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THEORIES OF DEPOLARIZED LIGHT SCATTERING (*)

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Résumé. — On passe en revue et on compare les théories existantes des spectres de la lumière dépolarisée diffusée par les liquides non associés. On présente une théorie complète qui dans diverses limites se réduit à toutes les théories qui existent dans la littérature.

Abstract. — Existing theories for the splittings of the depolarized light scattering spectra in non-associated liquids are compared and reviewed. A comprehensive theory is presented, which reduces in various limits to all of the theories that exist in the literature.

Introduction. — Several theories [1]-[7] have been offered to explain the recently observed splittings in the depolarized light scattering spectrum of certain non-associated molecular liquids [8], [9]. The observed spectrum consists of a diffuse band (sharp band that may be split) sitting on top of a broad background. Unfortunately, none of the theories that have appeared in the literature can account for the intensity ratio of the sharp and the broad bands [10].

In the present paper we point out (a) some drawbacks of the existing theories, and (b) show that it is possible, in principle, to construct a unified theory of the observed depolarized spectrum. We shall illuminate this by considering, specifically, the $I_{VH}$ spectrum.

II. Theories of depolarized light scattering. — It is generally well known [11] that the light scattering spectrum is determined by the spectrum of dielectric fluctuations. Thus, any theory of light scattering naturally divides into two parts:

(a) The determination of those fluctuations in the system which directly give rise to dielectric fluctuations. These we call « direct » fluctuations.

(b) The computation of the spectrum of the « direct » fluctuations. This involves deriving and solving « equations of motion » for the direct variables. The equations of motion often are such that the direct fluctuations are coupled to other fluctuations which for the sake of simplicity we call « indirect » fluctuations.

Previous calculations of the Brillouin spectra in liquids furnish an illustration of this [12]. In these theories the density fluctuation is a « direct » fluctuation whereas the longitudinal current and the energy density are « indirect ». The equations of motion that couple the direct and indirect variables are the equations of linear hydrodynamics.

The depolarized spectrum is in principle much more complicated than the isotropic Brillouin spectrum. The theories that have appeared in the literature are summarized in Table I. In this table $\rho, g, \varepsilon$ are respectively, the number, momentum, and energy densities, $S_j$ is the the molecular rotational angular momentum density, $\tau_{ij}^{(0)}, \tau_{ij}^{(1)}, \tau_{ij}^{(2)}$ are respectively the scalar, antisymmetric and symmetric traceless parts of the microscopic stress tensor, $u_i^{(2)}$ are the scalar, and symmetric parts of the distortion field $(u_i = V_j \rho_j$ where $u_j$ is the displacement field). $\alpha_{ij}$ and $\zeta_{ij}$ are the symmetric parts of the polarizability density and orientational fluctuations. From the table we see that the theories of A. B. F. I [5] and A. P. I [6] involve precisely the same sets of direct and indirect variables and, moreover, give precisely the same results. The theories of Rytov [1] and Volterra [2], are viscoelastic theories in the classical sense since they involve displacement and distortion fields. Since these concepts only have direct meaning in connection with crystals and amorphous solids, it is difficult to fit them into the conceptual framework of the other theories. Nevertheless, if we identify the time rate of change of the displacement field $u_i$ with the velocity field $V_i$ in the other theories, it immediately follows that A. B. F. I [5] and A. P. I [6] are equivalent to Rytov's earlier theory [1], and that A. P. II [6] is equivalent to Volterra's theory [2]. As a matter of fact, A. B. F. I [5] was formulated with this in mind.

In the theories of Ben-Reuven and Gershon [3], Keyes and Kivelson [4] and A. P. II [6], it is assumed that orientational fluctuations of the molecules cause the anisotropic dielectric fluctuations. From this point of view

$$\delta \varepsilon_{ij} \propto \zeta_{ij}.$$ 

In fact, A. P. I [6] is derived with any second rank symmetric traceless tensor which couples to hydrodynamic variables (be it $\varepsilon^{(2)}$ or $\zeta^{(2)}$). Thus, by choosing $\tau^{(2)}$, as they do, they arrive at the same results as A. B. F. I [5] or Rytov's [1]. If they had worked out the theory by taking $\zeta^{(2)}$ as the direct variable, they

(*) This work was supported by a grant from the N. S. F. GP. 
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TABLE I

