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Heterodyne detected transient gratings in supercooled molecular liquids

A phenomenological theory

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Abstract. We present an analysis, based on a phenomenological set of Generalised Navier-Stokes equations, of Heterodyne Detected Transient Gratings on supercooled molecular liquids of anisotropic molecules. This set of equations generalises equations proven in Franosch, Latz and Pick [24] for the same type of liquids. It also takes into account the three different sources generated by the laser pumping process pertinent for these experiments. We give analytical expressions for the response functions that can be measured using the different polarisation of the experimental set-up. Specialising to the case of parallel polarisation (where longitudinal phonons are launched), we show that each response function is a sum of the same seven "elementary response functions" (ERFs) whose time and temperature evolutions are individually analysed. We also show that the response functions corresponding to two of the sources can be directly connected to the Laplace Transform of a light scattering signal. The ERFs generated by the heat-absorption process, which is the third source, are of a different nature. They do not have the same time and temperature behaviours and they can provide, inter alia, unique information on the rotation-translation coupling function characteristic of these liquids.

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1 Introduction

In the early 1970s, researchers discovered the possibility of inducing in a material a transient grating, (TG), i.e. a periodic spatial modulation of its optical properties, using the interaction of the material with the interference field produced by a couple of laser pulses [1]. It was later realised [2–4] that one could monitor the relaxation towards equilibrium of this induced grating and thus measure important information on the dynamical properties of the material. The transient grating technique is a very useful and flexible method to investigate the dynamics of isotropic materials because one can measure, in a selective way, many of its dynamical properties depending on the characteristics of the material and on the frequency of the laser used to induce the grating.

In particular, Nelson and co-workers [5] proposed to study the dynamics of supercooled liquids by a TG technique in which a short (≈100 ps) pulse formed of two coherent light beams, with the same polarisation and propagating in slightly different directions, interfere in the liquid. The coherent interference field generates a density grating with wavevector $\vec{q}$. The latter is probed by a second light beam and the time evolution of the amplitude of the diffracted beam is the response function of the experiment. In the case discussed in [5], the optical grating is due to two effects. One is an electrostrictive interaction at optical frequency: it launches longitudinal phonons of equal amplitudes propagating with opposite wavevectors $\pm\vec{q}$. Their interference creates a time-dependent density grating. The corresponding response function has been called [3] the ISBS (Impulsive Stimulated Brillouin Scattering) response because both ISBS and Brillouin scattering probe the dynamics of these longitudinal phonons. The second effect, called [4] ISTS (Impulsive Stimulated Thermal Scattering) works in a

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somewhat different manner: a weak part of the intensity of the interference field is absorbed by the liquid and it is transformed into heat within a few picoseconds. A temperature grating with the same wavevector is thus created, which again launches these longitudinal phonons. However, as density changes with temperature, the thermal grating is also responsible for a density grating that disappears through the heat-diffusion process i.e. after times much longer than the phonon lifetime; the ISTS response function is thus basically different from the ISBS one.

Working out an elementary theory of these effects, Nelson and co-workers found that a TG-experiment could lead to two different methods of measuring the structural relaxation of a supercooled liquid. These are efficient on different time scales to measure the α-relaxation time, i.e. the time rate characterising the final decay of its relaxation. The first one uses the decay of the longitudinal phonons originating from both the ISBS and the ISTS effects as it was already mentioned in the original paper of Yan, Cheng, and Nelson [5]. This method is limited to relaxation times in the 10^{-2}–10 ns range and it was the starting point of a whole series of studies on α-relaxation dynamics in different glassformers (see, e.g., Ref. [9] in [6]). Duggal and Nelson [7] later realised that the ISTS signal could also provide information, on a much longer time scale (typically 1 ns to 10^6 ns), on a second relaxation time that they named "thermal expansion time". Though this second time was also measured in the TG-experiments as early as in 1991, the interpretation of the data still concentrated on the short-time window of the measurements. In 1995, Yang and Nelson [6] showed, on the basis of the set of equations used in [5], that this long relaxation time is due to the coupling of the structural relaxation to temperature. Their analysis was an important break through because it opened the possibility of measuring a collective relaxation time, τ, in a time window where alternative methods fail. It yielded precise results for $10 \text{ ns} < \tau < 10^4$ ns, while Photon Correlation Spectroscopy (PCS), the only alternative technique, is limited to $\tau > 10^2$ ns. Since that time, six different supercooled liquids [8–13] have been analysed along this line.

