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Local order in a liquid and the fine structure of vertical-horizontal light scattering

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In this paper we show that the fine structure of vertical-horizontal (V-H) light scattering is due to the local order in the liquid. Use is made of the hydrodynamics equations obtained in a previous paper which introduced two tensors to characterize the local order. When one of these tensors is neglected with regard to the other (the one-tensor approximation), the spectrum given previously by different authors is obtained. It is shown in which cases this approximation is valid. The V-H spectrum for the light scattered by a liquid of spherical molecules is also given. The spectrum is computed in the general case when the two tensors are of the same order. In such a case, a spectrum is obtained which gives the broad background observed some years ago, and also the experimental results obtained recently in supercooled liquids which cannot be explained with the one-tensor approximation. The results are compared with previous theories, and it is shown that a generalization of all the previous results is obtained.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as I) we emphasized the importance of the local order in a liquid when one deals with high frequencies and small-wavelength hydrodynamics. It was shown that it is necessary to introduce, with the usual hydrodynamic fields, two new vectorial fields characterizing the local rotations and two tensor fields, characterizing the local order, and microscopic expressions for these new fields were given. Using these microscopic expressions and the nonequilibrium thermodynamics, we were able to obtain hydrodynamic equations for a fluid, valid up to high frequencies and small wavelengths. It was stressed that the four new fields were necessary to describe the collective behavior if kL_1 was not negligible, where L_1 is the correlation length of the local order and k the wave number of interest.

We shall see in Sec. II that at least one of the tensors characterizing the local order is proportional to the tensor of polarizability responsible for the light scattering. Furthermore, we shall see equally that in a dense molecular liquid the correlation length L_1 can be estimated of the order to 100 Å, so that for light wavelengths, $kL_1 \simeq 0.12$ and is not negligible. Consequently, it appears that light scattering is a possible field of application of the equations given in I. We shall use them here and shall be able to check their validity with experimental results. Conversely, it will be seen that the spectrum of the scattered light is tightly linked to the local order in a liquid. This paper, deals particularly with the vertical-horizontal (V-H) scattered spectrum which has been widely studied in recent years.

In Sec. II, we recall in more detail the results (I) which are of interest here, and we recall some basic results about light scattering.

In Sec. III, we compute the V-H spectrum when one of the tensors characterizing the local order is negligible with regard to the other. In such a case we obtain the same spectrum as that given by different authors,[2-4] which is in agreement with the experiments for a great number of fluids.[5-7] We discuss the physical phenomena involved and particularly the role of the coupling of the transverse velocity with the local orientational order. We also give the V-H spectrum in the case of the depolarized light scattered by a monatomic fluid.[8]

In Sec. IV, we compute the spectrum in the general case, when two tensors are necessary to characterize the local order. This yields a spectrum which is more complex than the preceding one, and which gives the broad background observed some years ago[9-11] and the triplet observed more recently in supercooled liquids.[12-15] This last spectrum cannot be explained with the one-tensor theories,[2-4] as is shown for instance in Refs. 13 and 15.

Since the theoretical prediction by Leontovich more than 35 years ago of the fine structure of the V-H spectrum,[16] and its observation by Starunov and others[17] in 1966, a great number of theoretical[2-4,18-26] and experimental[5-7,9-15,27] papers have dealt with this phenomenon. We shall try in Sec. V to link our results with the more characteristic of these theories, to explain why, from our point of view, some of them are not correct, and to show that for the others the physical background underlying the hypothesis is the local order in the liquids.

II. THE USEFUL FORMULAS

In the first part of this section, we recall the results[1] which are of interest here. In the second part, we relate the tensor of polarizability to the local-order tensors. In the third part, we recall some basic results about light scattering. Finally, in the last part an outline of the computations is given.

A. Outline of the results (I)

To describe the hydrodynamics of a molecular fluid up to high frequencies and short wavelengths, it is necessary to take into account the local order. More precisely, if the correlation length L_1 is much shorter than the wavelength of interest, it is possible to neglect the local order and to use the usual Navier-Stokes equations. But if L_1 is not negligible compared to the wavelength, the situation is more complex.

It is known that in liquid nitrogen near the triple point, L_1 is at least 12 Å.[28] On the other hand, in the isotropic phase of a nematic, just above T_c, L_1 is estimated on the order of 200 Å.[29] We have no accurate information on this point concerning the molecular fluids giving a fine structure for the V-H spectrum, but they are more complex than nitrogen and it seems reasonable to take L_1 on the order of 100 Å for those liquids.

So, as was said in the Introduction, for the visible wavelengths, $kL_1 \simeq 0.12$ and is not negligible. To understand the light scattered by a liquid, it is necessary to take into account the local order, and conversely, light scattering is an accurate tool to study the local order in a liquid.

Two symmetric tensors are necessary to describe the local order. The first one, $\overleftrightarrow{G}$, characterizes the local order of the centers of gravity:

$$\overleftrightarrow{G}(\vec{r}, t) = \frac{m}{L_1^3} \sum_j [(\vec{r}_j - \vec{r})^2 \overleftrightarrow{U} - (\vec{r}_j - \vec{r})(\vec{r}_j - \vec{r})] U(\vec{r}_j - \vec{r}) , \tag{2.1}$$

where m is the mass and $\vec{r}_j$ the position of the center of gravity of the molecule j. $\overleftrightarrow{U}$ is the unit tensor. $U(\vec{r}_j - \vec{r})$ is equal to 1 if the center of gravity of the molecule j is inside the box of side L_1 centered at $\vec{r}$, and zero otherwise.

$\overleftrightarrow{G}(\vec{r}, t)$ is the tensor of inertia, with respect to the center of the box of the molecules inside. The traceless tensor $\overleftrightarrow{G}_s(\vec{r}, t)$ constructed from $\overleftrightarrow{G}(\vec{r}, t)$ is the quadrupolar mass density tensor. $\overleftrightarrow{G}_s(\vec{r}, t)$ is null if there is no local order of the center of gravity or if the local symmetry is cubic.

The local orientational order is characterized by the tensor

$$\overleftrightarrow{I}(\vec{r}, t) = \frac{1}{L_1^3} \sum_j \overleftrightarrow{I}_j(\vec{r}, t) U(\vec{r}_j - \vec{r}) , \tag{2.2}$$

where $\overleftrightarrow{I}_j$ is the tensor of inertia of the molecule j. The trace I_t of $\overleftrightarrow{I}$ is proportional to the density of the liquid, and the traceless tensor $\overleftrightarrow{I}_s$ is null if there is no local orientational order or if the local symmetry is fcc.

