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Light scattering by transverse waves in supercooled liquids and application to metatoluidine

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Abstract. We discuss the hydrodynamic equations which describe the shear dynamics of a liquid composed of anisotropic molecules, both in its normal and its supercooled phases. We use these equations to analyze 90° depolarized light scattering experiments performed in the supercooled phase of a glass forming liquid, metatoluidine, and show that the information extracted from this analysis is consistent with independent shear viscosity measurements performed on that liquid in the same temperature range.

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1 Introduction

The interpretation of the low-frequency part of the light scattering spectra of liquids is a very old problem. As early as 1910, it was proposed that the thermal density fluctuations of the liquid were the source of the polarized light scattering spectrum. Indeed, when the hydrodynamic equations of the fluid are solved in q-space, one finds that three out of its five roots correspond to longitudinal excitations, which can couple to the density fluctuations. Two of them are the propagating longitudinal phonons with wave vector $\mathbf{q}$ that give rise to the well-known Brillouin peaks seen as narrow lines at frequencies of the order of 10 GHz for visible light and not too small scattering angles. The third root corresponds to temperature fluctuations which are damped by heat conduction. The heat diffusion process gives rise to a Lorentzian spectrum centered at $\omega = 0$, with linewidth of the order of 0.1 GHz when observed in the same conditions as above. This is called the Rayleigh peak. Mountain [1] was the first to notice that those equations did not take into account the phenomenon of viscoelasticity first introduced by Maxwell, in the case of the shear viscosity, one hundred years earlier [2]. When such a mechanism is introduced on top of a relaxationless bulk viscosity, the relaxation process associated with the longitudinal viscoelasticity shows up as an additional contribution which increases the width of the Brillouin peaks. It also gives rise to an additional central peak, the width of which does not depend on the wavevector but may vary strongly with temperature. The effect is mostly visible when this width is smaller than but of the order of the Brillouin frequency. In this rather frequent case, the "Mountain" mode increases the magnitude of the scattered intensity between the Rayleigh and the Brillouin peaks, and can completely mask the Rayleigh contribution.

Actually, the hydrodynamic equations have two more solutions, not yet mentioned because they do not couple to the density fluctuations: these are the transverse modes, the behaviour of which, in viscoelastic conditions, is the subject of the present paper. The situation may seem simple for atomic liquids or molecular liquids formed of spherical top molecules: at low viscosity, a shear deformation, which involves the shear viscosity coefficient, η_s, does not propagate, while the molecular rotations which could be associated with this deformation have no effect on the polarizability tensors of the corresponding molecules which are proportional to the unit tensor. A naive analysis of this situation leads to the conclusion that the transverse solutions of the hydrodynamic equations are diffusive modes, characterized by a Lorentzian spectrum centered at $\omega = 0$, with a linewidth proportional to η_s but that such modes cannot couple to light; indeed, in such situations, they have never been detected by light scattering techniques; yet, their coupling to light needs to be discussed more carefully and we shall briefly come back to this point at the end of the present section.

The situation is different and much more intricate in fluids formed of anisotropic molecules, because this anisotropy has to be taken into account in two different ways. One aspect is the opening of a new light scattering channel: the rotation of an anisotropic molecule induces

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a fluctuation of the molecular polarizability tensor in the laboratory axes, and this channel is, in practice, the sole origin of the depolarized light scattering spectrum in this frequency range. The second aspect is the orientational dynamics of the molecules, which has to be included in the equations of motion of the fluid. This introduces one additional equation to the set of hydrodynamic equations and the coupling between this orientational motion and the hydrodynamic modes has to be properly taken into account.

In the backscattering geometry, the rotational dynamics and the hydrodynamic modes decouple (see Sect. 2): the rotational dynamics appears as an intense central mode with a linewidth of the order of 100 GHz for low viscosity liquids. The spectrum related to the Rayleigh mode is much narrower and falls below the resolving power of the instrumental technique used here. This explains why we shall neglect the thermal diffusion equation which leads to such a mode in the rest of the present paper, considering the whole process as adiabatic: we shall focus here on writing down the equations involving this rotational dynamics, on the influence of the coupling between the shear and the rotational motions on the corresponding spectra, and on the comparison between the present approach and experiments. Before doing that, let us review briefly the development of the subject over the past thirty years.

The first experiments [3,4] performed on liquids with typical shear viscosities of the order of 1 cp in a non-backscattering geometry revealed a depolarized spectrum with a minimum at $\omega = 0$, the so-called Rytov dip [5], located between two symmetric maxima in the vicinity of 1–2 GHz. At first, it was thought that this spectrum was the superposition of the rotational spectrum described above and of transverse propagative modes originating from the Maxwell viscoelastic effect. Shortly after, Keyes and Kivelson [6] and Andersen and Pecora [7] pointed out the necessity of taking into account the orientational dynamics of the molecules and their coupling with the shear motion. In both cases, as well as in all the following publications taking orientational dynamics into account, the solution was based upon a semi-phenomenological approach to the problem: writing down equations describing this rotation translation coupling, they showed that the interpretation given in [3,4] was incorrect: through a negative interference effect, the narrow diffuse shear mode, with a linewidth proportional to the static shear viscosity, was subtracted from the broad reorientational spectrum: viscoelasticity did not play any role in the explanation of these low viscosity experiments.

New developments took place when the same theory was applied to supercooled liquids in which the viscosity was typically larger by two or more orders of magnitude than in the preceding case. The Andersen Pecora theory predicted that a first increase of the viscosity would result in the disappearance of the Rytov dip. But, for still higher viscosities, provided that some cancellation effects would take place, damped propagating shear waves could appear. Indeed, such a phenomena was reported first by Bezot *et al.* [8], then by Enright *et al.* [9]: the Rytov dip disappeared for shear viscosities η_s of the order of 10 cp while transverse modes appeared for η_s one order of magnitude larger. Yet, in the latter case, the shape of the spectra could not be fitted with these theories using the known values of η_s. Several explanations were then proposed (see, *e.g.* [10–14]), each one introducing some additional internal mode, *i.e.* adding at least one more equation containing a linear coupling between this new variable, or its time derivative, and the variables already introduced in [6] or [7]. These models will be briefly reviewed in Section 5 but we must stress here that their fundamental and common characteristic was that, as in the original models [6,7], they assumed, at least formally, that the rotation-translation coupling was instrumental in producing the propagation of transverse modes at low temperature, ignoring the fact that, even in a simple fluid, transverse modes do propagate for high enough frequencies.

Ailawadi *et al.* [14] and, later, Wang [15] suggested combining viscoelastic effects and orientational dynamics in the description of the propagation of transverse modes in viscous liquids. In particular, Wang proposed to write down hydrodynamic equations, complemented by an equation of motion for the orientational dynamics of the molecules, in which retardation (memory) effects would systematically be taken into account. A natural consequence of the use of such equations was the appearance of propagating transverse waves at temperatures low enough for the relaxation times to be longer that the inverse of the frequency of such a mode. Wang was thus able to give a semiquantitative description of the low frequency depolarized light scattering spectra detected, *e.g.* in salol [16] or in orthoterphenyl [17]. Unfortunately, in [15] as well as in later versions of that theory (see, *e.g.* [18,19]), the way retardation effects were introduced was inconsistent, in some places, with his phenomenological approach (see Sect. 5.3).

The purpose of the present paper is to propose a coherent phenomenological way of writing down coupled equations which take into account the shear and rotational motions, include retardation effects in a natural way and to show that these equations correctly describe the different physical situations met in these molecular liquids. After analyzing the formal basis of these equations, we shall show that their low and high frequency limits represent, without further assumptions, either diffusive shear modes or propagative transverse modes coupled to orientational motions of the molecules. Furthermore, the retardation effects will be introduced in such a way that both the rotational dynamics of the molecules and the viscoelasticity related to the motion of the centers of mass may be properly identified and described. This last aspect may be tested because our formulation allows us to compare values of η_s determined from viscosity measurements with values obtained from the analysis of the Brillouin spectra of propagative transverse acoustic modes and we have proceeded to such a test. The different aspects of our work are presented in the following way.

Section 2 is devoted to writing down the equations of motion of the dynamical variables within a phenomenological approach. We shall study their solutions in the case of transverse motions and shall show from general considerations that they have the correct limits in the high and low temperature cases. We shall also show the relationship between some of the parameters extracted from fits of the low-temperature spectra and the static shear viscosity.

In Sections 3 and 4, we shall apply the preceding formalism to the study of a fragile glass forming liquid, metatoluidine (CH_3-C_6H_4-NH_2), an organic compound with melting temperature $T_{\mathrm{m}} = 243.5$ K and a calorimetric glass transition temperature $T_{\mathrm{g}} = 187$ K [20]. More information on this liquid and on the depolarized light scattering experiments will be given in Section 3. The 0.75 GHz–8 GHz part of these spectra have been fitted to the expressions obtained in Section 2, and a short report on this analysis has already appeared in [21]. Section 4 will give a detailed discussion of those results: we shall report the values of the parameters so obtained in a temperature range from 248 K, a temperature above T_{m}, to $T = 208$ K. We shall also compare the value of η_{s} deduced from those fits to the static viscosity, independently measured, and show that good agreement is obtained over a large range of viscosity values.

Finally, in Section 5, we shall briefly review the previous phenomenological approaches, some of which have been already mentioned in this introduction. We shall show that, once their structure has been transformed into a two variable approach including retardation effects similar to the one used in the present paper, it appears that the corresponding equations always imply some incorrect relationship with a physical aspect of the problem. A brief conclusion will summarize our results and propose further developments.

Before closing this introduction, let us note that mechanisms not requiring the existence of anisotropic molecules for the detection of the diffusive and/or of the propagative shear modes, have also been proposed. In particular, one of them [22], based on the Dipole-Induced Dipole mechanism should be active even in a monoatomic fluid. Another one [14b] implies only the existence of molecular entities and could be operative with spherical top molecules. It turns out that, in such liquids, the back-scattering depolarized spectra have a very weak intensity. For instance, at room temperature, in the GHz region, the depolarized intensity of CCl_4 (in which the two effects proposed in [14b] and [22] should permit the detection of the Rytov dip) is two orders of magnitude smaller than in a typical glass forming liquid, salol (see *e.g.* Fig. 4 of [23]). Since in these approaches as well as in all the other ones, the intensity of the Rytov dip or of the propagative modes have the same origin as the depolarized back scattering spectrum, we can neglect the two mechanisms mentioned at the beginning of this paragraph and assume, for the rest of this paper, that the sole origin of light scattering in molecular liquids formed of anisotropic molecules is the molecular reorientational motion.

2 The basic equations and their discussion

This section is devoted to (i) the setting up of a theoretical framework appropriate to the study of the low frequency depolarized light scattering spectra of supercooled molecular liquids and (ii) the discussion of the internal consistency of the formulas we obtain. This requires a careful analysis of the origin of each term we introduce in these equations, of their consequence for the possible expression of the corresponding retarded interactions and, finally, of the low and high frequency limits of our results. We shall take as a starting point the non-viscoelastic equations of Quentrec [11] who seems to be the first author who formulated the problem in terms amenable to the generalizations we look for. Section 2.2 will describe how these equations should be modified when retarded interactions have to be taken into account. The expression for the corresponding depolarized spectra will be derived in Section 2.3. The contribution of the rotational dynamics to these spectra is studied in Section 2.4. Finally, we shall examine in Section 2.5 the low and high frequency limits of the contribution of the shear viscosity to the spectrum and show that both agree, without further assumption, with the usual expression for those limits.

2.1 Hydrodynamic equations

Let us consider the set of hydrodynamic equations corresponding to our problem. The first two equations, describing mass conservation and momentum conservation, are written as usual:

$$\dot{\rho}(\mathbf{r},t) + \mathrm{div}\ \mathbf{J}(\mathbf{r},t) = 0, \tag{2.1}$$

$$\dot{J}_i(\mathbf{r},t) + \mathrm{div}_j \mathit{\Pi}_{ij}(\mathbf{r},t) = 0, \tag{2.2}$$

where $\rho(\mathbf{r},t)$ is the mass density and $\mathbf{J}(\mathbf{r},t)$ is the mass current (or momentum) density, $\mathit{\Pi}_{ij}(\mathbf{r},t)$ is the momentum current density tensor, i, j being Cartesian coordinates.

Difficulties arise when one wants to make precise the expression of $\mathit{\Pi}_{ij}(\mathbf{r},t)$ in the case of a fluid composed of anisotropic molecules and to write down the equations of motion describing the orientational dynamics of the molecules when retardation effects are taken into account. Let us discuss these different points in turn.