Direct and indirect fluctuations in different theories of the depolarized I\textsubscript{\textsc{vh}} spectrum observed in light scattering spectroscopy of molecular liquids

<table>
<thead>
<tr>
<th>Theory</th>
<th>Direct fluctuations</th>
<th>Indirect fluctuations</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. B. F. I (derivation of Ryvot's Theory)</td>
<td>{ \tau_{ij}^{(2)} }</td>
<td>{ g_1 }</td>
<td>A viscoelastic theory</td>
</tr>
<tr>
<td>A. B. F. II (*)</td>
<td>{ \tau_{ij}^{(1)}, \tau_{ij}^{(2)} }</td>
<td>{ g_1, S_j }</td>
<td>Uses « Newtonian form » of the stress tensor</td>
</tr>
<tr>
<td>K. K.</td>
<td>{ a_{ij}^{(2)} }</td>
<td>{ g_1 }</td>
<td>No account is taken of the antisymmetric stress tensor</td>
</tr>
<tr>
<td>A. P. I</td>
<td>{ \tau_{ij}^{(2)} }</td>
<td>{ g_1 }</td>
<td>Presence of antisymmetric stress tensor is recognized but is not considered either as a direct or indirect fluctuation</td>
</tr>
<tr>
<td>A. P. II</td>
<td>{ \tau_{ij}^{(2)} }</td>
<td>{ g_1, \tau_{ij}^{(2)} }</td>
<td>\tau_{ij} is the stress tensor corresponding to the distortion field u_{ij}</td>
</tr>
<tr>
<td>Ryvot</td>
<td>{ u_{ij}^{(2)} }</td>
<td>{ \tau_{ij}^{(2)} }</td>
<td></td>
</tr>
<tr>
<td>Volterra</td>
<td>{ \tau_{ij}^{(2)} }</td>
<td>{ g_1, u_{ij}^{(2)} }</td>
<td></td>
</tr>
<tr>
<td>Ben-Reuven and Gershon</td>
<td>{ a_{ij}^{(2)} }</td>
<td>{ g_1 }</td>
<td>The indirect fluctuation is not explicitly stated except that it is hydrodynamic</td>
</tr>
<tr>
<td>C. Y.</td>
<td>{ \tau_{ij}^{(2)} }</td>
<td>{ g_1, \tau_{ij}^{(2)} }</td>
<td>Reverses Volterra's results</td>
</tr>
</tbody>
</table>

would have obtained the KK theory [4]. Were we to assume further, following Leontovich [13], that the anisotropic dielectric fluctuations are determined entirely by the rigid molecule polarizability, \(\alpha_{ij}\), and furthermore that

\[\alpha_{ij} \propto \tau_{ij}\]

then all the theories except A. B. F. II [5] would be equivalent as far as the diffuse line of the observed depolarized spectrum is concerned. A. P. II [6], Volterra [2] and Chung and Yip [7] went further and tried to account for the existence of a broad background as well, by coupling \(\tau_{ij}\) to \(\zeta_{ij}\) dynamically. However, it has been pointed out by Keyes and Kivelson [10] that while it is possible to get the width of the broad background, these theories do not give the experimentally observed value of the relative intensity of the broad background with respect to the diffuse central line.

We would end up in a similar situation were we to couple the polarizability tensor \(\alpha\) which is a « direct » fluctuation with the « indirect » fluctuations such as the momentum density \(g\) and the intrinsic angular momentum density \(S\) (along with the number density and energy density). Thus, it is clear that the observed broad background in the depolarized spectrum cannot be obtained by coupling the dielectric constant to only one direct variable. We present here a two coupling constant theory which could in principle correctly give the observed integrated intensity ratio of the broad background and the diffuse line.