The equations of motion for $\overleftrightarrow{G}_s$ and $\overleftrightarrow{I}_s$ are

$$\begin{aligned} \overleftrightarrow{\sigma}_s &= -2\alpha_{11}(\vec{\nabla}\vec{v})_s - 2\alpha_{12}\frac{d}{dt}\overleftrightarrow{G}_s - 2\alpha_{13}\frac{d}{dt}\overleftrightarrow{I}_s , \\ a\overleftrightarrow{G}_s &= -2\alpha_{12}(\vec{\nabla}\vec{v})_s - 2\alpha_{22}\frac{d}{dt}\overleftrightarrow{G}_s - 2\alpha_{23}\frac{d}{dt}\overleftrightarrow{I}_s , \\ b\overleftrightarrow{I}_s &= -2\alpha_{13}(\vec{\nabla}\vec{v})_s - 2\alpha_{23}\frac{d}{dt}\overleftrightarrow{G}_s - 2\alpha_{33}\frac{d}{dt}\overleftrightarrow{I}_s . \end{aligned} \tag{2.3}$$

The matrice α is symmetric (Onsager relations), α_{11} is the usual shear viscosity. $\overleftrightarrow{\sigma}$ is the usual stress tensor which can be written as

$$\overleftrightarrow{\sigma} = \tfrac{1}{3}\sigma_t \overleftrightarrow{U} + \overleftrightarrow{\sigma}_s + \overleftrightarrow{\sigma}_a , \tag{2.4}$$

where $\overleftrightarrow{\sigma}_a$ is the antisymmetric part. The coefficients a and b are defined by Eq. (V.7) of I. We neglect the term c in this equation (we shall come back to this point).

The equation of motion for the velocity field $\vec{v}(\vec{r}, t)$ is

$$\rho \frac{d\vec{v}}{dt} = -\vec{\nabla} \cdot \overleftrightarrow{\sigma} \tag{2.5}$$

where ρ is the mass density.

The antisymmetric part $\overleftrightarrow{\sigma}_a(\vec{k}, t)$ is negligible if $1/k$ is much larger than the correlation length. So, for the light wavelengths $\overleftrightarrow{\sigma}_a(k, t)$ is small compared to $\overleftrightarrow{\sigma}_s(k, t)$, and in the following analysis we shall assume that the stress tensor is symmetric. The tensor $\overleftrightarrow{\sigma}_a$ correlates the linear velocity field $\vec{v}$ with the angular velocity fields $\vec{\omega}$ and $\vec{\Omega}$ [see Eq. (5.13) of I]. Consequently, when we assume that $\overleftrightarrow{\sigma}_a$ is null, the linear and the rotational velocity are no longer correlated, and the latter is not involved in the scattering process. Such an assumption is also explicitly made by Gershon-Oppenheim[4] and seems reasonable since the spectrum obtained is in good agreement with experiment. Yet, it is not possible to claim from a theoretical point of view that this assumption is always correct and an attempt to explain the depolarized spectrum with the rotational velocity is made in Ref. 25. Nevertheless, the role of the local order is certainly much more important than the role of the rotational velocity.

B. The density of polarizability

We call $\overleftrightarrow{Q}_j$ the tensor of polarizability of the molecule j. There is a linear relation between this tensor and the tensor of inertia $\overleftrightarrow{I}_j$:

$$\overleftrightarrow{Q}_j = \overleftrightarrow{B} \cdot \overleftrightarrow{I}_j . \tag{2.6}$$

This relation is written in the principal frame linked to the molecule j. If the molecule is linear, $\overleftrightarrow{B}$ is a scalar, and if the molecule is a symmetric top, $\overleftrightarrow{B}$ is diagonal. We define now the density of polarizability as

$$\overleftrightarrow{Q}(\vec{r},t)=\frac{1}{L_1^3}\sum_j \overleftrightarrow{Q}_j U(\vec{r}_j-\vec{r}) \tag{2.7}$$

The traceless part of this tensor, $\overleftrightarrow{Q}_s$, is responsible for the depolarized light scattering. Using (2.2) and (2.6), we see that there is a linear relation between $\overleftrightarrow{Q}(\vec{r},t)$ and $\overleftrightarrow{I}(\vec{r},t)$. Now if we use the Curie principles,[1] since the liquid is isotropic, we get

$$\overleftrightarrow{Q}_s(r,t)=\beta\overleftrightarrow{I}_s(r,t)\,, \tag{2.8}$$

where β is a scalar. The traceless part of the tensor of polarizability is proportional to the traceless part of the tensor characterizing the local orientational order.

In a liquid of spherical molecules, $\overleftrightarrow{I}_s$ is null since the tensors $\overleftrightarrow{I}_{js}$ are null if we neglect the collision effects. Yet there is a very weak depolarization[8] which is due to the fluctuations of the local order of the centers of gravity. In such a case, we have

$$\overleftrightarrow{Q}_s=\gamma\overleftrightarrow{G}_s\,, \tag{2.9}$$

where the scalar γ is very small, and we are still able to compute the spectrum of $\overleftrightarrow{Q}_s$ using (2.3).

Instead of (2.8), the actual general formula should be

$$\overleftrightarrow{Q}_s=\beta\overleftrightarrow{I}_s+\gamma\overleftrightarrow{G}_s \tag{2.10}$$

But in a liquid of nonspherical molecules, γ is negligible compared to β and we shall use (2.8) in such a case.

C. Basic results of light scattering

The spectrum of the scattered light is given by[30]

$$I(\omega_i+\omega)=\text{const}\times\int_{-\infty}^{+\infty}\left\langle\sum_{jl}[\vec{n}_f\cdot\overleftrightarrow{Q}_j(0)\cdot\vec{n}_i]\,[\vec{n}_f\cdot Q_l(t)\cdot\vec{n}_i]e^{i\vec{k}\cdot[\vec{r}_j(0)-\vec{r}_l(t)]}\right\rangle e^{-i\omega t}dt\,, \tag{2.11}$$

where $\omega_i, \vec{k}_i, \vec{n}_i$ are respectively the frequency, the wave vector, and the direction of polarization of the incident light, where $\vec{k}_f$ and $\vec{n}_f$ are the wave vector and the direction of the polarization of the scattered light, and $\vec{k}=\vec{k}_i-\vec{k}_f$.

Using (2.7), the fact that L_1 is small compared to $1/k$, and the translational invariance, we get

$$I(\omega_i+\omega)=\text{const}\times\int_{-\infty}^{+\infty}e^{-i\omega t}\int_V\langle[\vec{n}_f\cdot\overleftrightarrow{Q}(0,0)\cdot\vec{n}_i]\,[\vec{n}_f\cdot\overleftrightarrow{Q}(\vec{r},t)\cdot\vec{n}_i]\rangle e^{-i\vec{k}\cdot\vec{r}}d\vec{r} \tag{2.12}$$

This is the well-known result that the scattered spectrum is the space and time Fourier transform of the autocorrelation function of the tensor of polarizability.

Without any further calculation, we can have some ideas about the shape of the spectrum, using only this last formula. Consider a fluctuation $\delta Q(0,0)$. A part of this fluctuation will decay locally, i.e., within a distance $\leq L_1$, and the other part will couple with the hydrodynamic modes and will spread through the liquid. So we shall have

$$\langle[\vec{n}_f\cdot\overleftrightarrow{Q}(0,0)\cdot\vec{n}_i][\vec{n}_f\cdot\overleftrightarrow{Q}(\vec{r},t)\cdot\vec{n}_i]\rangle=f(t)\delta(\vec{r})+g(\vec{r},t) \tag{2.13}$$

and from (2.12)

$$I(\omega_i+\omega)=f(\omega)+g(\vec{k},t) \tag{2.14}$$

The scattered spectrum will be the summation of two terms. The first one, $\vec{k}$ independent, is due to the local decay of the fluctuations of the tensor of polarizability. The second one, $\vec{k}$ dependent, is due to the coupling, allowed by the geometry, of the tensor of polarizability with the hydrodynamic modes. This is actually what we shall find in the following parts.