Both Keyes and Kivelson [6] and Andersen and Pecora [7] used, for the additional variable which has to enter into the stress tensor associated with $\mathit{\Pi}_{ij}$ ($\sigma_{ij} = -\mathit{\Pi}_{ij}$) a symmetrical 2nd rank tensor which was assumed to describe a polarizability density (or, more accurately, the traceless part of the fluctuation of such a quantity). In order to write down the corresponding equations of motion, they made use of the Zwanzig-Mori formalism, introducing the symmetry properties of the correlation functions of this variable and of the momentum density rather than writing the explicit form of $\sigma_{ij}(\mathbf{r},t)$. Following some preliminary attempts by Ailawadi *et al.* [14], Quentrec [11] made use of this second route and simultaneously proposed a definite form for the polarizability density tensor or for any other tensor linearly related to it. Choosing for the tensorial quantity a local mean value of the molecular tensor of inertia[1], he showed that one should write:

$$\bar{\bar{\sigma}} = (-\delta P + \eta_{\mathrm{b}}\ \mathrm{div}\ \mathbf{v})\bar{\bar{I}} + \eta_{\mathrm{s}}\bar{\bar{\tau}} - \mu\dot{\bar{\bar{Q}}}, \tag{2.3}$$

where δP is the fluctuation of the hydrostatic pressure and $\bar{\bar{I}}$ the unit tensor. η_{b} and η_{s} are the bulk and shear viscosities respectively, Q_{ij} the local fluctuation of the traceless part of the tensor of inertia and μ a coupling constant. τ_{ij} is the traceless part of the strain rate tensor given by:

$$\tau_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\mathrm{div}\ \mathbf{v}\delta_{ij}. \tag{2.4}$$

Finally, on a phenomenological basis, Quentrec wrote the following equation of motion for $\bar{\bar{Q}}$:

$$-\bar{\bar{Q}} - \Gamma^{-1}\dot{\bar{\bar{Q}}} + \Lambda\mu\bar{\bar{\tau}} = 0, \tag{2.5a}$$

where Γ has the dimension of a frequency (or relaxation rate) which characterizes the linewidth of the spectrum associated with the pure orientational dynamics of the molecule and where Λ is a positive constant with the dimension of mass divided by velocity.

2.2 Discussion of the Quentrec hydrodynamic equations and introduction of memory functions

Equations (2.3) to (2.5a) clearly have the form expected for hydrodynamic equations. Indeed, in equation (2.3), η_{b} is the bulk viscosity, which complement the bulk modulus, K_{b}, while η_{s} replaces, for the liquid state, the shear modulus, G_{s}, of the theory of elasticity, the displacement field $\mathbf{u}$ being simultaneously replaced by its time derivative, the velocity field $\mathbf{v}$. Similarly, the last term of equation (2.3) represents the effect of $\bar{\bar{Q}}$, the additional variable of the problem, on the stress tensor $\bar{\bar{\sigma}}$: in the same way as the time derivative of a shear strain contributes to $\bar{\bar{\sigma}}$ through the shear viscosity η_{s}, the change in time of $\bar{\bar{Q}}$ produces an additional contribution to the stress tensor with a coupling constant, μ. This constant μ is the signature of a rotation-translation coupling in the liquid and this coupling is at the origin of both the flow birefringence effect (a consequence of Eq. (2.5) and of Eq. (2.14) mentioned below) and of the $\dot{\bar{\bar{Q}}}$ contribution to equation (2.3). The relative signs which appear in front of μ in the two equations (2.3, 2.5a) can be shown to be a direct consequence of this physical model.

Equation (2.5a) needs some further comments. It is the result of a simplification valid both in the theory of elasticity and in the equations of hydrodynamics when one considers the coupling of orientational motions with acoustic modes, *i.e.* when one is interested only in the low frequency regime. Actually, the general equation of motion of $\bar{\bar{Q}}$ should read:

$$\ddot{\bar{\bar{Q}}} = -\omega_0^2\bar{\bar{Q}} - \Gamma'\dot{\bar{\bar{Q}}} + \Lambda'\mu\bar{\bar{\tau}}. \tag{2.5b}$$

Equation (2.5b) makes it clear that we are looking here at an orientational motion characterized by $\bar{\bar{Q}}$ and that three forces act on this variable. The first one is an ordinary restoring force, which would lead to undamped librations of the molecules if one would neglect the two last terms of this equation. The libration frequencies are in the THz region. The two remaining terms correspond to the two origins of the damping: the $\dot{\bar{\bar{Q}}}$ term is the ordinary damping of the librations while the last term is the result of the rotation-translation coupling, the corresponding internal friction in the fluid creating a second damping mechanism for the orientation fluctuations.

When one performs a time Fourier transform of equation (2.5b), its l.h.s. yields a term in ω^2. Since we are interested only in frequencies below the THz range, this term is negligible with respect to the term in ω_0^2 which appears in its r.h.s. and with respect to the other terms of this r.h.s.. Equation (2.5a) is thus a simple rewriting of equation (2.5b) obtained by putting its l.h.s. to zero, and defining:

$$\Gamma^{-1} = \frac{\Gamma'}{\omega_0^2}; \quad \Lambda = \frac{\Lambda'}{\omega_0^2}, \tag{2.6a}$$

a harmless simplification in the present case.

The second step consists in generalizing equations (2.3) and (2.5b) in order to take into account retardation effects. For a consistent treatment, retardation must be included in all the friction terms appearing in those two equations: it is not sufficient to introduce these effects only through the Laplace transforms of the generalized viscosities η_{s} and η_{b}; retardation effects have also to be taken into account in the rotation-translation coupling term which appears in these two equations, and in the pure orientational damping term. Our phenomenological method for deriving these hydrodynamic equations precludes any attempt at a self-consistent description of these retarded interactions. Therefore, we shall make use of a phenomenological description of the memory functions, a method which has already been frequently used in such cases (see, for example, [24–27]); the validity of such a description can only be checked *a posteriori*, by looking at the consistency of the parameters so obtained. Introducing those retarded interactions, equations (2.3, 2.5b) become:

$$\bar{\bar{\sigma}} = (-\delta P + \eta_{\mathrm{b}} \otimes\ \mathrm{div}\ \mathbf{v})\bar{\bar{I}} + \eta_{\mathrm{s}} \otimes \bar{\bar{\tau}} - \mu \otimes \dot{\bar{\bar{Q}}}, \tag{2.7}$$

$$\ddot{\bar{\bar{Q}}} = -\omega_0^2\bar{\bar{Q}} - \Gamma' \otimes \dot{\bar{\bar{Q}}} + \Lambda'\mu \otimes \bar{\bar{\tau}}, \tag{2.8a}$$

where $\otimes$ means a convolution product. In the spirit of the Onsager theory, we consider that the same $\mu(t)$ acts in equations (2.7, 2.8a).

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[1] Making use of an averaging technique borrowed from the theory of electromagnetism where one defines a polarisation density from the individual dipole existing on each molecule.

From a formal point of view, we note that there are two differences between Wang's original work [15] and the present hydrodynamic equations. One is in the writing of the two first terms of the r.h.s. of equation (2.8a). Indeed, in the corresponding equation of [15], the memory function acts on the direct force (*i.e.* on a term proportional to $\bar{\bar{Q}}$) and not on the friction force (term proportional to $\dot{\bar{\bar{Q}}}$); we have indicated above why it is consistent with the present approach to use the expression adopted here. The second difference is in the necessary appearance of a nonzero l.h.s. in this equation, contrary to the case with no retardation (Eq. (2.5b)) for which we have argued that the $\ddot{\bar{\bar{Q}}}$ term could be neglected without difficulties. We shall come back to those two aspects in Section 2.4 and in Section 5.

2.3 Spectral shape of the depolarized light scattering spectrum

Equations (2.1, 2.2, 2.7, 2.8) can be easily solved using space-time Laplace techniques, briefly recalled in Appendix A.1, which consist in multiplying each equation by $i\mathrm{e}^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$ and integrating over the entire space and over $t > 0$.

Because of the vectorial character of $\mathbf{J}$, those equations have to be projected along three directions related to $\mathbf{q}$: we choose them to be $\mathbf{u}_{\|}$, which is the unit vector along $\mathbf{q}$, $\mathbf{u}_{\perp}$ and $\mathbf{u}'_{\perp}$, which are two orthogonal unit vectors, both perpendicular to $\mathbf{u}_{\|}$. We focus here on the Laplace transform of the thermal mean values $\langle Q_{\perp\perp'}(t)Q_{\perp\perp'}(0)\rangle$ and $\langle Q_{\perp\|}(t)Q_{\perp\|}(0)\rangle$.

Due to the particular definition of the Laplace transform used here (which differs from the form used in [28] by an opposite sign in front of ω):

$$f(\omega) \equiv LT\, f(t) = i\int_0^{\infty} f(t)\mathrm{e}^{-i\omega t}\mathrm{d}t, \tag{2.9}$$

one obtains[2] (see Appendix A.1):

$$\overline{Q^2_{\perp\perp'}(\omega)} \equiv LT\ \langle Q_{\perp\perp'}(t)Q_{\perp\perp'}(0)\rangle = \frac{1}{\omega}R(\omega)\langle\left|Q^0_{\perp\perp'}\right|^2\rangle \tag{2.10}$$

with:

$$R(\omega) = \frac{\omega\hat{\Gamma}(\omega)}{\omega_0^2 + \omega\,\hat{\Gamma}(\omega)}, \tag{2.11a}$$

$$\hat{\Gamma}(\omega) = \Gamma'(\omega) - \omega, \tag{2.11b}$$

$\langle\left|Q^0_{\perp\perp'}\right|^2\rangle$ being the thermal mean square value of the instantaneous fluctuations.
Similarly:

$$\overline{Q^2_{\perp\|}(\omega)} = \frac{1}{\omega}(R(\omega) + R_1(\omega))\langle|Q^0_{\perp\|}|^2\rangle \tag{2.12}$$

with:

$$R_1(\omega) = \frac{q^2\rho_{\mathrm{m}}^{-1}G(\omega)}{\omega^2 - q^2\rho_{\mathrm{m}}^{-1}\left[\omega\eta_{\mathrm{s}}(\omega) - G(\omega)(1-R(\omega))^{-1}\right]}, \tag{2.13a}$$

and:

$$G(\omega) = \Lambda'\,\omega_0^2\left(\frac{\mu(\omega)}{\hat{\Gamma}(\omega)}\right)^2 R^2(\omega). \tag{2.13b}$$

Let us consider a scattering geometry in which the scattering plane is the $[\mathbf{u}_{\|}, \mathbf{u}_{\perp'}]$ plane and the scattering angle is θ. In the introduction, we already mentioned that the only source of depolarized light scattering which is relevant at low frequency in molecular liquids is the traceless part, $\bar{\bar{\beta}}$, of the molecular polarizability tensor. We argue in Appendix A.2 that, in the frequency domain of interest here, it is consistent with our hydrodynamic approach to write:

$$\bar{\bar{\beta}} = b\bar{\bar{Q}}. \tag{2.14}$$

Within this approximation, in the usual VH geometry where the incident light is polarized along $\mathbf{u}_{\perp}$ and the scattered electric field is in the $[\mathbf{u}_{\|}, \mathbf{u}_{\perp'}]$ plane, the scattered intensity at frequency ω is proportional to:

$$I(\omega) \approx I^0 b^2 \mathrm{Im}\left(\sin^2\frac{\theta}{2}\,\overline{Q^2_{\perp\perp'}(\omega)} + \cos^2\frac{\theta}{2}\,\overline{Q^2_{\perp\|}(\omega)}\right), \tag{2.15}$$

where I^0 is the incoming light beam intensity. Taking into account that $\langle\left|Q^0_{\perp\perp'}\right|^2\rangle = \langle|Q^0_{\perp\|}|^2\rangle$, this yields:

$$I(\omega) \approx I^0\frac{b^2}{\omega}\mathrm{Im}(R(\omega) + \cos^2\theta/2\,R_1(\omega)), \tag{2.16}$$

where $R(\omega)$ does not depend on $\mathbf{q}$ and represents the uncoupled orientation fluctuation dynamics while $R_1(\omega)$ depends specifically on q.