III. Unified theory of depolarized spectrum. — It should be noted that the only theory that includes an antisymmetric tensor in either the direct or indirect set of fluctuations is A. B. F. II [5]. In A. P. [6] and K. K. [4] the existence of antisymmetric stress tensor is allowed but is not used in this way. This is rema-
kable since in fluids consisting of anisotropic molecules which interact through non-central forces, the microscopic stress tensor must contain an antisymmetric part, \( \tau_{ij}^{(1)} \), as well as symmetric parts \( \tau_{ij}^{(0)} \), and, \( \tau_{ij}^{(2)} \). The «Newtonian form» of these tensors is

\[
\begin{align*}
\tau_{ij}^{(0)} &= \eta_0 (\nabla \cdot \mathbf{V}) \delta_{ij} \\
\tau_{ij}^{(1)} &= \eta_1 (\nabla \times \mathbf{V})_i - 2 \alpha \tau_{ij}^{(0)} \\
\tau_{ij}^{(2)} &= \eta_2 (\nabla V_j + V_i \nabla \cdot \mathbf{V} - \delta V_j \delta V_i) \delta_{ij}
\end{align*}
\]

where \( \eta_0, \eta_1, \eta_2 \) are the bulk, shear and rotational viscosities, and \( \mathbf{V} \) and \( \omega \) are the linear and angular velocity fields respectively. The antisymmetric stress tensor arises because of intermolecular torques and is, in fact, the torque density.

The second thing that should be noted is that if the stress tensor has an antisymmetric part, it is necessary to consider the angular momentum density, \( S_j(r, t) \); otherwise the conservation laws are not obeyed. Although this last statement is correct without restriction, it is easy to see from the «Newtonian» stress tensors together with the momentum conservation law,

\[
d\frac{dt}{dt} \mathbf{g}_I + \nabla \cdot \mathbf{r}_{ij}^{(0)} + \tau_{ij}^{(1)} + \tau_{ij}^{(2)} = 0
\]

that the hydrodynamic equations are incomplete unless the angular momentum is considered. Unfortunately, only in A. B. F. II [5] is this fact realized and exploited. Nevertheless, even that theory is incomplete since it presents a purely «hydrodynamic theory» in which the «Newtonian form» of the stress tensor is used. This procedure gives rise to only the diffuse line. In what follows we show that when we take into account the microscopic relaxation of the stress tensor to its «Newtonian form», we can account for both the sharp and broad features of the depolarized Rayleigh spectrum.

First we note that since there are spontaneous fluctuations which give rise to antisymmetric and symmetric stress fields there is no reason to omit antisymmetric fluctuations in the dielectric tensor. In fact, we write the off-diagonal elements of the dielectric fluctuations, \( \delta \epsilon_{ij} \), as

\[
\delta \epsilon_{ij}(r, t) = X_1 \tau_{ij}^{(1)}(r, t) + X_2 \tau_{ij}^{(2)}(r, t).
\]

This was the form adopted in A. B. F. II [5] whereas in the other theories \( X_1 \) was taken as zero. That \( \delta \epsilon_{ij} \) couples to the stress tensor follows from the fact that we expect molecules to align in the presence of a stress field.

Some arguments have been raised, recently, which would require \( X_1 \) in the static limit, to be exactly-zero [15]. These arguments are not clear to us since eq. (2) is consistent with physically known principles; and leads to no dissipation of energy under either uniform translations or uniform rotations. This can be checked immediately from the «Newtonian form» of the stress tensor given in eq. (1).

In this paper, we do not assume local equilibrium values of the symmetric and antisymmetric stress tensor; but instead use the molecular expressions for these tensors. Also, we consider the set

\[
\{ \rho, g_0, \mathbf{v}, S_p, \tau_{ij}^{(0)}, \tau_{ij}^{(1)}, \tau_{ij}^{(2)} \}
\]

as the complete set of variables, where the symbols have usual meaning. This is the simplest set of variables since they correspond to the conserved properties, mass, momentum, angular momentum, and energy.

Equations of motion for these variables can be derived using Zwanzig-Mori projection operator techniques [16], [17]. These equations are particularly simple if: (a) the Markov approximation is made on the memory functions and (b) spin diffusion [18] is neglected. These equations are presented in Appendix A.

Given the equations of motion it is straightforward to calculate the depolarized light scattering spectrum. In particular, we compute the spectrum \( I_{vR}(q, \Omega) \) for 90° scattering which is

\[
I_{vR}(q, \Omega) = \int_{-\infty}^{+\infty} dt e^{iq \cdot \mathbf{r}(t)} \left[ < \delta \epsilon_{x x}(q, t) > < \delta \epsilon_{y y}(q, t) > + < \delta \epsilon_{y y}(q, t) > < \delta \epsilon_{x x}(q, t) > \right].
\]

Combining eq. (2) and (3), and solving the equations of motion in the Appendix A for the pertinent stress tensor correlation functions yields the spectrum.