Let us summarise the coupling that leads to this long time signal. The emitted phonons generated by the ISBS and ISTS effects decay through two channels. One corresponds to the fast anharmonic processes in ordinary liquids, characterised by a relaxation time $\tau_{anh} \approx 10$ ps, essentially temperature independent. The second is the phonon coupling to the structural relaxation of the liquid, whose characteristic time, τ, strongly increases with decreasing temperature. When τ becomes much larger than τ_{anh}, the latter dominates the phonon decay which becomes insensitive to τ. Meanwhile, the amplitude of the thermal grating decreases through the heat-diffusion process, characterised by the heat-diffusion relaxation time, $\tau_h \gg \tau_{anh}$. When $\tau_{anh} < \tau < \tau_h$, the amplitude of the emitted phonons has decayed to zero at a time t when the thermal grating has kept its initial shape and amplitude. Yet, for $t \approx \tau$, the density has not equilibrated with the temperature grating. As the change in the index of refraction is linearly related to the change in density, the amplitude of the index grating will increase on a time scale τ up to its equilibrium value. This is exemplified in Figure 5a where the increase of the signal in the 10^2–10^4 ns time window for the curves $\tau_L = 10^2$ ns and $\tau_L = 10^4$ ns is visible while those curves have been computed with $\tau_h = 3.3 \times 10^4$ ns and $\tau_{anh} = 5$ ns (see Sect. 4.4). To summarise, the interplay between the structural relaxation and the long-lived thermal grating allows for a direct measurement of this structural (or rather, as we shall see below, of the "longitudinal") relaxation time, τ_L. This interplay was, in fact, already pointed out in the pioneer work of Allain et al. [2] who gave a correct interpretation of the phenomenon. Though they thus recorded the first ISTS signal[1], their time resolution allowed them only to detect its long time decay.

Until 2001, the interpretations of the TG response relied (see [6]) on a series of approximations, one of them being that the anisotropy of the particles forming the liquid could be ignored. This resulted in the independence of the response function on the polarisation of the different beams involved in the experiment. Two recent HD-TG (Heterodyne Detected) experiments [12,14] on supercooled liquids have shown that this approximation had to be reconsidered. Indeed, those experiments were performed with liquids formed of strongly anisotropic molecules (salol and *m*-toluidine). Controlling the polarisation of all the laser fields (pumps, probe, and diffracted beams) showed the existence of long time signals that depended on these polarisations. The difference between the signals could only originate from orientational dynamics of these anisotropic molecules which gives rise to an anisotropic contribution to the dielectric tensor on the time scale of the ISTS signal. These two experiments demonstrated an effect that had been anticipated, in particular in [15]: analysing an experiment that mixed the simple geometry of an Optical Kerr Effect and the heat absorption inherent to an ISTS experiment, these authors pointed out the importance of introducing a coupling between the density and the molecular orientation to explain a similar dielectric anisotropy in the transient response obtained with supercooled salol.

The role of anisotropic molecules and, in particular, of the anisotropy of their molecular polarisability tensor in detecting local fluctuations in dense liquids had in fact been known for a very long time. The existence of the Rytov dip [16], first seen in depolarised light scattering experiments by Starunov et al. [17] and by Stegeman et al. [18], had been demonstrated, as early as 1971 [19,20], to originate from the coupling of a local shear to a local molecular orientation, the latter being detected through the corresponding polarisability anisotropy. Later on, Enright and Stoicheff [21] showed that the same effect, in supercooled liquids, provided a mechanism for the detection of transverse phonons. Yet, a proper description of the effect over the whole temperature range explored in those experiments only appeared in 1999 [22]. This description

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[1] The TG-technique is called, in their work, forced Rayleigh scattering.

required a generalisation of the usual Navier-Stokes equations that takes simultaneously into account, in a consistent way, both the molecular orientational dynamics and the retardation effects implied by the frequency dependence of the transport coefficients entering into these equations. Some of the present authors (C.D. and R.M.P.) showed that the set of generalised Navier-Stokes equations they proposed was necessary to properly describe both the low viscosity (normal liquid) and the high viscosity (supercooled liquid) experiments, and that the polarisability anisotropy mechanism was sufficient to explain the whole depolarised light-scattering spectrum. More recently, this set of equations was demonstrated to be derivable from a Mori-Zwanzig analysis of the dynamics of a liquid formed of anisotropic molecules [23,24].