2.4 The orientational part

The pure orientational spectrum is detected directly in the depolarized backscattering geometry ($\theta = \pi$) and is proportional to:

$$I(\omega) \approx \frac{1}{\omega}\mathrm{Im}\,R(\omega) = \mathrm{Im}\frac{\overline{Q^2_{\perp\perp'}(\omega)}}{\langle|Q^0_{\perp\perp'}|^2\rangle}\,\cdot \tag{2.17}$$

$R(\omega)$ is thus an observable quantity which can be determined experimentally and analyzed (see Sect. 3). In principle, equation (2.17) implies that the integral of its r.h.s. over ω is equal to π, independent of the value of ω_0 and of the exact form of $\Gamma'(\omega)$. Yet, the fulfilment of this relation

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[2] The $\mathbf{q}$-dependence of any quantity is written explicitly only when the algebra depends on the modulus of $\mathbf{q}$.

requires two conditions:

- First, as the spectrum related to equations (2.11) extends up to frequency higher than ω_0, *i.e.* up to few THz, one would need to record the spectrum up to such large frequencies.
- Second, one should be sure that the sole origin of the spectrum is the rotation of the molecular anisotropy tensor, and that the full dynamics is properly described by equations (2.11).

While the first condition could be met, we have no proof that the second condition is ever satisfied; in particular, other light scattering processes may play an important role at frequencies larger than, typically, 30 GHz [29,30]. The comparison between the full depolarized back scattering spectrum and equations (2.11) is thus meaningless.

However, equation (2.17) is only necessary to analyze the low-frequency orientational dynamics ($\omega \ll \omega_0$) of molecular glassforming liquids. Such a spectrum represents the low frequency part of the Laplace transform of some specific normalized orientational correlator. In real time, such a correlator first decreases from a value equal to unity to some smaller value on a time scale of the order of ω_0^{-1}, and ends up, at much longer times, as a stretched exponential. The low-frequency $R(\omega)$ spectra we need to study in the present experiments are mainly the Laplace transform of this final dynamics. This is why we shall represent $R(\omega)$ in the present paper by the Cole Davidson function:

$$R(\omega) = R^0 \left[1 - \left(\frac{1}{1 + i\omega\tau_{\mathrm{R}}}\right)^{\beta}\right]. \tag{2.18}$$

This function is frequently used to approximate, for not too large values of $\omega\tau_{\mathrm{R}}$, the Laplace transform of a stretched exponential, the relaxation time τ_{R} and the exponent β (that we shall, momentarily, call $\tau_{\mathrm{R_{CD}}}$ and β_{CD}) of equation (2.18) being related to the parameters of the stretched exponential by a set of formulas given by Lindsay and Patterson [31]. We want to stress here that the discussion preceding equation (2.18) implies that the integral of the l.h.s. of equation (2.17) is smaller than π; more precisely, it is equal to π multiplied by the $t = 0$ value of the stretched exponential, which is smaller than one. When one makes use of equation (2.18), this yields $0 < R^0 < 1$, a condition which will need to be fulfilled in the analysis we shall perform in Section 4.

In order to make clear the relationship between the present approach and previous approaches which will be discussed in Section 5, it is important to make the following remark. Equation (2.18) contains no signature of the frequency of the microscopic motion. This is also true for the ratio $\omega\hat{\Gamma}(\omega)/\omega_0^2$ through which $R(\omega)$ may be expressed (see Eq. (2.11a)) as well as for the quantity $G(\omega)$ when Λ'/ω_0^2 is replaced by Λ (see Eq. (2.13b)). This means that the signature of the microscopic dynamics, namely the term $-\omega$ in the r.h.s. of equation (2.11b), or the term in $\ddot{\bar{\bar{Q}}}(t)$ in equation (2.8a), does not need to appear in our equations. In agreement with equation (2.5a), we could have thus directly written, instead of equation (2.8a), the simpler equation:

$$0 = \bar{\bar{Q}} + \Gamma^{-1} \otimes \dot{\bar{\bar{Q}}} - \Lambda\mu \otimes \bar{\bar{\tau}}, \tag{2.8b}$$

with:

$$\Gamma^{-1}(t) = \frac{\hat{\Gamma}(t)}{\omega_0^2}; \quad \Lambda = \frac{\Lambda'}{\omega_0^2} \tag{2.6b}$$

provided that we accept to perform a Laplace transform of equation (2.8b) without questioning its mathematical meaning. Indeed, one can notice that equation (2.8b) has no solution for which $\bar{\bar{Q}}^0$, the $t = 0$ value of $\bar{\bar{Q}}$, is different from zero. This is easily seen for the $\perp\perp'$ component where the last term of equation (2.8b) is absent: for $t = 0$, the convolution product gives a contribution equal to zero which implies that $Q_{\perp\perp'}(t = 0)$ is equal to zero. Our long detour makes it clear that, provided we make use of the additional coefficient R^0 of equation (2.18), a purely relaxational form for Γ^{-1} and a careless use of the Laplace transform of equation (2.8b) give the correct form[3] for $R(\omega)$ and an expression for the spectral profile, $I(\omega)$, independent of the microscopic frequency, ω_0. This is the direction we shall take in the rest of this paper, replacing $\hat{\Gamma}(\omega)/\omega_0^2$ by $\Gamma^{-1}(\omega)$ and Λ'/ω_0^2 by Λ in equations (2.11) and (2.13).

2.5 Discussion of the term related to the shear viscosity

The second term of equation (2.16), $R_1(\omega)$, contains all the information on the shear dynamics through the frequency dependant shear viscosity, $\eta_{\mathrm{s}}(\omega)$, in its denominator, the rotation-translation coupling function, $\mu(\omega)$, and the rotational friction force, $\Gamma^{-1}(\omega)$ in both its numerator and its denominator. (Note that $R(\omega)$ is expressed through $\Gamma^{-1}(\omega)$.) Let us study $R_1(\omega)$ in the two regimes: ω small or ω large with respect to some relaxation rate. Three relaxation times are involved in, respectively, $\eta_{\mathrm{s}}(\omega)$, $\mu(\omega)$ and $\Gamma^{-1}(\omega)$ and we study in this section the two limiting cases where ω is small (or large) with respect to the inverse of these three times. One easily shows that the ω small (or large) limits of $\omega\mu(\omega)$, $\omega\Gamma^{-1}(\omega)$, $R(\omega)$ and $\omega\eta_{\mathrm{s}}(\omega)$, have the same analytic properties, namely:

$$\lim_{\omega\to 0} L(\omega) \approx i\omega L' \qquad L' \text{ real positive}, \tag{2.19a}$$

$$\lim_{\omega\to \infty} L(\omega) \approx L^{\infty} \qquad L^{\infty} \text{ real positive}, \tag{2.19b}$$

$L(\omega)$ being any of these four quantities.

2.5.1 The low-frequency limit

Let us call μ', Γ', R' and η', the values of L' when $L(\omega)$ is respectively equal to $\omega\mu(\omega)$, $\omega\Gamma^{-1}(\omega)$, $R(\omega)$ and $\omega\eta_{\mathrm{s}}(\omega)$.

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[3] Note that this quantity appears not only as the first term of the r.h.s. of equation (2.16) but also in the numerator and in the denominator of $R_1(\omega)$.

Equations (2.13b, 2.19a) imply that the low-frequency limit of $G(\omega)$ may be written as:

$$\lim_{\omega\rightarrow 0} G(\omega) = -\omega^2 G' \tag{2.20a}$$

with:

$$G' = \Lambda \left(\frac{\mu' R'}{\Gamma'}\right)^2 \cdot \tag{2.20b}$$

Since the low frequency limit of $G(\omega)$ is $-\omega^2 G'$ (see Eq. (2.20a)) while, in the denominator of $R_1(\omega)$ (Eq. (2.13a)), $1 - R(\omega)$ tends towards 1 in the same limit:

$$\lim_{\omega\rightarrow 0} R_1(\omega) = -\frac{\omega\, q^2 \rho_\mathrm{m}^{-1} G'}{\omega - i q^2 \rho_\mathrm{m}^{-1} \eta'} \cdot \tag{2.21}$$

Equation (2.21) requires some discussion.

First, in this $\omega \rightarrow 0$ limit, $(1/\omega)\,\mathrm{Im}\, R_1(\omega)$ is a Lorentzian with a negative intensity, a linewidth equal to $q^2 \rho_\mathrm{m}^{-1} \eta'$ and an integrated intensity proportional to q^2. $R_1(\omega)$ is exactly the Andersen-Pecora result [7], and, as in their case, η' must be identified with the static shear viscosity η_s. As noted by these authors and verified by *e.g.* Stegeman and Stoicheff [32], this result implies that Brillouin scattering experiments performed in non-viscous fluids ($\eta_\mathrm{s} \approx 1$ cp) allow for a direct determination of the static shear viscosity.

Second, the static shear viscosity does not contain any contribution from the rotation-translation coupling: this viscosity originates here only from the motion of the centers of mass of the liquid, as in Quentrec's approach [11] (see Sect. 5).

Third, in the next two sections of this paper, we shall analyze depolarized light scattering spectra performed in a 90° geometry, in a temperature regime where $\omega\tau_\mathrm{s} > 1$, ω being in the GHz region, and τ_s the relaxation time associated with η_s. Equation (2.21) will no longer be valid in the frequency window of the experiment, but our analysis will allow us to infer the whole function $\eta_\mathrm{s}(\omega)$, thus its $\omega \rightarrow 0$ limit, $i\eta'$. As $\eta' \equiv \eta_\mathrm{s}$, we shall be able to extract the value of the static shear viscosity, η_s, from spectra recorded in a frequency regime for which equation (2.21) is not applicable.

2.5.2 The high frequency limit

Using equation (2.19b), one easily obtains, for the high frequency limit of $R_1(\omega)$:

$$R_1(\omega) = \frac{q^2 \rho_\mathrm{m}^{-1} G^\infty}{\omega^2 - q^2 \rho_\mathrm{m}^{-1} \left[\eta^\infty - G^\infty (1 - R^\infty)^{-1}\right]} \tag{2.22}$$

with:

$$G^\infty = \Lambda \left(\frac{\mu^\infty R^\infty}{\Gamma^\infty}\right)^2, \tag{2.23}$$

R^∞, μ^∞, Γ^∞ and η^∞ being the high frequency limits, respectively, of $R(\omega)$, $\omega\mu(\omega)$, $\omega\Gamma^{-1}(\omega)$ and $\omega\eta_\mathrm{s}(\omega)$. $R_1(\omega)$ thus describes, in the $\omega \rightarrow \infty$ limit, a propagating transverse mode with zero linewidth and with velocity:

$$V_\mathrm{T} = \left[\frac{\eta^\infty}{\rho_\mathrm{m}}\left(1 - \frac{G^\infty}{\eta^\infty}(1 - R^\infty)^{-1}\right)\right]^{1/2} = \left[\frac{\eta^\infty}{\rho_\mathrm{m}}\right]^{1/2} r. \tag{2.24}$$

η^∞ plays here the same role as the shear modulus in the usual Maxwell theory of viscoelasticity, and, as in any other solid, the rotation-translation coupling, which enters into equation (2.24) through G^∞, decreases the sound velocity in this high frequency regime.

The two limiting cases have thus, without any additional constraint, the behaviour expected from general considerations for those quantities, a requirement which was not generally met in previous approaches to the problem (see Sect. 5). Furthermore, as we pointed out at the end of Section 2.5.1, the internal consistency of our approach can be checked through the direct measurement of the static shear viscosity. Such a check will be performed at the end of Section 4.

3 Experiment

An experimental test of the previous theoretical analysis has been performed on metatoluidine, CH_3-C_6H_4-NH_2. This is a molecular liquid which very easily remains in a supercooled state when cooled below its melting temperature. It is very difficult to crystallize and special techniques had to be used to obtain its melting temperature, $T_\mathrm{m} = 243.5$ K, and its thermodynamic glass transition temperature, $T_\mathrm{g} = 187$ K [20].

The thermal variations of its refractive index and of its density are given by [33]:

$$n(T) = -4.5 \times 10^{-4}\ T(\mathrm{K}) + 1.692(5) \tag{3.1a}$$

$$\rho(T) = -8.1 \times 10^{-4} \times T(\mathrm{K}) + 1.225(0). \tag{3.1b}$$

Low temperature, low frequency depolarized light scattering spectra of metatoluidine were measured in two different geometries for various temperatures. The first series of experiments was performed in order to measure and analyze the pure rotational α-relaxation spectrum over a large frequency range (experimental details and results are described in more details elsewhere [34,35]). They combined a backscattering tandem Fabry-Pérot experiment performed between 300 K and 260 K, a 90° scattering confocal VH Fabry-Pérot experiment (between 245 K and 227 K) and a 90° scattering VH Photon Correlation Spectroscopy (PCS) measurements performed between 198 K and 183 K.