To study the V-H scattering, we choose the usual geometry: $\vec{k}$ is along the z axis of the laboratory frame, θ is the scattering angle, $\vec{k}_i$, $\vec{k}_f$, and $\vec{n}_f$ are in the xz plane, and $\vec{n}_i$ is perpendicular to the xz plane.

Using the fact that the components Q_{xy} and Q_{yz} are independent variables, one can easily show with this geometry that

$$I_{\text{VH}}(\omega_i+\omega)\simeq\sin^2(\theta/2)\text{Re}\langle Q_{xy}(0,0)Q_{xy}(k,\omega)\rangle + \cos^2(\theta/2)\text{Re}\langle Q_{yz}(0,0)Q_{yz}(k,\omega)\rangle\,, \tag{2.15}$$

where

$$\overleftrightarrow{Q}(k,\omega)=\int_0^\infty e^{-i\omega t}\int_V e^{-i\vec{k}\cdot\vec{r}}\overleftrightarrow{Q}(\vec{r},t)\,d\vec{r}\,dt \tag{2.16}$$

$$\overleftrightarrow{Q}(0,0)=\overleftrightarrow{Q}(\vec{r},t)\ \text{for}\ \vec{r}=0\ \text{and}\ t=0$$

D. Outline of the computation

We shall compute the V-H spectrum, using Eq. (2.15). Since $\overleftrightarrow{Q}_s$ is proportional to $\overleftrightarrow{I}_s$ [formula (2.8)], we shall compute the space and time autocorrelation of I_{xy} and I_{yz}.

We saw in I that the natural fluctuations in a liquid obey Eqs. (2.3) and (2.5) if we are interested in wavelengths larger than a characteristic length L_2 which is on the order of 10Å. This is typically the case here.

The natural fluctuations in a liquid at equilibrium being weak, we shall linearize the equations. We take for $t=0$ the initial conditions $\overleftrightarrow{I}(k,0)$, $\overleftrightarrow{G}(k,0)$, and $\vec{v}(k,0)$. With these initial conditions, using the Fourier transform with respect to space and the Laplace transform with respect to time, we shall solve (2.3) and (2.5). Since the equations are linear, the solution will be linear with respect to the initial conditions. For instance, we have

$$I_{yz}(k,\omega)=I_{yz}(k,0)f_1(k,\omega)+G_{yz}(k,0)f_2(k,\omega)+v_y(k,0)f_3(k,\omega)\,, \tag{2.17}$$

and taking the equilibrium thermodynamic average

$$\begin{aligned}\langle I_{yz}(0,0)I_{yz}(k,\omega)\rangle &= \langle I_{yz}(0,0)I_{yz}(k,0)\rangle f_1(k,\omega)\\ &\quad+\langle I_{yz}(0,0)G_{yz}(k,0)\rangle f_2(k,\omega)\\ &\quad+\langle I_{yz}(0,0)v_y(k,0)\rangle f_3(k,\omega)\,.\end{aligned} \tag{2.18}$$

We must compute the averages appearing in (2.18).

Coming back to the $\vec{r}$ space, we have

$$\langle I_{yz}(0,0)I_{yz}(k,0)\rangle=\int_V e^{-i\vec{k}\cdot\vec{r}}\langle I_{yz}(0,0)I_{yz}(\vec{r},0)\rangle d\vec{r}\,,$$

and using the fact that $\langle I_{yz}(0,0)I_{yz}(\vec{r},0)\rangle = U(\vec{r})\langle I_{yz}^2(0,0)\rangle$, we get

$$\langle I_{yz}(0,0)I_{yz}(k,0)\rangle=L_1^3\langle I_{yz}^2(0,0)\rangle\,. \tag{2.19}$$

Following the same demonstration, we have

$$\langle I_{yz}(0,0)v_y(k,0)\rangle=L_1^3\langle I_{yz}(0,0)v_y(0,0)\rangle=0 \tag{2.20}$$

and

$$\langle I_{yz}(0,0)G_{yz}(k,0)\rangle=L_1^3\langle I_{yz}(0,0)G_{yz}(0,0)\rangle\simeq 0\,. \tag{2.21}$$

The second part of (2.20), is exact, as can be shown easily using the Boltzmann distribution. But the second part of (2.21) is an approximation which amounts to neglecting $\langle I_{yz}(0,0)G_{yz}(0,0)\rangle$ with regard to $\langle I_{yz}^2(0,0)\rangle$. This is equivalent to neglecting the coefficient c with regard to a and b in (5.7) of I. In the following we shall use this approximation, yet it is uncertain if this is always a good one. We have also performed the calculation without this approximation. The formulas obtained are rather tedious, but they are qualitatively the same as those given in Sec. IV.

Now we present some formulas which will be useful later. We consider a function $f(\vec{r})$ which tends towards zero when $|\vec{r}|$ tends towards infinity. This is the case if $f(\vec{r})$ is a natural fluctuation of the liquid. We have chosen $\vec{k}$ along the z axis, so

$$\begin{aligned}&f(k)=\int_V f(\vec{r})e^{-ikz}dx\,dy\,dz\,,\\ &\int_V \partial_x f(\vec{r})e^{-ikz}dx\,dy\,dz=\int_V \partial_y f(\vec{r})e^{-ikz}dx\,dy\,dz=0\,,\\ &\int_V \partial_z f(\vec{r})e^{-ikz}dx\,dy\,dz=ikf(k)\,.\end{aligned} \tag{2.22}$$

III. THE ONE-TENSOR APPROXIMATION

In this section, we shall compute the V-H spectrum assuming that one tensor is sufficient to describe the local order. This arises in three cases: (1) $\overleftrightarrow{G}_s$ is negligible with regard to $\overleftrightarrow{I}_s$. This is, for instance, the case in the isotropic phase of a nematic, or if the local order has a cubic symmetry. (2) $\overleftrightarrow{I}_s$ is negligible with regard to $\overleftrightarrow{G}_s$. This is, for instance, the case in a fluid of nearly spherical molecules. (3) The tensors $\overleftrightarrow{I}_s$ and $\overleftrightarrow{G}_s$ are proportional. This situation arises for instance if we assume that the liquid is a set of microcrystals.

We first compute the V-H spectra (Sec. III A) and then discuss the results (Sec. III B).

A. Calculation of the V-H spectra

It is assumed, for example, that $\overleftrightarrow{G}_s$ is negligible compared to $\overleftrightarrow{I}_s$ [case (1) above]. The other two cases give the same results with a straightforward permutation of the index. Equation (2.3) yields

$$\sigma_{xy}=-\alpha_{11}(\partial_x v_y+\partial_y v_x)-2\alpha_{13}\dot{I}_{xy}\,, \tag{3.1}$$

$$bI_{xy}=-\alpha_{13}(\partial_x v_y+\partial_y v_x)-2\alpha_{33}\dot{I}_{xy}\,, \tag{3.2}$$

where $\dot{I}_{xy}$ is the partial time derivative of I_{xy}. Taking the space Fourier transform of (3.2) and using (2.22), we get

$$bI_{xy}(k,t)=-2\alpha_{33}\dot{I}_{xy}(k,t)\,. \tag{3.3}$$

There is no coupling between $I_{xy}(k,t)$ and the transverse velocity. Solving this last equation, we get

$$I_{xy}(k,t)=I_{xy}(k,0)e^{-\Gamma t}\,, \tag{3.4}$$

where $1/\Gamma=2\alpha_{33}/b$ is the relaxation time of the local structure.