The spectrum is particularly simple if we neglect cross correlations between \( \tau_{ij}^{(1)} \) and \( \tau_{ij}^{(2)} \); i.e. if we assume that \( < \tau_{ij}^{(1)}(q, t) \tau_{ij}^{(2)}(q, t) > = 0 \). Then

\[
I_{vR}(q, \Omega) = \frac{1}{2} C_1 \left[ I_1 \left( \frac{\Omega^2 + \Omega_1^2}{\Omega^2 - \Delta \Omega_1 \left( 1 + \frac{4 m}{1q^2} \right)^2 + \Omega^2} \right) \right] + \frac{1}{2} C_2 \left[ I_2 \left( \frac{\Omega^2 \Gamma_2}{\Omega^2 + \Gamma_2} + \frac{\Omega^2 \Gamma_2}{\Omega^2 - \Delta \Omega_2} \right) \right]
\]

where

\[
\begin{align*}
C_1 &\equiv |X_1|^2 < |\tau_{ij}^{(1)}(q)|^2 > \\
C_2 &\equiv |X_2|^2 < |\tau_{ij}^{(2)}(q)|^2 >
\end{align*}
\]

Note that if the antisymmetric part of the stress tensor, \( \tau_{ij}^{(1)}(q, t) \) were not included as a direct variable, the term with \( C_1 \) in the spectrum would be zero and eq. (4) would reduce to the Rytov theory [1] or equivalently A. B. F. II [5] or A. P. I [6]. Assuming, as in the Rytov theory [1], that the second term in eq. (4) describes the diffuse (sharp) Rayleigh line (which for some liquids is split), the first term in eq. (4) would then describe the broad Rayleigh line if

\[
\begin{align*}
(a) &\quad C_1 = \frac{1}{2} C_2 \\
(b) &\quad \Gamma_1 \sim 100 \Gamma_2.
\end{align*}
\]
Condition (a) is a condition on the integrated intensity ratio of the diffuse and broad bands,

\[ \frac{I_1(q)}{I_2(q)} = \frac{C_2}{C_1} = \frac{|X_2|^2 < |\tau^{(1)}_{yz}(q)|^2 >}{|X_1|^2 < |\tau^{(1)}_{yz}(q)|^2 >} = \frac{|X_2|^2 \Omega^2_1}{|X_1|^2 \Omega^2_A} \sim 3 \tag{6} \]

and condition (b) is a condition on the relative ratio of relaxation of \( \tau^{(2)}_i \) and \( \tau^{(1)}_i \).

While in general we do not know the relative magnitudes of the frequencies \( \Omega_1(q) \) and \( \Omega_2(q) \), it is reasonable to assume that \( \Omega_1(q) \) and \( \Omega_2(q) \) are the same order of magnitude. With this assumption \( X_2/X_1 \sim \sqrt{3} \). Note that when \( \Omega_2(q) \) is comparable to \( \Omega_1(q) \) there may also be a splitting of even the broad background.

Let us recall that eq. (4) was determined on the assumption that \( \tau^{(1)}_{ij} \) and \( \tau^{(2)}_{ij} \) do not directly couple. This is not rigorously correct. This coupling will lead to an additional contribution to the \( I_{\text{inh}}(q, \Omega) \) spectrum of the form

\[ \frac{1}{2}(X_1^* X_2 + X_2^* X_1) \times \]

\[ \times [< \tau^{(1)}_{yx}(q) \tau^{(2)}_{yx}(q, \Omega) > + < \tau^{(1)}_{yz}(q) \tau^{(2)}_{yz}(q, \Omega) >]. \tag{7} \]

To the lowest order in \( q \) this term has a very complicated structure which is given explicitly in Appendix B. This interference term is of the order \( q^2 \) (to the lowest order in \( q \)) smaller than the contribution reported in eq. (4).

Since we are concerned with light scattering experiments where \( q \sim 10^5 \) cm\(^{-1} \), we surmise that these interference terms will be small compared to the terms already included in eq. (4). Needless to say, light scattering experiments are done at finite \( q \) so that we cannot be certain about the relative smallness of the interference terms. It should be noted, however, that if these terms are retained, the equations of motion in the Appendix A, and consequently eq. (4), must be corrected since these equations are derived by omitting terms of the same order in \( q \) as

\[ < \tau^{(1)}_{ij}(q) \tau^{(2)}_{ij}(q, t) >. \]

We think that we are on safe grounds in ignoring the terms which arise because of eq. (5). As a matter of fact, all the theories mentioned so far have omitted such terms. It would be very difficult to derive a consistent set of equations of motion to the order required by inclusion of these interference terms. Nevertheless, were these terms included, they would contribute to the splitting of both the diffuse line and the broad background.

