{s}}$ is the symmetric stress tensor

$$\sigma_0^{\mathrm{s}}=\frac{1}{2}\sum_j e^{ikx^j}\frac{d}{dt}(p_z^jx^j+p_x^jz^j) \tag{B6}$$

and

$$\Delta=\sum_j \mathbf{D}_2(\Omega^j)\exp(ik\cdot x^j) \tag{B7}$$

$$Y=\sum \mathbf{u}(\mathbf{r}^{jl})\,\mathbf{D}_2(\Omega^j)\,\mathbf{D}_2(\Omega^l)\exp(ikx^j) \tag{B8}$$

See Eqs. (15) and (16).

## APPENDIX C. DATA ANALYSIS

The data in Table I are for triphenyl phosphite and are taken from the work of Chappell and Kivelson.[3] These data refer to the $J_{xz}(\omega)$ component of the VH spectrum. [See Eq. (37).]

1. $k_{60}$ is the $k$ at a scattering angle of 60°,

$$k_{60}=1.930\times10^7\ \mathrm{m}^{-1}$$

2. $\delta\omega_s$ is the shift of the shear wave line (which is observed only at high $\eta_s$). The values are obtained by fits to the spectra generated by the

Table I. VH Scattering for Triphenyl Phosphite

| (°C) | $\eta_s$ (cP) | Scattering angle (deg) | $\delta\omega_s$ (GHz) | $\Delta\omega_s$ (GHz) | $\delta\omega_s k_{60}/k$ | $F$ (GHz) | $Gk_{60}^2$ (GHz) | $F\eta_s^{1/2}$ | $\eta_s^{1/2}M_{\phi\phi}/2$ | Integrated shear waves | $\tilde{I}^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| –27.7 | 652 | 90 | 3.2 | 0.35 | 2.3 | 0.20 | 0.15 | [5] | — | 0.12 | 0.11 |
| –22.7 | | 60 | 2.1 | 0.37 | 2.1 | | | | | | |
| | 406 | 90 | 3.0 | 0.49 | 2.1 | 0.26 | 0.12 | 5.2 | 2.4 | 0.14 | 0.14 |
| | | 120 | 3.7 | 0.60 | 2.1 | | | | | | |
| –17.8 | | 60 | 2.0 | 0.42 | 2.0 | | | | | | |
| | 264 | 90 | 2.8 | 0.54 | 2.0 | 0.30 | 0.12 | 4.9 | 2.3 | 0.17 | 0.17 |
| | | 120 | 3.4 | 0.66 | 2.0 | | | | | | |
| –12.7 | | 60 | 1.8 | 0.50 | 1.8 | | | | | | |
| | 173 | 90 | 2.6 | 0.62 | 1.8 | 0.38 | 0.12 | 5.0 | 2.6 | 0.18 | 0.22 |
| | | 120 | 3.2 | 0.74 | 1.8 | | | | | | |
| –7.7 | | 60 | 1.7 | 0.56 | 1.7 | | | | | | |
| | 118 | 90 | 2.4 | 0.68 | 1.7 | 0.44 | 0.12 | 4.8 | 2.5 | 0.20 | 0.28 |
| | | 120 | 3.0 | 0.80 | 1.7 | | | | | | |
| –2.7 | | 60 | 1.6 | 0.68 | 1.6 | | | | | | |
| | 83.1 | 90 | 2.3 | 0.79 | 1.6 | 0.58 | 0.10 | 5.3 | 2.9 | 0.23 | 0.34 |
| | | 120 | 2.8 | 0.89 | 1.6 | | | | | | |
| 17.4 | 25.7 | 90 | 1.5 | 1.2 | 1.0 | 0.96 | 0.12 | 4.9 | 3.1 | — | 0.50 |
| 87.5 | 2.9 | 90 | — | — | — | — | — | — | 6.0 | — | 0.50 |

four-variable theory of Chappell and Kivelson with the parameters given therein. The acoustic speed $v$, defined in Eq. (3), is proportional to the $\delta\omega_s k_{60}/k$ given in the table, and at high $\eta_s$ is more or less proportional to $(\mu^s/\rho)^{1/2}$, as indicated in Eq. (35b): thus, *at high* $\eta_s$

$$v \sim k_{60}\delta\omega_s/k \sim (\mu^s/\rho)^{1/2}$$

and, as indicated in Eq. (22), $m_{p\phi} = (\mu^s/\rho)^{1/2}$. See the $k_{60}\delta\omega_s/k$ column in the table; as expected, it changes only by a factor of 2, while $\eta_s$ changes by a factor of 225.

3. $\Delta\omega_s$ is the half-width at half-height of the shear wave line, obtained as indicated above. The parameters $F$ and $Gk_{60}^2$ are defined in Eq. (4) and are given in the table. In the high-$\eta_s$ region where the shear-wave side peaks are observed, we find that $Gk_{60}^2$ is quite constant, and $F$ varies roughly as $\eta_s^{1/2}$ (see $F$, $Gk_{60}^2$, and $F\eta_s^{-1/2}$ columns).

4. The integrated intensity of the *two* shear waves as a fraction of the total depolarized integrated intensity was obtained from the four-variable

fit of Chappell and Kivelson$^{(3)}$ and is given in the next to last column. The related $\tilde{I}^2$ parameter, specified by Eq. (5a), was obtained from a three-variable (with $M_{Dp}=0$) fit to the 90° angle data given by Chappell *et al.*$^{(10)}$ See Eq. (35c). These parameters seem to vary somewhat at high $\eta_s$, but very little at low $\eta_s$; it seems rather fortuitous that $\tilde{I}^2=0.5$ at low $\eta_s$.

5. The sharp central linewidth $\Delta\omega_s$ as given in both refs. 3 and 10 is associated with the parameter $M_{DD}$ and represents a rotational relaxation frequency. The data can be found in ref. 3 and 10; the most relevant point is that $\Delta\omega_s$ and $M_{DD}$ vary strongly with $\eta_s$ and $T$, more or less as $T/\eta_s$.

6. The broad central linewidth $\Delta\omega_b$ in the $J_{yz}(\omega)$ spectrum at high $\eta_s$ and in both the $J_{yz}(\omega)$ and $J_{xz}(\omega)$ spectra at low $\eta_s$ is closely related to the $M_{\Phi\Phi}$ parameter [see Eq. (34b)]. At high $\eta_s$,

$$F=M_{\Phi\Phi}/2$$

as indicated in Eq. (35a). The $M_{\Phi\Phi}\eta_s^{1/2}/2$ column indicates that $M_{\Phi\Phi}$ does indeed vary more or less as $\eta_s^{-1/2}$, but the relationship between $F$ and $M_{\Phi\Phi}$ seems to be off by a factor of 2. (The $M_{\Phi\Phi}$ are taken from the four-variable fits of ref. 3.)

7. The data at −27.7°C were obtained at 90° only. $F\eta_s^{1/2}$ was set at 5, and since $\eta_s$ is known, $F$ could be obtained. With $F$ and $\Delta\omega_s(90°)$ known, one can obtain $Gk_{60}^2$.

8. The resolution of side peaks at 17.4°C is poor, but $\delta\omega_s$, $\Delta\omega_s$, $F$, and $Gk_{60}^2$ were obtained by fits with the four-variable theory.$^{(3)}$ Above 17.4°C, one observes no side peaks, and a three-variable ($M_{Dp}=0$) fit yields $\tilde{I}^2\approx 0.5$. One such point (87.5°C) is given in the table.

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