We now study I_{yz}. Taking the space Fourier transform of (3.1) and (3.2) and using (2.22), we get

$$\sigma_{yz}(k,t) = -\alpha_{11} ikv_y(k,t) - 2\alpha_{13}\dot{I}_{yz}(k,t),$$
$$bI_{yz}(k,t) = -\alpha_{13} ikv_y(k,t) - 2\alpha_{33}\dot{I}_{yz}(k,t). \tag{3.5}$$

There is a coupling between $I_{yz}(k,t)$ and the transverse velocity $v_y(k,t)$. The equation of motion of v_y is given by (2.5). Taking the space Fourier transform, we get

$$\rho\dot{v}_y(k,t) = -ik\sigma_{yz}(k,t). \tag{3.6}$$

Taking the time Laplace transform, we are now able to solve Eqs. (3.5) and (3.6). Using (2.19) and (2.20), we give the autocorrelation functions directly:

$$\langle v_y(0,0)v_y(k,Z)\rangle = \frac{[Z+\Gamma]\langle v_y^2\rangle}{P(Z)} \tag{3.7}$$

$$\langle I_{yz}(0,0)I_{yz}(k,Z)\rangle = \frac{\langle I_{yz}^2\rangle}{Z+\Gamma} - \frac{ER\langle I_{yz}^2\rangle}{(\Gamma+\lambda_1)(\Gamma+\lambda_2)(\lambda_1-\lambda_2)} \times\left(\frac{\lambda_1-\lambda_2}{Z+\Gamma} + \frac{\Gamma+\lambda_2}{Z-\lambda_1} - \frac{\Gamma+\lambda_1}{Z-\lambda_2}\right), \tag{3.8}$$

where

$$E = \frac{k^2\alpha_{11}}{\rho}, \quad R = \frac{\alpha_{13}^2}{\alpha_{11}\alpha_{33}}, \tag{3.9}$$
$$P(Z) = Z^2 + [\Gamma + E(1-R)]Z + E\Gamma,$$

λ_1 and λ_2 are the roots of $P(Z)$, and $\langle I_{yz}^2\rangle$ means $\langle I_{yz}^2(0,0)\rangle$. Using (2.15), (3.4), (3.8) and the fact that $\langle I_{xy}^2\rangle = \langle I_{yz}^2\rangle$ since the liquid is isotropic, it is now easy to get the V-H spectrum. There are two cases depending on the sign of the discriminant Δ of $P(z)$.

1. Δ *is positive.* This arises if

$$\frac{E}{\Gamma} \le \frac{(1-R^{1/2})^2}{(1-R)^2} \quad \text{or} \quad \frac{(1+R^{1/2})^2}{(1-R)^2} \le \frac{E}{\Gamma} \tag{3.10}$$

The roots of $P(Z)$ are real and from (3.7) the transverse velocity v_y is diffusive. The V-H spectrum is given by

$$I_{\mathrm{VH}}(\omega_i+\omega) \simeq \langle I_{xy}^2\rangle \frac{\Gamma}{\omega^2+\Gamma^2} - \frac{\langle I_{yz}^2\rangle \cos^2(\theta/2) ER\Gamma}{(\Gamma+\lambda_1)(\Gamma+\lambda_2)(\lambda_1-\lambda_2)} \left(\frac{(\lambda_1-\lambda_2)\Gamma}{\omega^2+\Gamma^2} - \frac{(\Gamma+\lambda_2)\lambda_1}{\omega^2+\lambda_1^2} + \frac{(\Gamma+\lambda_1)\lambda_2}{\omega^2+\lambda_2^2}\right). \tag{3.11}$$

It is also possible to rewrite (3.11) in the more usual form[2-4]

$$I_{\mathrm{VH}}(\omega_i+\omega) \simeq \langle I_{xy}^2\rangle \sin^2\left(\frac{\theta}{2}\right) \frac{\Gamma}{\omega^2+\Gamma^2} + \langle I_{yz}^2\rangle \frac{\cos^2(\theta/2)}{\lambda_1-\lambda_2} \left(\frac{\lambda_2^2+\lambda_2 E(1-R)}{\omega^2+\lambda_2^2} - \frac{\lambda_1^2+\lambda_1 E(1-R)}{\omega^2+\lambda_1^2}\right). \tag{3.12}$$

2. Δ *is negative.* The roots of $P(Z)$ are complex and from (3.7) the transverse velocity v_y is propagative. (The spectrum is not given here. It can easily be obtained with a straightforward calculation.) There is a central peak and two symmetrically shifted peaks and the area of the two shifted peaks is equal to the area of the central one.[13-15,31]

B. Discussion

We discuss the results using formula (3.11). As expected from the previous discussion in Sec. II C, the V-H spectrum is the summation of two terms. The first one, $\vec{k}$ independent, is a Lorentzian which corresponds to the decay of the local order. The second one, which is $\vec{k}$ dependent through θ and E, gives the fine structure of the spectrum. As this fine structure is due to I_{yz}, we shall try to have a better understanding of the evolution of this quantity.

Returning to $\vec{r}$ space, we can rewrite the second equation (3.5) as

$$\dot{I}_{yz}(\vec{r},t) = -\Gamma I_{yz}(\vec{r},t) - \frac{1}{2}\left(\frac{\alpha_{11}}{\alpha_{33}}\right)^{1/2} R^{1/2}\partial_z v_y(\vec{r},t). \tag{3.13}$$

The first term of the right-hand side corresponds to the decay of the local order due to the thermal fluctuations which, as I_{xy}, does not couple with the transverse velocity. The second term corresponds to the coupling between I_{yz} and $\partial_z v_y$, R being the coupling parameter. It is easy to show, from the definition of R and using Eq. (5.6) of I giving the entropy production which is always positive, that R is always between 0 and 1.

We now consider a cube of side L_1 (the correlation length) in the liquid. It was observed in I that for some spans of time shorter than the lifetime of the local structure, the molecules in this cubic box are organized as those in a loose solid. The variations of I_{yz} are related to the evolution of this pseudosolid which is twofold: first, as a real solid, there is a linear velocity $\vec{v}$ and an angular velocity $\vec{\omega}$, and second, there is a deformation of the structure of this pseudosolid. Take one side of the box along the z axis and another side along the y axis. The transverse velocity along y on the face $z=0$ is $V_1 = v_y(\vec{r},t)$; the transverse velocity on the face $z=L_1$ is V_2. Since L_1 is small compared to the light wavelength,

$$V_2 \simeq V_1 + L_1\partial_z v_y(\vec{r},t). \tag{3.14}$$

The variation of I_{yz} due to the transverse velocity v_y is proportional to the shear $V_2 - V_1$. Thus, from (3.14),

$$\dot{I}_{yz}(\vec{r}, t) \simeq -L_1 \partial_z v_y(\vec{r}, t) \tag{3.15}$$

But for a given shear and a given L_1, the variation of I_{yz} depends also on the "softness" of the pseudosolid. We have, for instance, three characteristic cases:

(1) The "stone case": the pseudosolid is very rigid. In such a case the shear stress gives to the pseudosolid a rotation along the x axis which induces a variation of I_{yz} in the laboratory frame. This variation of I_{yz} is important.