IV. Theory involving the orientational fluctuations. —
In this section we consider, in addition to the set (A.1), the anisotropic orientational fluctuations \( \zeta_{ij} \) as well.
The correlation function (9) has a third pole

\[ s_3 = -\frac{\Omega_i^2}{(\Gamma_2 + \Gamma_3 - \Gamma_2 \Gamma_3 - \Gamma_2 \Gamma_3)} \]

which is the cause of the splitting in the diffuse line. In this limit, \( \Gamma_1 \) is the width of the central diffuse line and \( \Gamma_3 \) would be the width of what in Volterra [2], A. P. II [6] and Chung and Yip theories correspond to the broad background. If \( \Gamma_2 \ll \Gamma_3 \), i.e., when the shear stress relaxation is slower than the relaxation due to reorientations,

\[ \Gamma_4 \approx \Gamma_2 - \frac{\Gamma_2 \Gamma_3}{\Gamma_3} \approx \Gamma_2. \]

The width of the central line is then given by \( \Gamma_2 \). This case corresponds to Volterra [2] and A. P. II [6] theories. In the reverse case corresponding to C. Y. theory [7] \( \Gamma_3 \ll \Gamma_2 \) the reorientation relaxation is slower than the shear stress relaxation and accordingly, the central line has a width given by the reorientation relaxation. The integrated intensity ratio of the central line to the broad background is still given by eq. (6).

V. Conclusion. — In this paper we presented a viscoelastic theory which is and extension of the Rytov theory [1], by taking into account the presence of the antisymmetric part of the microscopic stress tensor. This theory gives rise to a central split line and to a broad background. Moreover it suggests that in certain circumstances interference effects (cross terms might be important). This theory is quite different from other theories that have appeared in the literature [1]-[7] and can account in principle for the intensity ratio of the sharp line to the broad background.

Our previous work on the antisymmetric fluctuations [5] was based on the local equilibrium form of the stress tensor and could only account for the existence of the sharp line. The magnitude of the rotational viscosity \( \eta_r \) required for such a fit is about four-orders of magnitude smaller than the shear viscosity \( \eta_s \). While an experimental value of \( \eta_r \) is unknown, estimates of McCoy, Sandler and Dahler [20] for dilute gas of rough spheres give a value for rotational viscosity of the same magnitude as shear viscosity. It is not quite clear if the same estimate for \( \eta_r \) holds even for dense systems; the situation can be quite different for dense molecular fluids. It is, therefore uncertain if our previous work could account for the sharp line. There is no such problem in our present work.

In section IV, we have presented a general scheme in which the ideas of all the previous work on this subject is incorporated. While, it is too early to tell physically what mechanisms are responsible for the observed depolarized spectra, it is fairly clear that two different coupling coefficients are needed in the dielectric fluctuations to account for the observations [21].

Acknowledgements. — We have benefited from numerous conversations with Professor Daniel Kivelson and Mr. Thomas Keyes.

Appendix A. — We restrict ourselves to the consideration of \( \mathcal{I}_{\text{vis}}(q, \Omega) \) spectrum only; therefore only the reduced set of variables

\[ A = \{ g_i, S_{ij}, \tau_{ij}^{(1)}, \tau_{ij}^{(2)} \} \]  

is considered. We use Zwanzig-Mori projection operator techniques to derive equations of motion for these quantities. Using the approximations given in the text, namely,

i) Markov approximation on the memory functions, and

ii) neglecting spin diffusion,

the relevant equations of motion for the geometry used in our previous paper are

\[ \frac{d}{dt} g_i(q, t) = i q [\tau_{ij}^{(1)}(q, t) + \tau_{ij}^{(2)}(q, t)] \]  

\[ \frac{d}{dt} S_{ij}(q, t) = -2 \tau_{ij}^{(1)}(q, t) \]  