- The tandem Fabry-Pérot intensity spectra were analyzed by fitting to equation (2.17), with $R(\omega)$ given by equation (2.18). This yielded an almost constant value for $\beta_\mathrm{CD} = 0.5$, clearly different from $\beta_\mathrm{CD} = 1$, when the data were analyzed in a large enough frequency range (typically two decades), and a set of relaxation times $\tau_{\mathrm{R}_\mathrm{CD}}(T)$.

- The PCS data were analyzed assuming that the α-relaxation could be described by a stretched exponential (or Kohlrausch-Williams-Watts function). The $\tau_{\mathrm{R_K}}(T)$ and $\beta_{\mathrm{K}}(T)$ values so obtained were converted into similar constants in the Cole Davidson representation, $\tau_{\mathrm{R_{CD}}}(T)$ and $\beta_{\mathrm{CD}}(T)$, using the equivalence formulas given by Lindsay and Patterson [31].

- Because of a problem of overlapping orders, the spectra obtained with the confocal interferometer cannot be analyzed with both τ and β free. Therefore, the values of $\beta_{\mathrm{CD}}(T)$ were interpolated in the intermediate region of the confocal measurements, the analysis of which then yielded the corresponding $\tau_{\mathrm{R_{CD}}}(T)$ for this last series of measurements. The whole set of orientational relaxation times was fitted by a Vogel-Fulcher law, from which values of $\tau_{\mathrm{R_{CD}}}(T)$ were obtained for the intermediate temperature values used here; we shall simply call them, from now on, $\tau_{\mathrm{R}}(T)$, or τ_{R}. They are given in the second column of Table 1 and were used, in the data analysis performed in Section 4, in conjunction with $\beta_{\mathrm{CD}} = 0.5$.

The second series of experiments consisted of 90° VH light scattering experiments performed on the 8 pass tandem Fabry-Pérot instrument already used for the backscattering experiments, the light source being a Coherent Innova 90 monomode Ar$^+$ laser ($\lambda = 514.5$ nm). The spectra were recorded between 0.75 GHz and 8 GHz, each spectrum consisting of about 300 data points on the Stokes and Anti-Stokes sides. The spectra were symmetrized afterwards in order to improve the signal to noise ratio. The sample was placed in a cryostat with temperature regulation better than 0.25 K and the measurements were performed every 5 K from 248 K down to 208 K with one additional measurement at $T = 176$ K, below T_{g}.

After completing the analysis of these 90° VH light scattering spectra, some of the resulting parameters were compared with the values of the static shear viscosity at different temperatures. As previous measurements of this shear viscosity did not extend, to our knowledge, below 245 K [36], we performed in Mainz lower temperature measurements using a Rheometrics RHS-800 viscometer which allowed us to obtain the shear viscosity from mechanical friction measurements down to 191 K.

4 Data analysis and discussion

4.1 Data analysis

90° VH spectra for $T = 248$ K, 233 K and 208 K are shown in Figure 1. At the highest temperature (248 K), a weak bump (see also Fig. 2) emerges around 2.5 GHz from a broad central peak while, at 208 K, the transverse phonon appears as a narrow peak located at ≈ 4.5 GHz. Following the analysis performed in Section 2 and the necessary simplifications discussed in Section 2.4, these spectra were fitted to:

$$I(\omega) \approx \frac{I^1}{\omega} \mathrm{Im}\left(R(\omega) + \cos^2 \frac{\theta}{2} R_1(\omega)\right), \tag{4.1}$$

with:

$$R_1(\omega) = \frac{q^2 \rho_{\mathrm{m}}^{-1} G(\omega)}{\omega^2 - q^2 \rho_{\mathrm{m}}^{-1} \left[\omega \eta_{\mathrm{s}}(\omega) - G(\omega)(1 - R(\omega))^{-1}\right] - i\omega\gamma}, \tag{4.2}$$

where $R(\omega)$ is given by equation (2.18) and $G(\omega)$ by:

$$G(\omega) = \Lambda \left(\frac{\mu(\omega)}{\Gamma^{-1}(\omega)}\right)^2 R^2(\omega), \tag{4.3}$$

$\Gamma^{-1}(\omega)$, which is the Laplace transform of $\Gamma^{-1}(t)$ appearing in equation (2.8b), being related to $R(\omega)$ by:

$$R(\omega) = \frac{\omega \Gamma^{-1}(\omega)}{1 + \omega \Gamma^{-1}(\omega)} \cdot \tag{4.4}$$

$\eta_{\mathrm{s}}(t)$ is a memory function which describes a viscoelastic phenomenon; we postulated for it a form similar to $R(\omega)$:

$$\omega \eta_{\mathrm{s}}(\omega) = \eta_{\mathrm{s}}^0 \left[1 - \left(\frac{1}{1 + i\omega\tau_{\mathrm{s}}}\right)^{\beta}\right] \tag{4.5}$$

where, in the absence of further information, we chose the same $\beta = 0.5$ value as for $R(\omega)$.

In principle, we should have had also to postulate some form for $\omega\mu(\omega)$. This would have meant introducing at least two new parameters for this function while $\Gamma^{-1}(\omega)$ was entirely determined by $R(\omega)$ through equation (4.4). A fit with so many parameters being unreliable, we postulated that the functional forms, the relaxation times and the stretching coefficients of $\omega\Gamma^{-1}(\omega)$ and $\omega\mu(\omega)$ were close enough to take their ratio as a frequency-independent quantity. This assumption allowed us to treat $\Lambda(\mu(\omega)/\Gamma^{-1}(\omega))^2$ in equation (4.3) as a temperature-dependent constant in the data analysis.

Such a simplifying assumption was all the more necessary because of our neglect of any high-frequency contribution to $R(\omega)$ and $\omega\eta_{\mathrm{s}}(\omega)$. It has been recognized for several years that there is a need for additional damping mechanisms which originate from the high frequency part of the relaxation functions of the liquid [27], the so-called fast relaxation processes. As a precise description of these effects was out of the scope of the present paper, we assumed, as a first-order approximation, that this additional damping could be taken into account by adding a conventional "fast damping" term, $-i\omega\gamma$ in the denominator of $R_1(\omega)$, as shown in equation (4.2). Furthermore, γ which might be taken as a temperature dependent quantity [37] was assumed here not to depend on temperature in order to avoid increasing the number of parameters to be fitted. γ was thus determined by fitting a VH 90° spectrum measured at 176 K, *i.e.* at a temperature below T_{g} to equation (4.2). At such a low temperature, the only operative relaxation term is $-i\omega\gamma$, the relaxation times related to $\eta_{\mathrm{s}}(\omega)$ and $R(\omega)$ being essentially infinite. This procedure fixed the value of γ to $\gamma = 0.085$ GHz.

A first series of fits was performed using equations (4.1) to (4.5), in which we took $\tau_{\mathrm{R}} = \tau_{\mathrm{s}}$ as a fitting parameter.

Table 1. Fitting parameters for metatoluidine VH spectra. τ_{R} is taken from [34], (see footnote 4); τ_{s}, η_{s}^{0}, $\Lambda(\mu/\Gamma^{-1})^2$ and R^0 are obtained from the fits of the spectra to equations (4.1) to (5.5), using the additional parameters $\beta = 0.5$ and $\gamma = 0.085$ GHz; r and V_{T} are deduced from the fitting parameters (Eq. (2.24)) as well as $\beta\eta_{\mathrm{s}}^{0}\tau_{\mathrm{s}}$. η_{s} is the static shear viscosity (values interpolated from the mechanical spectroscopy measurements).

T [K]	τ_{R} [ns]	τ_{s} [ns]	η_{s}^{0} [10^8Pa]	$\Lambda\left(\frac{\mu}{\Gamma^{-1}}\right)^2$ [10^8Pa]	R_0	r	V_{T} [m/s]	$\beta\eta_{\mathrm{s}}^{0}\tau_{\mathrm{s}}$ [Pa.s]	η_{s} [Pa.s]
248	0.9	0.23	4.8	0.8	0.58	0.93	640	0.05	0.06
243	1.6	0.25	5.9	1.0	0.61	0.91	690	0.075	0.07
238	3.2	0.35	7.6	1.4	0.63	0.89	778	0.13	0.13
233	6.9	0.45	8.5	1.8	0.60	0.89	805	0.19	0.29
228	17.2	1.0	9.1	2.1	0.53	0.92	844	0.45	0.75
223	50.4	2.1	9.9	2.2	0.56	0.91	883	1.05	2.0
218	182	4.1	10.2	2.6	0.46	0.94	926	2.1	8.4
213	870	5.8	11.0	1.5	0.68	0.89	960	3.2	37
208	6112	12.0	13.8	1.6	0.71	0.89	1020	8.3	246

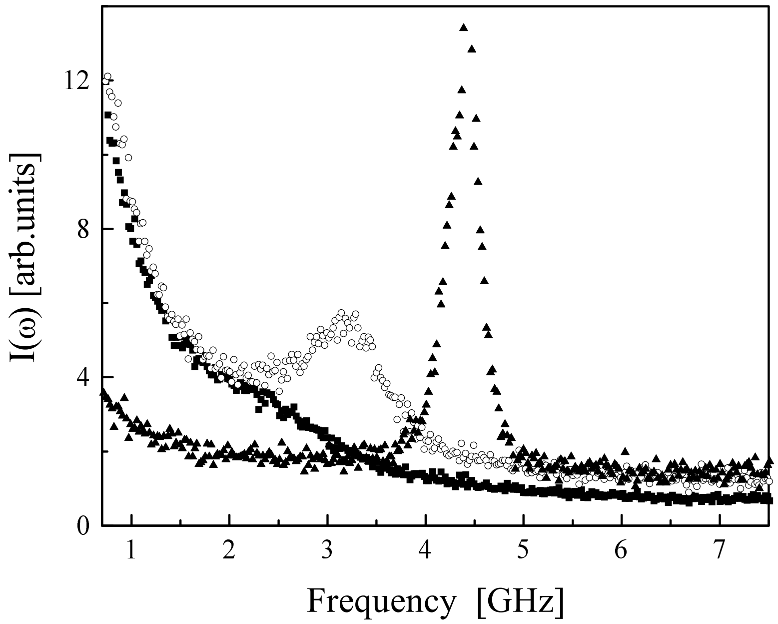

Fig. 1. VH 90° scattering spectra at 248 K (■), 233 K (○) and 208 K (▲), respectively.

The fitting parameters were thus τ_{R}, η_{s}^{0}, R^0, $\Lambda(\mu/\Gamma^{-1})^2$ and the normalization factor I^1. Though quite reasonable fits could be obtained at nearly all temperatures, the relaxation times so obtained were, at each temperature, much shorter than the value of τ_{R} determined from the depolarized backscattering spectra by a factor of close to 3 at 248 K and larger than 10 at 218 K. This indicated that our assumption of an unique relaxation time for all the memory functions was unrealistic [28].

A second series of fits was thus performed fixing $\tau_{\mathrm{R}}(T)$ at the value determined in [34,35] and fitting all the other parameters as before with τ_{s} free. Though we did not increase the number of parameters, the quality of the fit improved and, as expected, the values of $\tau_{\mathrm{s}}(T)$ were systematically shorter than $\tau_{\mathrm{R}}(T)$. In Figure 2, examples of the quality of the fits are given for two temperatures, $T = 248$ K and $T = 233$ K. The entire set of parameters either used as input data (T and τ_{R}) or obtained from those fits is given in Table 1.

4.2 Discussion of the results

4.2.1 Relaxation times

The values of the two relaxation times τ_{R} and τ_{s} are given[4] in columns 2 and 3 of Table 1, and shown in Figure 3. Although no error bars are given in this figure, two points need to be made.

- First, there are some uncertainties in the values of τ_{R} (called $\tau_{\mathrm{R_{CD}}}$ in Sect. 3) obtained through the methods

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[4] Due to an error in a file, the values of τ_{R} were incorrectly reported in the corresponding column of [21]. Column 2 of the present Table 1 gives the correct values for these rotational times.