(2) The ”rubber case”: the shear stress induces a deformation of the bulk of the pseudosolid. The resulting variation of I_{yz} is still important.

(3) The "butter case": the shear stress induces a deformation near the faces $z=0$ and $z=L_1$ which does not disturb the bulk of the pseudosolid. The variation of I_{yz} is then weak.

We may characterize these different behaviors by a phenomenologic coefficient ϕ which can be named a local "softness" coefficient. This coefficient is large in the first case and small in the third one.

Using (3.13), (3.15), and the preceding discussion, we can write

$$R^{1/2} = \phi L_1 \tag{3.16}$$

which gives the mathematical definition of ϕ.

From this last formula, we can qualitatively understand why the experimental values of R are approximately the same for a great number of compounds,[5,7,15] since there are two opposed effects: when the correlation length L_1 is large, the softness modulus is generally weak and vice versa.

We return now to the second term of the right-hand side of (3.11) giving the fine structure of the V-H spectrum. As expected, this term is proportional to the coupling parameter R. Using the definition of E and (3.16), we see that this term is also proportional to $(kL_1)^2$, which is the characteristic number of the theory[1] as was emphasized in the Introduction.

Thus if L_1 is much smaller than the light wavelength, the V-H spectrum is a single Lorentzian. This is, for instance, the case of a highly depolarizing molecule diluted in a liquid of spherical molecules. In such a case the V-H scattering is due to the diluted molecule and the correlation length is the length of the molecule ($\simeq 5$ Å). $(KL_1)^2$ is then very small and the coupling of the scattering object (the molecule) with the transverse velocity is very weak. Actually, the observed spectrum is a Lorentzian with no fine structure.[32]

This argument and this experiment show that the theories of the V-H light scattering based on the coupling of the individual molecule with the transverse velocity are not accurate. The k dependent term of the V-H spectrum is due to the coupling of the local order, which is a *collective* quantity, with the transverse velocity.

Equation (3.12) (or similar expressions) is given by different authors,[2-4] the definition of the coefficients E, Γ, and R being different for each theory, but having essentially the same meaning. The experimental spectra are in agreement with this formula for a great number of compounds in a large range of temperatures and densities.[5-7] Thus, the one-tensor approximation seems valid in a great number of cases. In the studied liquids, this approximation holds because the liquids are in case one or case three described at the beginning of this section. The second case corresponds to the depolarized light scattered by a fluid of spherical molecules[8] and the formula (3.11) gives the V-H spectrum in such a case.

It was observed recently in supercooled fluids[12-15] that the V-H spectrum disagrees with (3.11) or with the equivalent formula when $\Delta < 0$. Thus the one-tensor approximation is not always valid and we shall now compute the V-H spectrum in the general case.

IV. THE GENERAL CASE

We now assume that the two tensors $\overleftrightarrow{I}$ and $\overleftrightarrow{G}$ are necessary to describe the local order. As in the preceding section, we begin with the computation of the V-H spectrum (Sec. IV A) and then discuss the results (Sec. IV B).

A. Computation of the V-H spectrum

Let us begin with Q_{xy}. If we perform a space Fourier transform of (2.3) using (2.22), we get

$$\begin{aligned} aG_{xy}(k,t) &= -2\alpha_{22}\dot{G}_{xy}(k,t) - 2\alpha_{23}\dot{I}_{xy}(k,t), \\ bI_{xy}(k,t) &= -2\alpha_{23}\dot{G}_{xy}(k,t) - 2\alpha_{33}\dot{I}_{xy}(k,t). \end{aligned} \tag{4.1}$$

G_{xy} and I_{xy} are coupled to each other but are not coupled to the transverse velocity.

Using the time Laplace transform, it is easy to solve (4.1). We give the autocorrelation function directly, using (2.8) and (2.19)–(2.21):

$$\langle Q_{xy}(0,0)Q_{xy}(k,t)\rangle = \frac{\langle Q_{xy}^2\rangle}{Z_1 - Z_2}\left[\left(\frac{Z_1+\Gamma_2}{1-R_{23}}\right)e^{Z_1 t} - \left(\frac{Z_2+\Gamma_2}{1-R_{23}}\right)e^{Z_2 t}\right], \tag{4.2}$$

where

$$R_{23} = \frac{\alpha_{23}^2}{\alpha_{22}\alpha_{33}}, \quad \Gamma_2 = \frac{a}{2\alpha_{22}}, \quad \Gamma_3 = \frac{b}{2\alpha_{33}} \tag{4.3}$$

and Z_1 and Z_2 are the roots of

$$D(Z) = (1 - R_{23})Z^2 + (\Gamma_2 + \Gamma_3)Z + \Gamma_2\Gamma_3 \tag{4.4}$$

These roots are always real and negative, and the coefficients before the two exponentials in (4.2) are always positive.

Equation (4.2) is valid when $R_{23} \neq 1$. We shall study the case $R_{23} = 1$ in Sec. IV B.

It is now easy to compute the first term of the V-H spectrum:

$$\mathrm{Re}\langle Q_{xy}(0,0)Q_{xy}(k,\omega)\rangle = \frac{\langle Q_{xy}^2\rangle}{Z_1 - Z_2}\left(\frac{Z_2^2 + Z_2\Gamma_2/(1-R_{23})}{\omega^2 + Z_2^2} - \frac{Z_1^2 + Z_1\Gamma_2/(1-R_{23})}{\omega^2 + Z_1^2}\right). \tag{4.5}$$

This term is the summation of two positive Lorentzians.

We now compute Q_{yz}. Performing a space Fourier transform of (2.3) and using (2.22), we get

$$\begin{aligned} \sigma_{yz}(k,t) &= -\alpha_{11} ikv_y(k,t) - 2\alpha_{12}\dot{G}_{yz}(k,t) \\ &\quad -2\alpha_{13}\dot{I}_{yz}(k,t), \\ aG_{yz}(k,t) &= -\alpha_{12} ikv_z(k,t) - 2\alpha_{22}\dot{G}_{yz}(k,t) \\ &\quad -2\alpha_{23}\dot{I}_{yz}(k,t), \\ bI_{yz}(k,t) &= -\alpha_{13} ikv_y(k,t) - 2\alpha_{23}\dot{G}_{yz}(k,t) \\ &\quad -2\alpha_{33}\dot{I}_{yz}(k,t). \end{aligned} \tag{4.6}$$

G_{yz} and I_{yz} now couple with the transverse velocity. The following calculations are straightforward but tedious, and we give here the main lines only. The time Laplace transform of the second and third equations (4.6) gives $G_{yz}(k,Z)$ and $I_{yz}(k,Z)$ as a linear function of $G_{yz}(k,0)$, $I_{yz}(k,0)$, and $v_y(k,Z)$. Using these results, the Laplace transform of the first equation (4.6) and (3.6), we get $v_y(k,Z)$ as a linear function of $v_y(k,0)$, $G_{yz}(k,0)$, and $I_{yz}(k,0)$. With this value of $v_y(k,Z)$ we are then able to obtain $G_{yz}(k,Z)$ and $I_{yz}(k,Z)$.