\[ \frac{d}{dt} \tau_{ij}^{(1)}(q, t) = \frac{i}{q^2} \Omega_i^2 g_i(q, t) + 2 \frac{m}{Iq^2} \Omega_i^2 S_{ij}(q, t) - \Gamma_1(q) \tau_{ij}^{(1)}(q, t) - q^2 \Gamma_2(q) \tau_{ij}^{(2)}(q, t) \]  

\[ \frac{d}{dt} \tau_{ij}^{(2)}(q, t) = \frac{i}{q^2} \Omega_i^2 g_i(q, t) - q^2 \Gamma_2(q) \tau_{ij}^{(1)}(q, t) - \Gamma_2(q) \tau_{ij}^{(2)}(q, t) \]  

\[ \frac{d}{dt} \tau_{ij}^{(1)}(q, t) = -\Gamma_1(q) \tau_{ij}^{(1)}(q, t) - q^2 \Gamma_2(q) \tau_{ij}^{(2)}(q, t) \]  

\[ \frac{d}{dt} \tau_{ij}^{(2)}(q, t) = -\Gamma_2(q) \tau_{ij}^{(2)}(q, t) - q^2 \Gamma_2(q) \tau_{ij}^{(1)}(q, t) \]
where

\[ \Omega_1^2(q) = q^2 \frac{< | \tau_{12}^{(2)}(q) |^2 >}{< | g_s(q) |^2 >} = \frac{q^2 \mu_\infty(q)}{\rho_0} \]  

(A.3a)

and

\[ \Omega_2^2(q) = q^2 \frac{< | \tau_{11}^{(2)}(q) |^2 >}{< | g_s(q) |^2 >} = \frac{q^2 \mu_A(q)}{\rho_0} \]  

(A.3b)

Note that eq. (A.3) define \( \mu_\infty(q) \) and \( \mu_A(q) \) where \( \mu_\infty \) is the usual high-frequency shear modulus at a wave vector \( q \). \( \mu_A(q) \), for want of a previous name, we call the high frequency rotational modulus. We have explicitly written in eq. (A.2) the dependence on \( q \) to the lowest order. Also

\[ \Gamma_1(q) = [ < | \tau_{12}^{(1)}(q) |^2 > - | < \tau_{12}^{(1)*}(q) \tau_{12}^{(2)}(q) |^2 ]^{-1} \times \]

\[ \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. 
- \left. < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(2)}(q) > < \tau_{12}^{(1)}(q) \tau_{12}^{(2)}(q) > \right] \]  

(A.4a)

\[ \Gamma_2(q) = [ < | \tau_{12}^{(2)}(q) |^2 > - | < \tau_{12}^{(1)*}(q) \tau_{12}^{(2)}(q) |^2 ]^{-1} \times \]

\[ \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. 
- \left. < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(2)}(q) > < \tau_{12}^{(1)}(q) \tau_{12}^{(2)}(q) > \right] \]  

(A.4b)

\[ q^2 \Gamma_{12}(q) = [ < | \tau_{12}^{(1)}(q) |^2 > - | < \tau_{12}^{(1)*}(q) \tau_{12}^{(2)}(q) |^2 ]^{-1} \times \]

\[ \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. 
- \left. < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(2)}(q) > < \tau_{12}^{(1)}(q) \tau_{12}^{(2)}(q) > \right] \]  

(A.4c)

\[ q^2 \Gamma_{21}(q) = [ < | \tau_{12}^{(1)}(q) |^2 > - | < \tau_{12}^{(1)*}(q) \tau_{12}^{(2)}(q) |^2 ]^{-1} \times \]

\[ \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. 
- \left. < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(2)}(q) > < \tau_{12}^{(1)}(q) \tau_{12}^{(2)}(q) > \right] \]  

(A.4d)

In the low \( q \) limit

\[ \Gamma_1 = \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. \]  

(A.5a)

\[ \Gamma_2 = \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. \]  

(A.5b)

\[ \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. 
- \left. < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(2)}(q) > < \tau_{12}^{(1)}(q) \tau_{12}^{(2)}(q) > \right] \]  

(A.5c)

\[ \int_0^\infty \text{d}q \left[ < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(1)}(q) > < | \tau_{12}^{(2)}(q) |^2 > \right. 
- \left. < \tau_{12}^{(1)*}(q) e^{i(1-P)L}(1 - P) \tau_{12}^{(2)}(q) > < \tau_{12}^{(1)}(q) \tau_{12}^{(2)}(q) > \right] \]  

(A.5d)
Appendix B. — We now use equations (A.2) and (2) and (3) to calculate the depolarized $I_{\text{VH}}(q, \Omega)$ spectrum. First we assume no coupling between $\tau_{11}^{(1)}(q, t)$ and $\tau_{12}^{(2)}(q, t)$.