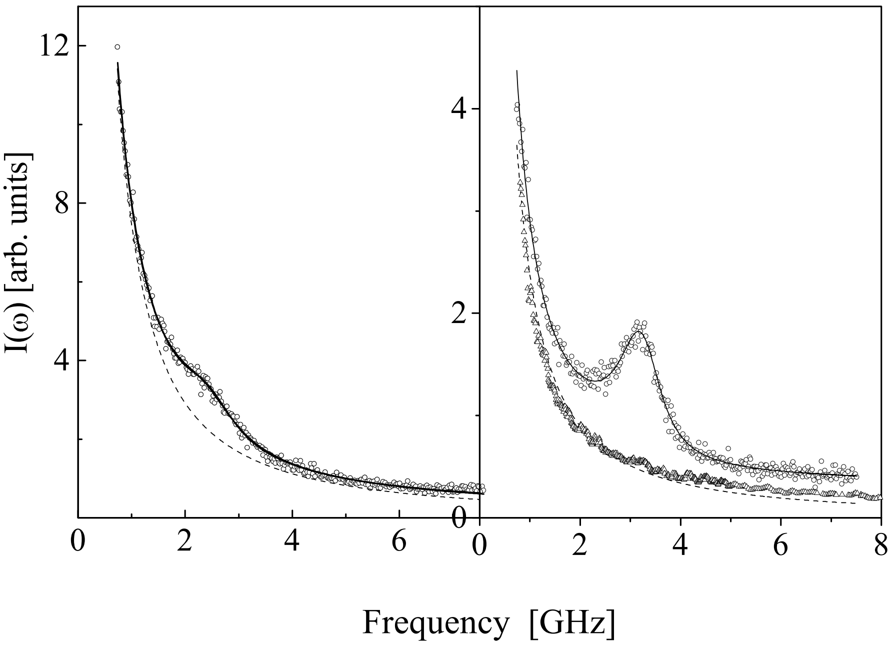

Fig. 2. Continuous line (—): fits to the data, using equations (4.1) to (5.5): at left, 248 K; at right, 233 K; dashed line (– – –): $R(\omega)$ contribution (Eq. (2.18)) to the spectra; (△): corresponding backscattering spectrum at 233 K.

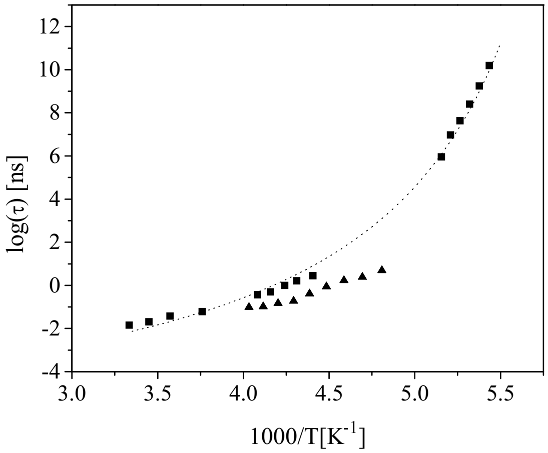

Fig. 3. Reorientational relaxation time, τ_R(■), [34] and viscoelasticity relaxation time, τ_s(▲), obtained from the fitting of spectra similar to those of Figure 1 with equations (4.1) to (4.5), as a function of temperature.

described in that Section. We estimated [34,35] the corresponding relative error on τ_R to be approximately 40%. This error is by far the largest uncertainty in the whole fitting procedure, and it gives nearly the same value for $\Delta\tau_s/\tau_s$, the two quantities being strongly correlated.

- Second, the magnitude of this relative error is correct only as long as the value of γ introduced in the denominator of $R_1(\omega)$ plays a minor role in the determination of τ_s. With $\gamma = 0.085$ GHz, this is the case for $\tau_s < 1$ ns. The situation is different for longer relaxation times: the low-frequency cut-off of our experiment, 0.75 GHz, makes no longer accessible the contribution of the corresponding relaxation mechanism to the Rayleigh wing; τ_s is then mostly deduced from the bare linewidth of the transverse phonon peak, which correlates the values of γ and τ_s. As in the fitting of the data, γ mimics all the fast relaxation processes which take place in a supercooled liquid, it is the neglect of the temperature variation of these processes which is the main source of error on τ_s at the lowest temperatures.

Keeping those remarks in mind, we see that the result of our data treatment, which can be represented by an Arrhenius behaviour for τ_s over the whole temperature range, is, presumably, largely artificial at low temperature. Conversely, the factor 3, seen in Figure 3 between τ_R and τ_s at 248 K, cannot be accounted for by the uncertainty on τ_R or additional uncertainties on τ_s; similarly, the increase of the ratio τ_R/τ_s between 248 K and 223 K may not be related to the uncertainty on γ at those temperatures. This difference between two relaxation times, τ_R and τ_s in the present case, is not new in the field of the liquid-glass transition of molecular liquids; it originates from the fact that τ_R is related to an orientational dynamics while the relaxation times corresponding to other variables may be related to different damping mechanisms: here, τ_s characterizes the shear friction forces related to the centers of mass motion (see Eqs. (2.7, 4.2)) decoupled from the associated rotations. Similar differences have been found between τ_R and the relaxation times τ_L associated with the damping of the longitudinal acoustic phonons: for instance, at the highest temperature where it has been measured, τ_L is 12 times shorter than the corresponding τ_R in salol [26] and 4 times shorter in metatoluidine [34,35].

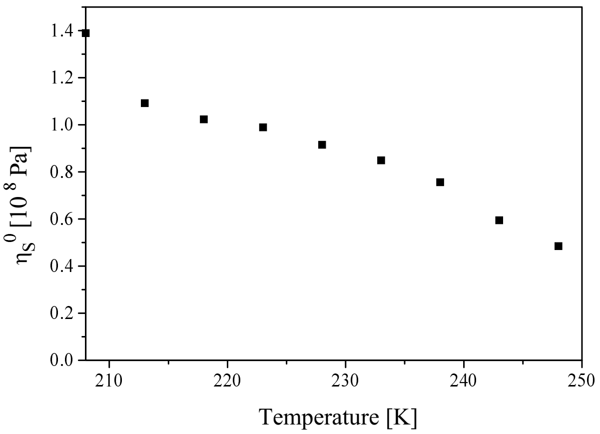

Fig. 4. Temperature dependence of η_s^0, shear modulus at infinite frequency, obtained by the same technique as for Figure 3.

4.2.2 Infinite frequency shear modulus $\eta_s^0(T)$ and the transverse sound velocity

Figure 4 represents the thermal variation of $\eta_s^0 \equiv \eta^\infty$, the infinite frequency limit of $\omega\eta_s(\omega)$. As recalled in the introduction and shown more precisely in equations (2.22, 2.19b), in the absence of rotation-translation coupling, the square root of this quantity divided by $\rho_m^{-1/2}$, should give the velocity of the transverse modes for $\omega\tau_s \gg 1$. In the Maxwell treatment of viscoelasticity, this quantity has been supposed to be temperature independent. We see that it is not at all the case, an extrapolation of η_s^0 to higher temperatures suggesting a rather low value ($\approx 10^8$ Pa) at 280 K, *i.e.* approximately 100 K above T_g.

Table 1 gives also the value of r, the reduction factor, (see Eq. (2.24)), which is the ratio between the actual velocity of transverse waves at infinite frequency and the value it would have in the absence of rotation-translation coupling. We find that r is nearly constant over the whole temperature range. As the position of the peak in the spectra is not very sensitive to the value of $\omega\tau_s$, when that quantity is larger than 1, the absence of thermal variation of r allows us, in the present case, to read off the value of η_s^0, up to a r^{-1} scale factor, directly from the recorded spectra.

Let us finally note that r depends on R^∞, which is equal to the coefficient R^0 in equation (2.18) discussed in Section 2.4. Column 6 of Table 1 shows that, this coefficient is always smaller than one, as predicted in that section.

4.2.3 Comparison with static shear viscosity data

A severe test of the validity of the theory can be obtained from a comparison between the values of the static shear viscosity deduced from the analysis of our light scattering spectra, and their direct measurement briefly described at the end of Section 3. Using equations (2.19a, 2.21, 4.5), one finds that the static shear viscosity, η_s, should be equal to:

$$\eta_s = \beta\,\eta_s^0\tau_s, \tag{4.6}$$

where each term of the r.h.s. is known, either from [35] or from the present fits. Figure 5 presents those results as the logarithm of the shear viscosity *versus* temperature and the corresponding values are also reported in Table 1. Both sets of values agree well, within the possible accuracy of the measurements, between 248 K, just above the melting temperature, and 223 K, that is, for a variation of η_s from 0.06 Pa.s (0.6 p) to 2 Pa.s (20 p). The divergence which takes place at lower temperatures is due to the effects of fast relaxation processes in this temperature range, as discussed in Section 4.2.1.

5 Relationship with previous studies

In nearly every paper published since 1975 on the simultaneous appearance of a central peak and a transverse Brillouin doublet in the depolarized spectra of supercooled liquids formed of anisotropic molecules, the relationship between the model used for the data fitting and previous models has been discussed. In particular, the problem of the relative intensity of these two spectral features and of the form of the dispersion relation, $\omega(q)$, have been frequently dealt with. However, there has been very little discussion on the consistency of the equations appearing in these papers with respect to the phenomena they describe. Concentrating on that aspect of the problem, we proposed to write down a set of equations in which the temperature evolution of the relaxation times leads naturally to correct high and low temperature limits, and which give equally good fits to the recorded spectra with a minimal number of parameters. In this penultimate section, we shall review some aspects of the earlier works concerning the appearance of transverse waves in these supercooled molecular liquids and analyze the mechanism(s) through which these transverse modes appear, emphasizing their relationship to and their differences with the present work. In order to simplify the discussion and the writing of the equations, throughout this section, we shall renormalize the various variables $\bar{\bar{Q}}$ so that they have the same dimension (inverse of a time) as $\bar{\bar{\tau}}$.

5.1 Equations of motion in the two-variable theories without retardation effects

The original papers of Keyes and Kivelson [6] and of Andersen and Pecora [7] were the first to propose a two-variable theory which could explain the existence of the Rytov dip at high temperature and its change into propagative transverse modes at lower temperatures. They did not make use of an equation of motion for the mass current density (Eq. (2.2)), *i.e.* they did not make explicit the expression of the shear tensor. Nevertheless, one can recast their equations into the formalism of the present paper. Restricting oneself, as they did, to the traceless parts of the strain rate tensor $\bar{\bar{\tau}}$ and of a tensor $\bar{\bar{Q}}$ assumed to be proportional to the anisotropic part of the polarizability

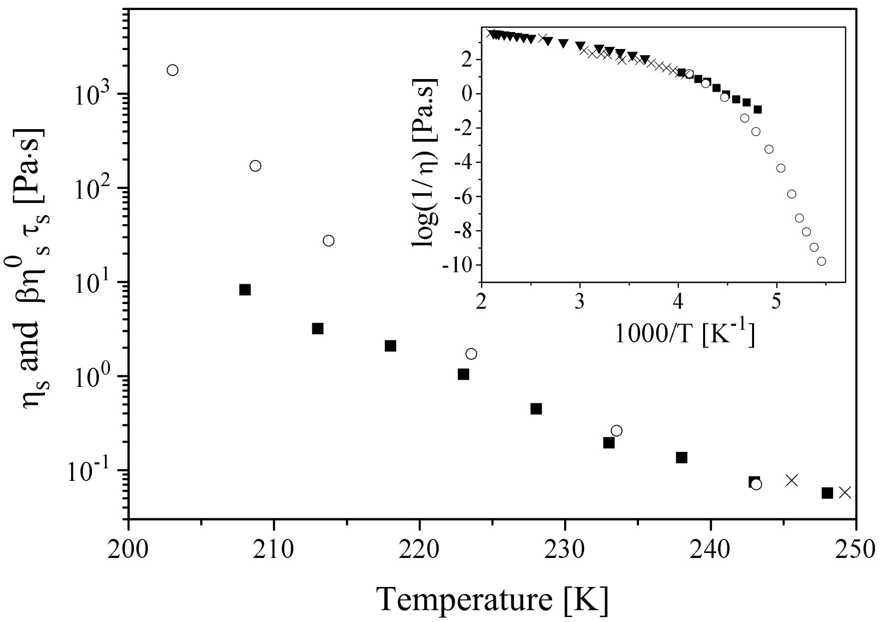

Fig. 5. Comparison between $\beta\eta_s^0\tau_s$ (■) as obtained from the fit parameters reported in Table 1, and the Couette's viscosity measurements (○), as a function of temperature. The inset presents static viscosity data over a larger range of temperature: (▼) from [48] and (×) from [36].

tensor, one obtains, in the case of Andersen and Pecora [7]:

$$\bar{\bar{\sigma}} = \eta_s(1-R)\bar{\bar{\tau}} - \Gamma_{12}\,\bar{\bar{Q}} \tag{5.1a}$$

$$0 = -\Gamma_{12}^*\bar{\bar{\tau}} - \Gamma_{22}\,\bar{\bar{Q}} - \dot{\bar{\bar{Q}}} \tag{5.1b}$$

using here notations as close as possible to their original paper. These equations make clear that, as their coefficient R lies between zero and one, only part of the full static shear viscosity, η_s, couples the shear strain rate $\bar{\bar{\tau}}$ to $\bar{\bar{\sigma}}$ and also that the molecular orientations are taken into account through the variable $\bar{\bar{Q}}$, (and not its time derivative, $\dot{\bar{\bar{Q}}}$) in equation (5.1a). As we shall see in equation (5.3), this difference is responsible for the fact that the static shear viscosity is renormalized by the rotation-translation coupling, which explains the introduction of the additional parameter R in their equations (we do not discuss here the Keyes and Kivelson paper because both papers obtain exactly the same final formula, though they start from slightly different points of view).