We give the results which are of interest to us [we use again (2.8) and (2.19)–(2.21)]:

$$\langle v_y(0,0)v_y(k,Z)\rangle = \langle v_y^2\rangle\frac{D(Z)}{ZD(Z) + EN(Z)}, \tag{4.7}$$

$$\begin{aligned} \langle Q_{yz}(0,0)Q_{yz}(k,Z)\rangle &= \langle Q_{xy}(0,0)Q_{xy}(k,Z)\rangle + \langle Q_{yz}^2\rangle ER_{13}\Gamma_3 \\ &\quad \times \frac{A_1Z^2 + A_2Z + A_3}{D(Z)[ZD(Z) + EN(Z)]}, \end{aligned} \tag{4.8}$$

where $D(Z)$ is defined by (4.4) (its roots are Z_1 and Z_2), and

$$\begin{aligned} &E = \frac{k^2\alpha_{11}}{\rho}, \quad R_{12} = \frac{\alpha_{12}^2}{\alpha_{11}\alpha_{22}}, \quad R_{13} = \frac{\alpha_{13}^2}{\alpha_{11}\alpha_{33}}, \\ &N(Z) = [1 - R_{12} - R_{13} - R_{23} + 2(R_{12}R_{13}R_{23})^{1/2}]Z^2 \\ &\qquad + [\Gamma_2(1 - R_{13}) + \Gamma_3(1 - R_{12})]Z + \Gamma_2\Gamma_3, \\ &A_1 = 2\left(\frac{R_{12}R_{23}}{R_{13}}\right)^{1/2} - \frac{R_{12}R_{23}}{R_{13}} - 1, \\ &A_2 = 2\Gamma_2\left[\left(\frac{R_{12}R_{23}}{R_{13}}\right)^{1/2} - 1\right], \\ &A_3 = -\Gamma_2^2. \end{aligned} \tag{4.9}$$

If we call X_1, X_2, and X_3 the roots of the third-degree polynomial, $ZD(Z) + EN(Z)$, we can rewrite (4.8) as

$$\begin{aligned} \langle Q_{yz}(0,0)Q_{yz}(k,Z)\rangle &= \langle Q_{xy}(0,0)Q_{xy}(k,Z)\rangle + \langle Q_{yz}^2\rangle ER_{13}\Gamma_3 \\ &\quad \times\left[\frac{B_1}{Z - Z_1} + \frac{B_2}{Z - Z_2} + \frac{B_3}{Z - X_1}\right. \\ &\quad \left. + \frac{B_4}{Z - X_2} + \frac{B_5}{Z - X_3}\right], \end{aligned} \tag{4.10}$$

where the B_i are easily obtained from the A_i, the Z_i, and the X_i.

Now, using (2.15), (4.5), and (4.10), we are able to obtain the V-H spectrum in the general case.

We must consider two cases depending on the sign of the discriminant Δ_1 of $ZD(Z) + EN(Z)$:

1. $\Delta_1 < 0$. The three roots X_1, X_2, and X_3 are real. From (4.7) the transverse velocity v_y is diffusive, and

$$\begin{aligned} I_{\mathrm{VH}}(\omega_i + \omega) &\simeq \mathrm{Re}\langle Q_{xy}(0,0)Q_{xy}(k,\omega)\rangle - \cos^2(\theta/2)\langle Q_{xy}^2\rangle \\ &\quad \times ER_{13}\Gamma_3\left(\frac{B_1Z_1}{\omega^2 + Z_1^2} + \frac{B_2Z_2}{\omega^2 + Z_2^2} + \frac{B_3X_1}{\omega^2 + X_1^2}\right. \\ &\quad \left. + \frac{B_4X_2}{\omega^2 + X_2^2} + \frac{B_5X_3}{\omega^2 + X_3^2}\right). \end{aligned} \tag{4.11}$$

2. $\Delta_1 > 0$. The root X_1 is real, the other roots X_2 and X_3 are complex conjugate: $X_2 = x + iy$, $X_3 = x - iy$. From (4.7), the transverse velocity is now propagative, and

$$\begin{aligned} I_{\mathrm{VH}}(\omega_i + \omega) &\simeq \mathrm{Re}\langle Q_{xy}(0,0)Q_{xy}(k,\omega)\rangle \\ &\quad - \cos^2(\theta/2)\langle Q_{xy}^2\rangle ER_{13}\Gamma_3 \\ &\quad \times\left(\frac{C_1}{\omega^2 + Z_1^2} + \frac{C_2}{\omega^2 + Z_2^2} + \frac{C_3}{\omega^2 + X_1^2}\right. \\ &\quad \left. + \frac{C_4}{(\omega - y)^2 + x^2} + \frac{C_5}{(\omega + y)^2 + x^2}\right). \end{aligned} \tag{4.12}$$

To compute the C_i we must take into account that now the B_i are complex.

B. Discussion

As in the one-tensor approximation, the V-H spectrum is the summation of two terms. The first one is $\vec{k}$ independent and the second is $\vec{k}$ dependent. But now each of these terms is more complex. Furthermore, the spectrum depends on five parameters: Γ_1, Γ_2, R_{12}, R_{13}, and R_{23}. For the same reasons as those given in the previous section for R, R_{12}, R_{13}, and R_{23} are always between 0 and 1.

We shall now try to understand the physical meaning of these parameters.

Let us begin with R_{23}. If $R_{23}=1$, it is easy to show from (4.1) that

$$\begin{aligned} I_{xy}(k,t) &= I_{xy}(k,0)e^{-\Gamma_2\Gamma_3 t}, \\ G_{xy}(k,t) &= I_{xy}(k,0)\Gamma_3/\Gamma_2(\alpha_{33}/\alpha_{22})^{1/2}e^{-\Gamma_2\Gamma_3 t}, \end{aligned} \tag{4.13}$$

with the condition that $\Gamma_2+\Gamma_3=1$.

The components $I_{xy}(k,t)$ and $G_{xy}(k,t)$ are proportional. If $R_{23}=0$, we can easily show from (4.1) that

$$\begin{aligned} I_{xy}(k,t) &= I_{xy}(k,0)e^{-\Gamma_3 t}, \\ G_{xy}(k,t) &= G_{xy}(k,0)e^{-\Gamma_2 t}. \end{aligned} \tag{4.14}$$

Now $I_{xy}(k,t)$ and $G_{xy}(k,t)$ are two independent functions. Thus, R_{23} plays the role of a coupling parameter between $\overleftrightarrow{I}_s$ and $\overleftrightarrow{G}_s$. When $R_{23}=1$, these two tensors are proportional; when $R_{23}=0$, they are not correlated.

Furthermore, from (4.14) we see that $1/\Gamma_2$ and $1/\Gamma_3$ are respectively the relaxation times of $\overleftrightarrow{G}_s$ and $\overleftrightarrow{I}_s$ if there is no coupling between them.

Using the same arguments as in the previous section for R, we can see that R_{12} and R_{13} are respectively the coupling parameter between the transverse velocity and the tensors $\overleftrightarrow{G}_s$ and $\overleftrightarrow{I}_s$. Actually, the parameter R defined by (3.9) is nothing else but the parameter R_{13}. As in the one-tensor approximation, the $\vec{k}$ dependent term of the V-H spectrum is proportional to the coupling parameter R_{13}.