From eq. (2) and (3) in the text, the $I_{\text{VH}}(q, \Omega)$ spectrum is

$$I_{\text{VH}}(q, \Omega) = \frac{1}{2} | X_1 |^2 \left[ < \tau_{11}^{(1)*}(q) \tau_{12}^{(1)}(q, \Omega) > + < \tau_{12}^{(1)*}(q) \tau_{11}^{(1)}(q, \Omega) > ight] +$$

$$+ \frac{1}{2} | X_2 |^2 \left[ < \tau_{12}^{(2)*}(q) \tau_{12}^{(2)}(q, \Omega) > + < \tau_{11}^{(2)*}(q) \tau_{11}^{(2)}(q, \Omega) > \right]. \quad (B.1)$$

Neglecting terms involving $q^2 \Gamma_{12}(q)$ in eq. (A.2) [which amounts to just disregarding the coupling between $\tau_{11}^{(1)}(q)$ and $\tau_{12}^{(2)}(q)$], we can calculate the spectrum in eq. (B.1)

$$I_{\text{VH}}(q, \Omega) = \frac{1}{2} C_1 \left[ \frac{\Gamma_1}{\Omega^2 + \Gamma_1^2} + \frac{2 \Omega^2}{\Omega^2 - \Omega^2 \left( 1 + \frac{4m}{Iq^2} \right)^2} \right] +$$

$$+ \frac{1}{2} C_2 \left[ \frac{\Gamma_2}{\Omega^2 + \Gamma_2^2} + \frac{2 \Omega^2}{\Omega^2 - \Omega^2 \left( 1 + \frac{4m}{Iq^2} \right)^2} \right] \quad (B.2)$$

which is just eq. (4) in the text.

Next we do not disregard the coupling between $\tau_{11}^{(1)}(q, t)$ and $\tau_{12}^{(2)}(q, t)$ but calculate the spectrum $I_{\text{VH}}(q, \Omega)$ only to the lowest order in $q$.

In this case, the spectrum $I_{\text{VH}}(q, \Omega)$ is not obtainable from only eq. (B.1) but has, in addition, the cross terms given by eq. (5). Thus

$$I_{\text{VH}}(q, \Omega) = \frac{1}{2} | X_1 |^2 \left[ < \tau_{11}^{(1)*}(q) \tau_{12}^{(1)}(q, \Omega) > + < \tau_{12}^{(1)*}(q) \tau_{11}^{(1)}(q, \Omega) > \right] +$$

$$+ \frac{1}{2} | X_2 |^2 \left[ < \tau_{12}^{(2)*}(q) \tau_{12}^{(2)}(q, \Omega) > + < \tau_{11}^{(2)*}(q) \tau_{11}^{(2)}(q, \Omega) > \right] +$$

$$\frac{1}{2} (X_1^2 X_2 + X_1 X_2^2) \left[ < \tau_{11}^{(1)*}(q) \tau_{12}^{(2)}(q, \Omega) > + < \tau_{12}^{(1)*}(q) \tau_{11}^{(2)}(q, \Omega) > \right]. \quad (B.3)$$

To the lowest order in $q$, the first two terms in eq. (B.3) are given by eq. (B.2). The interference (or cross terms) term has a very complicated structure,

$$< \tau_{11}^{(1)*}(q) \tau_{12}^{(2)}(q, \Omega) > = < \tau_{12}^{(1)*}(q) \tau_{11}^{(2)}(q, \Omega) > \times \frac{2 \Omega^2 \Gamma_1 + \Gamma_2 (\Gamma_1 \Gamma_2 - q^2 \Gamma_{12} \Gamma_{21})}{[\Omega^2 + q^2 (\Gamma_{12} \Gamma_{21} - \Gamma_1 \Gamma_2)]^2 + \Omega^2 (\Gamma_1 + \Gamma_2)^2} +$$