On the contrary, Quentrec [11], who made explicit use of the stress tensor, took into account the molecular orientation through the variable $\dot{\bar{\bar{Q}}}$, and, in the two-variable form of his theory, his equations of motion reduce to:

$$\bar{\bar{\sigma}} = \eta_s\bar{\bar{\tau}} + 2\alpha_{12}\dot{\bar{\bar{Q}}} \tag{5.2a}$$

$$0 = -2\alpha_{12}^*\bar{\bar{\tau}} - 2\alpha_{22}\dot{\bar{\bar{Q}}} - a\bar{\bar{Q}} \tag{5.2b}$$

sticking again here as closely as possible to the notations of the corresponding paper; in contradistinction with equation (5.1a), his approach does not require the use of the extra parameter R and it is the total static shear viscosity, η_s, which appears, in equation (5.2a).

In this Section 5.1, we briefly discuss some consequences of these two sets of equations. It is easily seen that it is not possible to measure separately the coefficients entering into equations (5.1, 5.2) and that one cannot discriminate between the two equations in the high temperature regime, where the Rytov dip is detected. One can also examine the consequences of these equations at low temperature, *i.e.* for viscous fluids in which propagative transverse waves can be observed. This second situation also does not allow for an independent determination of the coefficients entering those equations but we shall show that the very existence of propagative waves at such temperatures involves a nearly complete cancellation between some of these coefficients which have no fundamental reason to take place. These equations will also give an incorrect role to the rotation translation coupling because they make it responsible for the appearance of the transverse waves while it should actually decrease their velocity: they propose the wrong sign for this effect. Though no low temperature spectrum of a supercooled liquid could be fitted to either of those two sets of equations [8,9,11], it is worth demonstrating those two incorrect low temperature effects here because they will show up, under rather similar but more complex forms, in the three (or more) variable theories we shall discuss in Section 5.2. The two cases we shall treat in this part will be free from the mathematical intricacies introduced by the use of more variables.

Let us start with the Andersen-Pecora approach. Solving equations (5.1) together with equation (2.2), the denominator of the correlation function related to $\bar{\bar{Q}}$ is easily found to be, in the general case:

$$D_{\mathrm{AP}} = i\omega + q^2\rho_{\mathrm{m}}^{-1}\left(\eta_{\mathrm{s}}(1-R) + \frac{\eta_{\mathrm{s}}R}{1+i\omega\tau}\right), \qquad (5.3)$$

where, following [7], we have transformed the notations of equations (5.1) into $\Gamma_{22}^{-1} = \tau$ and $|\Gamma_{12}|^2/\Gamma_{22} = \eta_{\mathrm{s}}R$ (we note that the purpose of introducing the additional parameter R into that equation is to identify the parenthesis of the r.h.s. of equation (5.3) with the static viscosity, η_{s}, in the high temperature regime where $\omega\tau \ll 1$). At low temperature, one expects η_{s} to increase roughly as quickly as the α-relaxation time τ. To get the same kind of variation for $\eta_{\mathrm{s}}R$ requires that Γ_{12} stays approximately constant. Taking thus $\omega\tau \gg 1$ and multiplying both sides of equation (5.3) by $-i\omega$ yields, in leading orders:

$$-i\omega D_{\mathrm{AP}} = \omega^2 - q^2\rho_{\mathrm{m}}^{-1}\left(\frac{\eta_{\mathrm{s}}R}{\tau} + i\omega\,\eta_{\mathrm{s}}(1-R)\right). \qquad (5.4)$$

Equation (5.4) makes it clear that propagative shear modes with a finite sound velocity are possible at low temperature because η_{s}/τ does not diverge, even in this temperature region. But, in order for these modes not to be overdamped, $\eta_{\mathrm{s}}(1-R)$ must remain finite and small with respect to η_{s}/τ. Thus, R must tend towards 1 with $\eta_{\mathrm{s}}(1-R) \approx$ const., a condition which does not seem to be very physical. Furthermore, as mentioned above, the transverse-mode velocity originates from $\eta_{\mathrm{s}}R/\tau \equiv |\Gamma_{12}|^2$: the existence of such propagative modes is the consequence of the rotation-translation coupling rather than of viscosity. This result is counter-intuitive.

The same discussion can be made in the Quentrec case [11] because its dynamical equation can be cast in exactly the same mathematical form as for the Andersen-Pecora's theory. Let us demonstrate it for the denominator of the correlator discussed in equation (5.3). Using equations (5.2) this denominator reads:

$$D_{\mathrm{Q}} = i\omega + q^2\rho_{\mathrm{m}}^{-1}\left(\eta_{\mathrm{s}} - \frac{4i\omega|\alpha_{12}|^2}{a + 2i\omega\alpha_{22}}\right) \qquad (5.5)$$

which can be transformed into:

$$D_{\mathrm{Q}} = i\omega + q^2\rho_{\mathrm{m}}^{-1}\left(\eta_{\mathrm{s}} - \eta_{\mathrm{s}}' + \frac{\eta_{\mathrm{s}}'}{1+i\omega\tau}\right) \qquad (5.6\mathrm{a})$$

with:

$$\eta_{\mathrm{s}}'\tau = 4|\alpha_{12}|^2/a \qquad \tau = 2\alpha_{22}/a. \qquad (5.6\mathrm{b})$$

The Quentrec condition for the existence of underdamped transverse propagative modes is that $\eta_{\mathrm{s}} - \eta_{\mathrm{s}}'$ remains finite and small with respect to $\eta_{\mathrm{s}}\tau^{-1}$ (compare with Eq. (5.3)). As, in Quentrec's theory, both α_{12} and α_{22} are roughly proportional to τ, such a condition is not impossible but it requires, again, a cancellation between *a priori* uncorrelated coefficients; also, the non zero value of the transverse-wave velocity originates, once more, solely from the orientation-translation coupling.

Before closing this part, let us note that [6,7] were published at the same time as the papers by Ailawadi *et al.* [14] who proposed to describe, in hydrodynamic terms, the orientational motion of the molecules and their coupling with the centers of mass motions through equations first derived by de Groot and Mazur [38]. These equations introduce a variable $\bar{\omega}$ which is the local average of the molecular angular velocity and an antisymmetric contribution to the stress tensor: the two equations which replace equations (5.1) or (5.2) in their theory read, for the case of transverse waves [14b]:

$$\bar{\bar{\sigma}} = \eta_{\mathrm{s}}\bar{\bar{\tau}} + \eta_{\mathrm{r}}\,\bar{\bar{\bar{L}}} \cdot (\mathrm{rot}\;\mathbf{v} - 2\bar{\omega}) \qquad (5.7\mathrm{a})$$

$$\rho_{\mathrm{I}}\dot{\bar{\omega}} = 2\eta_{\mathrm{r}}(\mathrm{rot}\;\mathbf{v} - 2\bar{\omega}) \qquad (5.7\mathrm{b})$$

where we have, again, used notation as close as possible to the original paper, $\mathbf{v}(\mathbf{r},t)$ being the velocity field of the particles, ρ_{I} the mean density of the average moment of inertia and $\bar{\bar{\bar{L}}}$ the usual Levi-Civita tensor. Furthermore, it was proposed in [14b] that the Rytov dip would be detected through the antisymmetric part of a local dielectric tensor which would read:

$$\bar{\bar{\varepsilon}} = X_1\bar{\bar{\bar{L}}} \cdot (\mathrm{rot}\;\mathbf{v} - 2\bar{\omega}), \qquad (5.8)$$

the rot $\mathbf{v}$ contribution being negligible with respect to that of $\bar{\omega}$ in the case of light scattering by a liquid in thermal equilibrium. Though the form of equation (5.8) is rather awkward, one may note that, through the neglect of the rot $\mathbf{v}$ term and the form of the Levi-Civita tensor, $\varepsilon_{\perp\perp'}$ is proportional to $\omega_{\parallel}$ and $\varepsilon_{\perp\parallel}$ to $\omega_{\perp'}$. If one performs a transformation in equations (5.7, 5.8) in which $\omega_{\parallel}$ is changed into $\sqrt{\rho_{\mathrm{I}}}\,Q_{\perp'\perp}$ and $\omega_{\perp'}$ into $\sqrt{\rho_{\mathrm{I}}}\,Q_{\perp\parallel}$ one finds, after a lengthy but straightforward calculation, that, as far as the transverse modes are concerned, the solutions of equations (5.7) and the spectrum derived from equation (5.8) are identical to the solutions which can be derived from:

$$\bar{\bar{\sigma}} = (\eta_{\mathrm{s}} - \eta_{\mathrm{r}})\bar{\bar{\tau}} \pm \frac{2\eta_{\mathrm{r}}}{\sqrt{\rho_{\mathrm{I}}}}\,\bar{\bar{Q}} \qquad (5.9\mathrm{a})$$

$$0 = \pm\frac{2\eta_{\mathrm{r}}}{\sqrt{\rho_{\mathrm{I}}}}\,\bar{\bar{\tau}} - \frac{4\eta_{\mathrm{r}}}{\rho_{\mathrm{I}}}\,\bar{\bar{Q}} - \dot{\bar{\bar{Q}}} \qquad (5.9\mathrm{b})$$

the motion of $\bar{\bar{Q}}$ being detected through a local dielectric tensor of the form:

$$\bar{\bar{\varepsilon}} = b\,\bar{\bar{Q}}. \qquad (5.10)$$

As already noticed by Ailawadi and Berne [39], from a formal point of view, the equations proposed in [14b] are thus, for the transverse modes, identical to those of [6] or [7]. Nevertheless, the comparison between equation (5.1b) and equation (5.9b) shows an important difference, namely that the width of the central peak predicted by equations (5.9) is proportional to η_{r}. In order to reproduce the experimental facts, η_{r} has thus to decrease with decreasing temperature, contrary to an usual viscosity coefficient. In such a case, the role of η_{r} becomes negligible at low temperature in equation (5.9a) and the whole shear dynamics is governed by the shear viscosity.

As noted in [14b], transverse modes could still propagate if the constant η_s would be transformed into a memory function, but the rotation-translation coupling would play no role in the value of the velocity of the transverse waves, a result which is, again, counter intuitive.

5.2 Equations of motions in the three-variable theories without retardation effects

As early as 1976, it was recognized that these two variable theories could not fit correctly the depolarized spectra containing propagative waves but the two theoretical difficulties pointed out at the beginning of Section 5.1 were not identified. Most authors rather tried to improve the quality of their fit by introducing at least one more dynamical variable linearly coupled to the two variables already introduced, a technique which was actually suggested by some theoreticians even before this failure was reported (see, *e.g.* [40,41]). Because we are only interested here in the role of these extra variables in changing the origin of propagative transverse waves at low temperature, we shall ignore these two early papers.