We shall see now that the formulas (4.5), (4.11), and (4.12) could explain the experimental spectrum which cannot be explained with the one-tensor approximation. If $\Gamma_3 \ll \Gamma_2$, we have from (4.4) and (4.5)

$$\operatorname{Re}\langle Q_{xy}(0,0)Q_{xy}(k,\omega)\rangle = \langle Q_{xy}^2\rangle\Gamma_3\left[\frac{R_{23}}{1-R_{23}}\left(\frac{1}{\omega^2+[\Gamma_2/(1-R_{23})]^2}\right)+\frac{1}{\omega^2+\Gamma_3^2}\right]. \tag{4.15}$$

The second one of these Lorentzians is high and narrow and corresponds to the decay of the local orientational order, as in the one-tensor approximation. But the first Lorentzian is very broad and very low and could give the broad background observed experimentally.[9,10]

Formula (4.12) could gives the spectra observed in the supercooled liquids,[12-15] since there is a central peak and two shifted propagative ones, and the area under the central peak is larger than the area under the two shifted ones, which is not the case with the one-tensor approximation where the two areas are equal.[31]

From our point of view, the best way to compare our results with the experimental ones would be first to compare (4.5) from an experimental spectrum with $\theta \simeq 180°$ (since in such a case only this term appears in the V-H spectrum) and to fit the parameters Γ_2, Γ_3, and R_{23}. Then it would be easier, knowing three parameters, to solve numerically (4.8) and fit the last two parameters on an experimental spectrum with $\theta \neq 180°$.

There is a last point to understand: why is the one-tensor approximation a good one in the normal liquid for high temperatures, but becomes a bad one for low temperatures in the supercooled liquid? It is a very difficult problem since it deals with the evolution of the local order as a function of the temperature. Nevertheless, we can imagine two different explanations:

(1) The molecule is elongated. Then, in the normal liquid at high temperature, the orientational local order is much more important than the order of the center of gravity, and the one-tensor approximation is valid. But in the supercooled liquid, the local order recalls much more a real solid, and we must now take into account the order of the center of gravity.

(2) The molecule is not elongated. In the normal fluid the two local orders are of the same importance, but since the molecule is rather spherical the local order is cubic. Then, the tensor $\overleftrightarrow{G}$ is null and the one-tensor approximation is also valid. But if at low temperature the symmetry of the local order is no longer cubic, it should be necessary to take into account the two tensors.

V. COMPARISON WITH OTHER THEORIES

A great number of theories deal with V-H light scattering. We shall try in this last section to give a short summary of those which are from our point of view the most characteristic. We shall relate them to our own work, bringing up the main differences and pointing out the new results we have derived.

The theories dealing with V-H light scattering can be roughly divided into two subsets: the first one uses the technique usually called the Mori formalism[33-35]; the second one uses the older technique of nonequilibrium thermodynamics.

A. The Mori technique

The utilization of the Mori technique in this kind of problem is very well summarized in the work of Andersen and Pecora.[2] The main difficulty with such a technique is to guess the good set of variables. One must have a set of "slow" variables with relaxation times larger than the molecular one, and this set must be a "complete" set which includes all the variables coupling with the variable which is of interest (the off-diagonal part of the polarizability tensor for the V-H light scattering). When one has chosen the set of variables and assumed that this set is the good one, the Mori technique is a powerful tool to obtain the dynamics of these variables.

The more elaborate papers dealing with the V-H light scattering using the Mori's formalism are those of Andersen and Pecora,[2] Keyes and Kivelson,[3] and Gershon and Oppenheim.[4] From symmetry considerations, all these authors agree that the transverse velocity is a good variable.

As a second variable, Andersen and Pecora choose a second-rank tensor with the adequate symmetry, without further precision. Keyes and Kivelson choose a tensor characterizing the molecular orientation density, and Gershon and Oppenheim choose the polarizability tensor directly.

These authors all make two fundamental assumptions: these variables are slow, and they form a complete set.

The transverse velocity is actually a slow variable since it is a real hydrodynamic variable. But concerning the second variable, the preceding authors are not able to prove their assumption. We are able to claim that this second variable is really a slow variable since it is proportional to the tensor $\overleftrightarrow{I}_s$ characterizing the local orientational order, and we know (see discussion in I) that the relaxation time of the local order is much larger than the molecular relaxation time.

Concerning the second assumption, we can claim that it is generally wrong since we saw that $\overleftrightarrow{G}_s$, which is also a slow variable, couples with $\overleftrightarrow{I}_s$ and the transverse velocity. If we neglect the antisymmetric part of the stress tensor (see preceding discussion, Sec. II A), the complete set of variables is formed with the transverse velocity and the two tensors of the local order $\overleftrightarrow{I}_s$ and $\overleftrightarrow{G}_s$. Yet, we pointed out at the beginning of Sec. III the cases in which this second assumption is valid.

Andersen and Pecora[2] introduce also another variable, but they choose as their third variable the stress tensor. They obtain the same results as Volterra[19] and we shall discuss them later. Gershon and Oppenheim[4] claim that the relaxation time of the stress tensor is of the same order as the molecular one, and consequently that it is a wrong variable. But a further molecular dynamic calculation in dense argon[36] shows that its autocorrelation function has a very long positive tail. So it appears that the stress tensor can be regarded as a slow variable, and it is difficult to say with this argument if it is a wrong variable or not.

We also believe that the stress tensor is a wrong variable but for a different reason: the velocity and the stress tensor are not variables of the same order. If we are interested in the behavior of the velocity, the stress tensor plays the role of the random force and of the memory function in the generalized Langevin equation; so it is not consistent to have them both in a "complete" set of observables and to assume that the memory function of this set is a delta function. We shall come back to this point later.

B. Nonequilibrium thermodynamic method

The second category of theories dealing with the depolarized light scattering employs nonequilibrium thermodynamics. One assumes that locally the liquid is at thermodynamic equilibrium, so that it is possible to define locally the usual thermodynamic quantities, free energy, entropy, etc. Then, performing a limited expansion up to the second order of the free energy, it is possible to get the equations of motions of the fluid. Our theory (I) enters this last category.

Leontovich[16] was the first to use this technique for depolarized light scattering. He introduced a tensor $\overleftrightarrow{\zeta}$ which characterizes the local orientational order and which is equivalent to our tensor $\overleftrightarrow{I}_s$. He assumes also that this tensor is proportional to the polarizability tensor. But, to obtain the evolution equation of $\overleftrightarrow{\zeta}$ he implicitly assumes, as was shown by Volterra,[19] that $\overleftrightarrow{\zeta}$ is proportional to the stress tensor. Thus, instead of getting the spectra (3.12), he gets analogous spectra but with the coupling factor $R=1$. We can easily find this previous result using (3.1) and (3.2). If $R=1$, the determinant $\alpha_{11}\alpha_{22}-\alpha_{12}^2=0$, which implies that the stress tensor $\overleftrightarrow{\sigma}_s$ must be proportional to the tensor $\overleftrightarrow{I}_s$. This was Leontovich's hypothesis.