$$+ < \tau_{11}^{(1)*}(q) >^2 \frac{2 \Omega^2 \Gamma_1 + \Gamma_2 (\Gamma_1 \Gamma_2 - q^2 \Gamma_{12} \Gamma_{21})}{[\Omega^2 + q^2 (\Gamma_{12} \Gamma_{21} - \Gamma_1 \Gamma_2)]^2 + \Omega^2 (\Gamma_1 + \Gamma_2)^2} \quad (B.4)$$

$$< \tau_{12}^{(1)*}(q) \tau_{11}^{(2)}(q, \Omega) > = < \tau_{11}^{(1)*}(q) \tau_{12}^{(2)}(q, \Omega) > \times \frac{2 \Omega^2 \Gamma_2 + \Omega^2 (\Gamma_1 \Gamma_2 - q^2 \Gamma_{12} \Gamma_{21})}{[\Omega^2 + q^2 (\Gamma_{12} \Gamma_{21} - \Gamma_1 \Gamma_2)]^2 + \Omega^2 (\Gamma_1 + \Gamma_2)^2} +$$

$$+ < \tau_{12}^{(1)*}(q) >^2 \left[ \Omega^2 \Omega_1^2 \left[ \Gamma_1 \Omega_1 - \Omega_1 \Omega_2 \Omega_2 \left( 1 + \frac{4m}{Iq^2} \right) \right] \times \right. \left. \times \left[ \Omega^2 - \Omega_1^2 \left( 1 + \frac{4m}{Iq^2} \right) - \Gamma_1 \Gamma_2 \Omega_2 \right]^2 \right]^{-1} \quad (B.5)$$

The interference terms (B.4) and (B.5) are at least of the order $q^2$ smaller than the terms in eq. (B.2).

Appendix C. — Equations of motion when the orientational fluctuations are included. — These equations are

$$\frac{d}{dt} \sigma_s(q, t) = i q [ \tau_{11}^{(1)}(q, t) + \tau_{12}^{(2)}(q, t) ] \quad (C.1)$$

$$\frac{d}{dt} S_s(q, t) = -2 \tau_{12}^{(1)}(q, t) \quad (C.2)$$
The quantities \( r_1(q), r_2(q), r_{12}(q) \) and \( r_{21}(q) \) are defined by eqs (A.3) and (A.4). The other quantities are

\[
q^2 \Gamma_{13}(q) = \int_0^\infty dt \left< \frac{\tau_{1y}^{(2)}(q)}{\tau_{1y}^{(2)}} (1 - P) \frac{\tau_{1y}^{(1)}(q)}{\tau_{1y}^{(2)}} \right> \frac{\tau_{1y}^{(1)}(q)}{\tau_{1y}^{(2)}}.
\]

\[
q^2 \Gamma_{33}(q) = \int_0^\infty dt \left< \frac{\tau_{1y}^{(2)}(q)}{\tau_{1y}^{(2)}} (1 - P) \frac{\tau_{1y}^{(1)}(q)}{\tau_{1y}^{(2)}} \right> \frac{\tau_{1y}^{(1)}(q)}{\tau_{1y}^{(2)}}.
\]

In the limit \( q \to 0 \), the off-diagonal elements of the friction matrix are related.

The \( yx \) components of \( \tau^{(2)}, \tau^{(2)} \) and \( \zeta^{(2)} \) do not couple to \( g \) or \( S \) and the equations of motion for these involve only the friction coefficients \( \Gamma_{ij} \).

**References**


[14] In this context, the word «Newtonian» implies local-equilibrium value. For more information, the reader is referred to: de GROOT (S. R.) and MAZUR (P.), in Non-Equilibrium Thermodynamics (North-Holland, Amsterdam, 1962).


[18] Spin diffusion is not rotational relaxation. It has to do with translational diffusion processes which bring spin into and out of a volume element. This has been analyzed by AILAWADI (N. K.), BERNE (B. J.) and FORSTER (D.), Phys. Rev., 1971, A 3, 1462.

[19] This seems to be the case for diatomic liquids where molecular dynamics calculations have been done. For example in liquid CO $\Omega_2$ and $\Omega_4$ appear to be of the same order of magnitude.


[21] A different theory has been proposed by KEYES (T.), KIVELSON (D.) and MCTAGUE (J. P.), «Theory of k-Independent Depolarized Rayleigh Wing», submitted to J. Chem. Phys. This theory arrives at the same result that slow and fast direct variables couple with two different coupling constants to the dielectric fluctuations.