Let us start by discussing a very simple case which will allow us easily to correlate the many variable technique with the two variable memory function technique used in Section 2. Analyzing salol data over a large temperature range, Vaucamps *et al.* [10] proposed to improve over the original Andersen-Pecora model by (i) ignoring the existence of an intrinsic viscosity of the liquid, and (ii) imposing that the mass current couples to two dynamical variables not directly coupled one with the other; finally, only one of these variables was supposed to couple with light. Using the Andersen-Pecora notations of equation (5.1), one thus obtains the following set of equations:

$$\begin{aligned}\bar{\bar{\sigma}} &= -\Gamma_{12}\bar{\bar{Q}}_2 - \Gamma_{13}\bar{\bar{Q}}_3\\ 0 &= -\Gamma_{12}^*\bar{\bar{\tau}} - \Gamma_{22}\,\bar{\bar{Q}}_2 - \dot{\bar{\bar{Q}}}_2\\ 0 &= -\Gamma_{13}^*\bar{\bar{\tau}} - \Gamma_{33}\,\bar{\bar{Q}}_3 - \dot{\bar{\bar{Q}}}_3. \end{aligned}\qquad (5.11)$$

In such a case, it is a simple matter of algebra to eliminate the variable which does not couple with light, say Q_3. This yields the new set of equations:

$$\begin{aligned}\bar{\bar{\sigma}} &= \eta_s \otimes \bar{\bar{\tau}} - \Gamma_{12}\bar{\bar{Q}}_2\\ 0 &= -\Gamma_{12}^*\bar{\bar{\tau}} - \Gamma_{22}\,Q_2 - \dot{\bar{\bar{Q}}}_2 \end{aligned}\qquad (5.12)$$

with:

$$\eta_s(t) = |\Gamma_{13}|^2 \mathrm{e}^{-\Gamma_{33}t} \equiv \eta_s^0 \mathrm{e}^{-t/\tau}. \qquad (5.13)$$

In other words, Vaucamps' method introduces, implicitly, a viscoelasticity of the Maxwell type, as can be seen through the appearance of a convolution product in the first equation of equations (5.12). The unrealistic condition of a small value for the coefficient $\eta_s(1-R)$ at low temperature which was necessary with the Andersen-Pecora equations (see Eq. (5.3)) is then automatically eliminated. Yet, as in that theory, the "normal" variable Q_2 contributes to a renormalization of the static shear viscosity at high temperature and gives a positive contribution to the transverse-wave velocity at low temperature, the ratio $|\Gamma_{12}|^2/\Gamma_{22} \equiv \eta_s R$ still playing the same role: it is thus not surprising that, in the numerical analysis of their experiment, Vaucamps *et al.*, who determined R through a direct determination of η_s, obtained a value of R approximately constant and low in the region of the Rytov dip, constant and close to unity in the region of the propagative transverse waves, with an abrupt jump from one value to the other in the temperature region where none of those features was visible.

In the general case where the third variable Q_3 (or its time derivative) is linearly coupled to the two other dynamical variables, the technique of eliminating it through a Laplace Transform of the initial equations, followed, after its elimination by an inverse Laplace Transform can be generalized for the two cases studied in Section 5.1. Let us start with the Quentrec case where the introduction of Q_3 was already proposed in [11]. The generalization of equations (5.2) to three variables leads to the new set of equations:

$$\bar{\bar{\sigma}} = \eta_s\,\bar{\bar{\tau}} + 2\alpha_{12}\dot{\bar{\bar{Q}}}_2 + 2\alpha_{13}\dot{\bar{\bar{Q}}}_3 \qquad (5.14a)$$

$$0 = -2\alpha_{12}^*\,\bar{\bar{\tau}} - 2\alpha_{22}\dot{\bar{\bar{Q}}}_2 - a\bar{\bar{Q}}_2 - 2\alpha_{23}\dot{\bar{\bar{Q}}}_3 \qquad (5.14b)$$

$$0 = -2\alpha_{13}^*\,\bar{\bar{\tau}} - 2\alpha_{23}^*\dot{\bar{\bar{Q}}}_2 - 2\alpha_{33}\dot{\bar{\bar{Q}}}_3 - b\bar{\bar{Q}}_3. \qquad (5.14c)$$

The elimination technique recovers equations (5.2) where each product is replaced by a convolution product where, *e.g.*, η_s is replaced by:

$$\eta_s(t) = \left(\eta_s - \frac{2|\alpha_{13}|^2}{\alpha_{33}}\right)\delta(t) + \frac{2b|\alpha_{13}|^2}{\alpha_{33}^2}\exp\left(-\frac{bt}{2\alpha_{33}}\right), \qquad (5.15a)$$

similar expressions holding for $\alpha_{12}(t)$ and $\alpha_{22}(t)$. The modified equations (5.2) are thus formally identical to the set of equations (2.7, 2.8b). There are, nevertheless, two important differences between those two sets of equations:

- One is that the second part of the memory function of equation (5.15) is a Debye relaxation function with a relaxation time $2\alpha_{33}/b$ totally determined by the dynamics of the individual variable Q_3. The same relaxation time will appear for the memory functions $\alpha_{12}(t)$ and $\alpha_{22}(t)$: adding one variable always results in a Debye relaxation mechanism identical for the shear viscosity and the rotational dynamics; if more than one variable would be linearly added, a more complex dynamics could be found, $\eta_s(t)$, $\alpha_{12}(t)$ and $\alpha_{22}(t)$ being the sum of different Debye relaxation processes with the same relaxation times but different weighting factors for the three functions.

- A second difference with equations (5.7, 5.8b) is that, unless $\eta_s = 2|\alpha_{13}|^2/\alpha_{33}$ (with similar conditions for the delta functions appearing in α_{12} and α_{22}), the high frequency behaviour of $Q_2(\omega)$ at low temperature will still be dominated by these delta functions, *i.e.* by the terms studied in Section 5.1: the propagation of transverse acoustic phonons will still require a special cancellation between the amplitudes of these delta functions and this propagation will still be due to the rotation-translation coupling.

These aspects of the three variable theory of Quentrec [11] and of a further generalization to a four variable theory [42] were not noticed in a study of benzyl benzoate [43,44] because the authors concentrated their analysis on restricted parts of the spectra.

The same type of problems arise in the case of the Andersen-Pecora formulation. Its generalization to three variables was performed by Chapell *et al.* [12] and to four variables by some of the same authors in [13]. Their elimination recovers the set of equations (5.1) where each product is changed into a convolution product with, *e.g.*, in the case of a three variable theory:

$$\eta_{\mathrm{s}}(1-R) \rightarrow \eta_{\mathrm{s}}'(t) = \eta_{\mathrm{s}}(1-R)\,\delta(t) + \frac{|\varGamma_{13}|^2}{\varGamma_{33}}\exp(-\varGamma_{33}t) \tag{5.15b}$$

which is exactly the expression found in the case of Vaucamps *et al.* [10], similar expressions holding now for $\varGamma_{12}(t)$ and $\varGamma_{22}(t)$, though with different signs. These quantities trivially generalize those of equations (5.1). One can thus make the same remarks for the Chapell *et al.* generalizations as for the Quentrec's one about the uniqueness of the relaxation times or their Debye character, about the condition for propagation of transverse acoustic waves at low temperature or the origin of their velocity; in particular, in the case of the iono-organic molecular glassformer, triphenylphosphite, though Chapell *et al.* [12] assumed, as Vaucamps *et al.* did, that $\eta_{\mathrm{s}}(1-R)$ of equation (5.15b) is equal to zero, a definition of R similar to the one discussed in this previous case led to results not substantially different: R changed from a value of 0.4 at high temperature to a value of ~ 0.8 for viscosities of a few poise, the change being simply smoother than in [10].

5.3 Equations of motion with explicit retardation effects

After the introduction of viscoelastic phenomena in the hydrodynamic equations by Maxwell [2] and Mountain [1] and an allusion to their role by Ailawadi *et al.* [14b], Wang was the only author, to our knowledge, to make explicit use of this notion and, more generally, of the idea of phenomenological retarded interactions related to variables appearing explicitly in these equations. This method appeared in several papers, the most important being presumably [15,18,19,45].

Wang's first attempt [18] is formally equivalent to the two equations (5.12) which describe the model of Vaucamps *et al.* [10] once the variable Q_3 has been eliminated; indeed, this model may be summarized as follows:

a) $\eta_{\mathrm{s}}(T)$ is represented by the sum of two relaxation phenomena:

$$\eta_{\mathrm{s}}(T) = \eta_{\mathrm{s}}^{0_1}\mathrm{e}^{-t/\tau_1} + \eta_{\mathrm{s}}^{0_2}\mathrm{e}^{-t/\tau_2}. \tag{5.16}$$

b) For all the temperatures used and in the frequency window of the Brillouin experiment, τ_1 is so short that $\omega\tau_1 \ll 1$, while, conversely, τ_2 is so long that $\omega\tau_2 \gg 1$. Also, $\eta_{\mathrm{s}}^{0_1}$ and $\eta_{\mathrm{s}}^{0_2}$ may vary strongly with temperature.

As a consequence, one obtains:

$$\omega\eta_{\mathrm{s}}(\omega) = i\omega\eta_{\mathrm{s}}^{0_1}\,\tau_1 + \eta_{\mathrm{s}}^{0_2} \equiv i\omega\eta + G_0 \tag{5.17}$$

where, for some temperatures, G_0 may be equal to zero.

This model described successfully a parametrized form of the data obtained by Enright *et al.* [9] in salol, the supercooled liquid which had already been successfully fitted by Vaucamps *et al.* [10]. In Wang's analysis, G_0 is equal to zero as long as the transverse modes do not appear in the spectra and represents the unrenormalized shear modulus at infinite frequency when these modes are visible. Yet, the equivalence between this model and the model of Vaucamps *et al.* make them suffer from the same defects: in particular, at low temperatures, one can obtain a decent fit to the spectra but the corresponding physics is not correctly described.

In later papers, [15,19,45], Wang introduced retardation effects more formally in $\eta_{\mathrm{s}}(t)$ and also in the description of the rotational dynamics and of its coupling with the transverse current. As mentioned in Section 2, in Wang's formalism [15], equation (2.8a) reads:

$$0 = -\omega_0^2 \otimes \bar{\bar{Q}} - \varGamma'\dot{\bar{\bar{Q}}} + \varLambda'\mu \otimes \bar{\bar{\bar{\tau}}} \tag{5.18a}$$

which is equivalent to:

$$\dot{\bar{\bar{Q}}} = -\gamma \otimes \bar{\bar{Q}} + \tilde{\mu} \otimes \bar{\bar{\bar{\tau}}} \quad \text{with} \quad \gamma(t) = \frac{\omega_0^2(t)}{\varGamma'}\,\cdot \tag{5.18b}$$

Equation (5.18b) shows that retardation acts on the direct force, $\gamma(t)$, in Wang's formalism, and not on the friction force, as in equation (2.8b). Such an equation is definitely more legitimate from a mathematical standpoint that our equation (2.8b): its Laplace transform is always well behaved. In particular, if one considers its projection on the two directions $\mathbf{u}_\perp$ and $\mathbf{u}_{\perp'}$ defined in Section 2, one obtains with notations similar to those of equations (2.9) to (2.11):

$$\overline{Q^2_{\perp\perp'}(\omega)} = \frac{1}{\omega}R(\omega)\langle|Q^0_{\perp\perp'}|^2\rangle \tag{5.19a}$$

with:

$$R(\omega) = \frac{\omega\varGamma'}{\omega\varGamma' - \omega_0^2(\omega)}\,\cdot \tag{5.19b}$$

We may remark that, if we forget about the mathematical difficulties related to the Laplace transformation, in principle, equation (5.19b) and equation (4.4) should represent the same physics and this could be, in principle, achieved by imposing the relation:

$$\frac{\omega_0^2(\omega)}{\omega\varGamma'} = -\left[\frac{\omega\hat{\varGamma}(\omega)}{\omega_0^2}\right]^{-1}. \tag{5.20}$$

But the spirit of the phenomenological approaches discussed in this paper is different: the memory functions which are introduced must represent some plausible form of a relaxation process because one assumes that the corresponding variables have a relaxing dynamics. That was the approach used in Section 2 and we have seen that it is always the case with the memory functions which can be built from Section 5.2. Following the same line of reasoning and in agreement with the generalizations found there, the simplest possible form for $\omega_0^2(t)$ is:

$$\omega_0^2(t) = \frac{\Omega^2}{\tau} \exp\left(-\frac{t}{\tau}\right) \tag{5.21}$$

which yields:

$$\frac{1}{\omega} \operatorname{Im} \frac{\overline{Q^2_{\perp\perp'(\omega)}}}{\langle |Q^0_{\perp\perp'}|^2 \rangle} = \frac{\Gamma' \Omega^2}{(\omega^2 \tau \Gamma' - \Omega^2)^2 + \omega^2 \Gamma'^2} \cdot \tag{5.22}$$

If $2\Omega^2 > \Gamma'^2$, equation (5.19) will have a minimum at $\omega = 0$ and a maximum at $\omega^2 = (\Omega^2 - \Gamma'^2/2)(\tau\Gamma')^{-1}$. This simple example emphasizes the fact that equation (5.19b) does not allow for a fit of the rotational part of the spectrum unless one imposes an unphysical form for the supposed retarded interaction. The modifications of these equations performed in [45] or [19] did not change equation (5.18a) and they thus lead to the same difficulty.