Volterra[19] was the first to stress that two processes are involved in depolarized light scattering. The first one is (as for Leontovich) the "reorientation of the molecules" and the second is the "rearrangement of the molecules into new equilibrium positions." To characterize the first process, he introduces the same tensor $\overleftrightarrow{\zeta}$ as Leontovich, but to characterize the second process, he assumes that the liquid is solid-like, and he introduces a deformation tensor $\overleftrightarrow{S}$ as in the elastic theory of solids. But in a liquid this tensor $\overleftrightarrow{S}$ cannot be defined rigorously and has no real physical meaning. The only way to define such a tensor is to write $\dot{\overleftrightarrow{S}} = \vec{\nabla}\vec{v}$, but then $\overleftrightarrow{S}$ is defined with an arbitrary constant. Furthermore, in our opinion the Volterra theory fails on two points. First, there is confusion between the tensor $\overleftrightarrow{S}$ and the real tensor characterizing the rearrangement of the center of gravity of the molecules which is our tensor $\overleftrightarrow{G}_s$. Particularly, this confusion leads to an incorrect expression for the free energy. We shall come back to this point. Second, the equation of motion of $\overleftrightarrow{\zeta}$, as stressed by Volterra himself, is derived from an arbitrary assumption of minimizing the free energy, and does not give a direct coupling between $\overleftrightarrow{\zeta}$ and the transverse velocity.

We get Volterra's fundamental equations $A(1, 2)$ from our equations (4.6) if we assume that the stress tensor $\overleftrightarrow{\sigma}_s$ is proportional to $\overleftrightarrow{G}_s$ and that $\alpha_{13} = 0$.

Nevertheless, the Volterra theory gives an accurate qualitative interpretation of the two processes involved in light scattering. He gives the same expression as we do for $\mathrm{Re}\langle Q_{xy}(0, 0)Q_{xy}(k, \omega)\rangle$ (4.5) and stresses the fact that this expression gives the broad background observed by experimentalists.[9,10]

Rytov, using the paper of Romanov, Solov'ev, and Filatova[20] gave a new version of his previous theory[18] in 1970.[21,22] His new theory is essentially equivalent to the Volterra theory, but instead of two, he assumes there is in the liquid a number n of relaxation processes without further physical explanations. Furthermore, he assumes that the polarizability tensor is not only proportional to the local orientational order but is also proportional to the other relaxation processes.

We disagree with him on these two points. The discussion (Sec. II B) shows that in a molecular fluid the tensor of polarizability is only proportional to $\overleftrightarrow{I}_s$ and $\overleftrightarrow{G}_s$ and that under normal conditions, for a fluid of nonspherical molecules, it is essentially proportional to $\overleftrightarrow{I}_s$. Furthermore, in I we stressed that in a simple liquid there are only two relaxation processes ($\overleftrightarrow{I}$ and $\overleftrightarrow{G}$), if we do not take into account the internal modes of the molecule.

As for Volterra's theory, our equations (4.6) yield the Rytov fundamental equations (9) when there is a single relaxation process (namely $\overleftrightarrow{I}_s$), if we assume that the tensor $\overleftrightarrow{G}_s$ is proportional to the deformation tensor $\overleftrightarrow{S}$ and if we take $\alpha_{13} = 0$.

We return now to an important point on which we disagree with the previously mentioned theories.

The three preceding authors, having in mind that for high frequencies a liquid behaves like a solid, introduce a deformation tensor $\overleftrightarrow{S}$. Assuming then that the deformation is small, they express the density of free energy F as a quadratic function of the tensor $\overleftrightarrow{S}$ and of the other tensors characterizing the internal relaxation processes, which are essentially the local orientational order characterized by $\overleftrightarrow{I}_s$. So they write, in our notation,

$$F = F_0 + \tfrac{1}{2} a \overleftrightarrow{S}^2 + \tfrac{1}{2} b \overleftrightarrow{I}_s^2 + c \overleftrightarrow{I}_s : \overleftrightarrow{S}, \tag{5.1}$$

$$\dot{\overleftrightarrow{S}} = \vec{\nabla} \vec{v}. \tag{5.2}$$

These two equations are the basic ones for their theories.

We think there is a confusion between the tensor $\overleftrightarrow{S}$ and the tensor characterizing the local order of the centers of gravity, which is our tensor $\overleftrightarrow{G}_s$. The density of free energy F is the free energy of the molecules contained in the little box of side L_1, these molecules being organized as in a loose solid. A deformation of this loose solid is characterized by a variation of the tensor $\overleftrightarrow{I}_s$ and of the tensor $\overleftrightarrow{G}_s$. The time derivative, $\vec{\nabla}\vec{v}$, of the tensor $\overleftrightarrow{S}$ is an *external stress* with regard to this loose solid, and this external stress induces an *internal strain* which is characterized by a variation of the tensors $\overleftrightarrow{G}_s$ and $\overleftrightarrow{I}_s$. Thus the formula (5.1) is wrong and must be replaced by

$$F = F_0 + \tfrac{1}{2} a \overleftrightarrow{G}_s{}^2 + \tfrac{1}{2} b \overleftrightarrow{I}_s{}^2 + c \overleftrightarrow{I}_s : \overleftrightarrow{G}_s \tag{5.3}$$

which is the formula (5.7) of I.

In other words, we find the conclusions of our discussion about the third variable of the Andersen and Pecora theory. Here, there is confusion between strain and stress. In the Andersen and Pecora theory there is a mixing between the variables (the transverse velocity and the orientational tensor $\overleftrightarrow{I}_s$) and the force acting on them (the stress tensor).

Finally, a paper dealing with light scattering and using nonequilibrium thermodynamics is one by de Gennes on the short-range order in the isotropic phase of nematics.[23] This author computes the spectrum of the light scattered by a shear flow and he finds the same expression as we do: $\mathrm{Re}\langle Q_{yz}(0, 0)Q_{yz}(k, \omega)\rangle$ in the one-tensor approximation. We emphasized in I that our theory is a generalization of de Gennes's theory when the two tensors $\overleftrightarrow{I}$ and $\overleftrightarrow{G}$ are necessary to describe the local order.

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[31] We give here an elegant demonstration of this point, thanks to the Bordeaux group on light scattering. First, from (2.15) we can see easily that the area under the spectrum is proportional to $\langle Q_{xy}^2\rangle + \langle Q_{yz}^2\rangle$ (we choose $\theta = 90°$). Furthermore, since the liquid is isotropic, $\langle Q_{xy}^2\rangle = \langle Q_{yz}^2\rangle$. In the one-tensor approximation, in the propagative case ($\Delta < 0$), the central peak is given by $\langle\langle Q_{xy}(0,0)Q_{xy}(k,\omega)\rangle\rangle$ and the two shifted peaks by $\langle\langle Q_{yz}(0,0)Q_{yz}(k,\omega)\rangle\rangle$ [each shifted peak corresponds to a root of the second-degree polynomial $P(Z)$], and, since $\langle Q_{xy}^2\rangle = \langle Q_{yz}^2\rangle$, the area under the central peak must be equal to the area under the two shifted ones. In general propagative case ($\Delta_1 > 0$) the central peak is given by $\langle\langle Q_{xy}(0,0)Q_{xy}(k,\omega)\rangle\rangle$ but also by a part of $\langle\langle Q_{yz}(0,0)Q_{yz}(k,\omega)\rangle\rangle$ coming from the real root x_1 of the third degree polynomial $ZD(Z)+EN(Z)$, the two other roots x_2 and x_3, giving the shifted peaks. So in the general propagative case, the area under the central peak is larger than the area under the two shifted ones.

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