6 Summary and perspectives

In this paper, we have discussed the structure of the hydrodynamic equations pertinent to the case of a fluid formed of anisotropic molecules. Pointing out the physical origin of the interactions which need to be taken into account, we have indicated that the form proposed by Quentrec [11] was consistent with the usual expression of the stress tensor, in the case of liquids with small shear viscosities. We have also shown that this form was conveniently amenable to a phenomenological introduction of retardation effects, when the latter have to be taken into account as is the case for supercooled liquids. This led, for one of these equations, to a form which differed from the expression originally proposed by Wang [15]. We have discussed the low and high frequencies limits of our results and we have shown that they behave as expected in those two regimes. This was generally not the case with other formulations in their high frequency (or low temperature) limit: shear waves could propagate in this regime but this propagation always required accidental cancellation effects; also, the coupling between the shear motion and the molecular reorientations did not have the expected influence on the transverse mode velocity.

Metatoluidine, a molecular fragile glass forming liquid was chosen to test the validity of our equations. Making use of two (90° and 180°) scattering geometries, we have analyzed the corresponding depolarized Rayleigh-Brillouin spectra; those were measured with the excellent contrast and large free spectral range available with an 8 pass tandem Fabry-Pérot interferometer which allowed for a precise description of their intensity profiles. Making as few approximations as possible for the theoretical expressions, we have found a good consistency between the value of the static shear viscosity, η_s, from direct viscosity measurements and from experiments performed in a regime where the shear waves were propagative (and not diffusive, as *a priori* implied by the use of such a constant). This was true for temperatures at which we expect our spectra to give a reasonable determination of the shear viscosity relaxation time, τ_s, and the discrepancy found at low temperature is understood as a consequence of the neglect of the temperature variation of the fast relaxation processes.

Our analysis of metatoluidine and the equations obtained in the present paper lead to a certain number of new problems. Let us mention two of them:

We have measured, for the first time, the shear relaxation time, τ_s, and found it to be always shorter than the reorientation relaxation time, τ_R associated with the reorientation of the molecules. Experiments performed on the propagation of longitudinal phonons in the supercooled molecular glass forming liquids have been, up to now, analyzed with the help of phenomenological expressions (see, *e.g.*, [26,27,34,35]) making use of only one relaxation function for the longitudinal viscosity. Once $\eta_s(\omega)$ and $R(\omega)$ are determined, the expression (A.14) proposed in the Appendix A of the present paper for the spectral shape of these phonons allows us, in principle, to determine a bulk viscosity relaxation time, τ_b, associated with an expression of a bulk-viscoelasticity function, $\eta_b(\omega)$, analogous to equation (4.1). It will be important to find out whether there is some measurable difference between τ_s and τ_b in the temperature range where the difference we found between τ_R and τ_s cannot be attributed to our use of a constant value of the additional damping constant, γ.

Another question is related to the temperature variation of the coefficient η_s^0, the infinite frequency limit of $\omega\eta_s(\omega)$ (see Eq. (4.5)). Measurements of transverse spectra similar to those reported here have already been made. This is, in particular, the case for Wang and his collaborators who recorded spectra in fragile molecular glass-forming liquids such as orthoterphenyl [17] or salol [16]. In those supercooled liquids, the frequency of the peak associated with the transverse phonon also decreases with increasing temperature: in both cases, its extrapolated frequency appears to go to zero approximately 100 K above T_g, as it is the case for metatoluidine (see Sect. 4.2). Those papers proposed that the thermal evolution of the rotation-translation coupling , the r factor of Section 4.2.2, could play an important role in the decrease of the shear velocity of the corresponding liquid but they could not base this statement on a really quantitative analysis of the corresponding spectra. As metatoluidine appears to be similar in many respects to those two other molecular glassformers [46,47], a complete analysis of those transverse spectra needs to be made before a firm conclusion on the thermal evolution of their η_s^0 and r factor can be made. The similarity between the published spectra and those analyzed here suggests that, as in metatoluidine, it is η_s^0, rather than r, which decreases strongly with increasing temperature; this problem clearly needs to be looked at more carefully in further studies.

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Appendix A.1

We briefly describe here how one obtains equations (2.11) and (2.13), which are the basis of the interpretation of our experimental data.

We make use here of a Laplace-Fourier transform technique in which:

$$f(\mathbf{q},\omega) = i \iiint \mathrm{d}^3\mathbf{r} \int_0^\infty \mathrm{d}t f(\mathbf{r},t)\mathrm{e}^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)} \tag{A.1}$$

and we thus look for the frequency dependence of the Laplace transform of normalized correlation functions $\langle f(\mathbf{q},t)f(\mathbf{q},0)\rangle$, the time derivative of which are equal to zero at time $t=0$.

Also, we assume, for the sake of simplicity, that the memory functions are local in space. Omitting the $\mathbf{q}$ dependence when not necessary, we first perform the space Fourier transform of equations (2.1, 2.2, 2.7 and 2.8a). This yields:

$$\dot{\rho}(t) - iqJ_{\parallel}(t) = 0 \tag{A.2}$$

$$\dot{J}_i(t) + iq\sigma_{i\parallel}(t) = 0 \tag{A.3}$$

$$\begin{aligned}\sigma_{i\parallel}(t) = &-(c^2\rho(t) + iq(\eta_\mathrm{b}(t) + \frac{1}{3}\eta_\mathrm{s}(t)) \otimes v_\parallel(t))\delta_{i\parallel} \\ &- iq\,\eta_\mathrm{s}(t) \otimes v_i(t) - \mu(t) \otimes \dot{Q}_{i\parallel}(t)\end{aligned} \tag{A.4}$$

$$\begin{aligned}&\ddot{Q}_{ij}(t) + \Gamma'(t) \otimes \dot{Q}_{ij}(t) + \omega_0^2 Q_{ij}(t) \\ &+ iq\Lambda'\mu(t) \otimes (v_i(t)\delta_{j\parallel} + v_j(t)\delta_{i\parallel} - \frac{2}{3}v_\parallel(t)\delta_{ij}) = 0\end{aligned} \tag{A.5}$$

where $c^2 = (\rho_\mathrm{m}\chi)^{-1}$, ρ_m being the thermal mean value of the mass density and χ the adiabatic compressibility of the fluid.

One can now solve these equations by Laplace transforms, in the three different cases: (1) $i=\perp$, $j=\perp'$; (2) $i=\perp$, $j=\parallel$; (3) $i=j=\parallel$. Noting with an upper index 0, the value of a fluctuation at time $t=0$, one easily obtains:

- Case (1):

$$Q_{\perp\perp'}(\omega) = \frac{1}{\omega}R(\omega)Q^0_{\perp\perp'} \tag{A.6}$$

where:

$$R(\omega) = \frac{\omega\hat{\Gamma}(\omega)}{\omega_0^2 + \omega\hat{\Gamma}(\omega)} \tag{A.7}$$

$$\hat{\Gamma}(\omega) = \Gamma'(\omega) - \omega. \tag{A.8}$$

Multiplying both sides of equation (A.6) by $Q^0_{\perp\perp'}$ and taking the thermal mean value of both sides yields:

$$\overline{Q^2_{\perp\perp'}(\omega)} \equiv LT\langle Q_{\perp\perp'}(t)Q_{\perp\perp'}(0)\rangle = \frac{1}{\omega}R(\omega)\langle|Q^0_{\perp\perp'}|^2\rangle \tag{A.9}$$

the corresponding spectral profile being the imaginary part of $\overline{Q^2_{\perp\perp'}(\omega)}$.

- Case (2):

The calculation is a little more intricate because of the coupling between equations (A.4) and (A.5). Once the Laplace transform is performed, one obtains the two equations:

$$\begin{aligned}&\rho_\mathrm{m}(\omega v_\perp(\omega) - v^0_\perp) - q^2\eta_\mathrm{s}(\omega)v_\perp(\omega) \\ &\qquad - q\mu(\omega)(\omega Q_{\perp\parallel}(\omega) - Q^0_{\perp\parallel}) = 0\end{aligned} \tag{A.10a}$$

$$\begin{aligned}&\hat{\Gamma}(\omega)(\omega Q_{\perp\parallel}(\omega) - Q^0_{\perp\parallel}) + \omega_0^2 Q_{\perp\parallel}(\omega) \\ &\qquad + q\Lambda\mu(\omega)v_\perp(\omega) = 0\end{aligned} \tag{A.10b}$$

which yields:

$$\begin{aligned}&Q_{\perp\parallel}(\omega)\left(\omega_0^2 + \omega\hat{\Gamma}(\omega) + \frac{q^2\Lambda'[\omega\mu(\omega)]^2}{\omega^2\rho_\mathrm{m} - q^2\omega\eta_\mathrm{s}(\omega)}\right) \\ &\quad = \frac{Q^0_{\perp\parallel}}{\omega}\left(\omega\hat{\Gamma}(\omega) + \frac{q^2\Lambda'[\omega\mu(\omega)]^2}{\omega^2\rho_\mathrm{m} - q^2\omega\eta_\mathrm{s}(\omega)}\right) + Kv^0_\perp\end{aligned} \tag{A.11}$$

where K is a function of q and ω. When one multiplies both sides of equation (A.11) by $Q^0_{\perp\parallel}$, and takes its thermal mean value, the term proportional to $\langle Q^0_{\perp\parallel}v^0_\perp\rangle$ drops out, because the product in the thermal mean value is not invariant through time reversal symmetry. Some algebraic manipulations then lead to:

$$\overline{Q^2_{\perp\|}(\omega)} \equiv LT\langle Q_{\perp\|}(t)Q_{\perp\|}(0)\rangle = \frac{1}{\omega}(R(\omega)+R_1(\omega))\langle|Q^0_{\perp\perp'}|^2\rangle \qquad \text{(A.12)}$$

with:

$$R_1(\omega) = \frac{q^2\rho_{\rm m}^{-1}G(\omega)}{\omega^2 - q^2\rho_{\rm m}^{-1}[\omega\eta_{\rm s}(\omega) - G(\omega)(1-R(\omega))^{-1}]} \qquad \text{(A.13a)}$$

$$G(\omega) = \Lambda'\omega_0^2\left(\frac{\mu(\omega)}{\hat{\Gamma}(\omega)}\right)^2 R^2(\omega). \qquad \text{(A.13b)}$$

- Case (3):
Though we shall not discuss the case of the longitudinal current in this paper, we simply quote here the result which makes use of the fact that both $\langle Q^0_{\|\|}J^0_{\|}\rangle$ and $\langle\rho^0 J^0_{\|}\rangle$ are equal to zero, due to the same time reversal symmetry argument as above. A tedious calculation yields:

$$\overline{J^2_{\|}(\omega)} = \frac{\langle|J^0_{\|}|^2\rangle}{\omega^2-q^2\rho_{\rm m}^{-1}\left[c^2\rho_{\rm m}+\omega\eta_{\rm b}(\omega)+\frac{4}{3}\left(\omega\eta_{\rm s}(\omega)-G(\omega)(1-R(\omega))^{-1}\right)\right]}, \qquad \text{(A.14)}$$

a result formally similar to the one obtained in [15].

Appendix A.2

The light scattering mechanism which gives rise to the low frequency spectrum we study in the present paper may be considered from two different points of view. One is the formal expression of the dielectric tensor associated with a rotation of the molecules, within the framework of the present study; the second is the physical origin of the mechanism and its potential calculation. We shall only discuss here the first aspect which is only a problem of group theory. The general method used in this paper consists in working in the hydrodynamic regime, *i.e.* in a limit where the liquid is considered as a continuous medium which has the full symmetry of the complete rotational group, O_3. A symmetrical secund rank traceless tensor transforms as the $l = 2$ irreducible representation of that group, which is $2l + 1 = 5$ fold degenerate. This implies that the 5 non trivial components of such a tensor depend only on one number; in other words, if this tensor is expressed in the axes in which it is diagonal, it reduces to $\beta_{XX} = \beta_{YY} = -1/2\beta_{ZZ}$, while $\beta_{XY} = \beta_{YZ} = \beta_{ZX} = 0$, by definition. Such a property is valid for any second rank symmetrical traceless tensor, so that, if one tensor is linearly related to the other (one being the origin of the second), the two tensors can only be proportional one to the other. This implies that the relationship between the two tensors $\bar{\bar{\beta}}$ and $\bar{\bar{Q}}$ must be:

$$\bar{\bar{\beta}} = b\bar{\bar{Q}},$$

as written in equation (2.14).

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