The coupling between molecular orientation and shear deformation also creates an optical anisotropy in the case of an inhomogeneous density fluctuation. Though this second effect has been known for a long time, the role of the polarisability anisotropy in Brillouin lineshape of longitudinal phonons has only recently begun to be studied [23]. It turns out that the generalised Navier-Stokes equations proposed in [22] are a convenient way to handle this problem [25] and to describe the extra features implied by this coupling. The latter have very recently been recorded and analysed in supercooled salol [26]. The explanation of the HD-TG experiments reported in [12,14] relies on the same orientation-translation coupling. Reference [13] contains a brief summary of the results that the generalised Navier-Stokes equations lead to in the case of such an experiment, while [14] presents a more primitive explanation based on a less systematic use of the molecular anisotropy (see Sect. 6).

The present paper is the first of an ensemble of three [27,28] in which a general scheme is developed for the calculation and analysis of HD-TG experiments performed on supercooled liquids composed of anisotropic molecules. In this case, one takes advantage of the different possible polarisation of the pumps, probe, and detected beams to obtain a maximum of information. We give in this first paper a phenomenological version of the theory and analyse some consequences of this description when, as in [24,25], the scattering of light is only due to density and orientation modulations. In particular, we show that:

- different response functions, obtained with different polarisation of the pumps, probe, and detected beams, may be recorded when one studies such molecular supercooled liquids;
- each response function splits into a weighted sum of the same seven “elementary response functions” (ERFs);
- for any parallel polarisation of the pumps, on the one hand, and of the probe and diffracted beams, on the other hand, the contribution of five of these ERFs can be related, through the Fluctuation-Dissipation theorem, to a CW light-scattering spectrum. This contribution constitutes the “generalised ISBS” part of the response function;
- one can also define “generalised ISTS” response functions that only depend on the polarisation of the probe and diffracted beams and are linear combinations of the two remaining ERFs. They originate from an irreversible process, the heat absorption, and have thus no equivalent in the light-scattering spectra. They are responsible for the two long time signals that can be obtained with different polarisation and each of these ERFs brings information that could not be obtained otherwise;
- different scenarios involving relaxation processes not explicitly taken into account until now might have to be considered to understand the behaviour of the ISTS response function at very long time and low temperature. This effect had been noticed as soon as the origin of that signal was understood and it has been recently analysed in [29] within a limited framework.

In order to show these and other aspects of the problem, this paper is organised as follows:

- Section 2 introduces the phenomenological set of generalised Navier-Stokes equations, with the corresponding sources and relaxation mechanisms, which have to be used to interpret those HD-TG experiments;
- in Section 3, we study the number of independent response functions that can be recorded by varying the polarisation of the pumps, probe and detected beams. We show that each of them is a weighted sum of the same seven ERFs, each ERF being characterised by the source that generates it and by the mechanism, density or orientation fluctuation, through which the ERF is detected;
- neglecting some relaxation processes, we give in Section 4 usable expressions for each ERF, explain their time evolution and show the correlations that exist between them. We define the “generalised ISBS” response functions and prove the Fluctuation-Dissipation relation that relates them to light-scattering spectra. We also define the “generalised ISTS” response functions and show why each of the corresponding ERFs contains information not easily obtainable by other techniques;
- in Section 5, we show that most of those ERFs can be individually obtained as specific combinations of the response functions measured with different polarisations. We also show that, when the generalised ISBS response functions can be neglected, the two generalised ISTS response functions can be broken-up into an isotropic and an anisotropic signal, one measuring the longitudinal relaxation time τ_L in the $10-10^4$ ns time scale, the second its coupling with the molecular orientation in the same time window;
- Section 6 compares the present phenomenological formulation to previous ones proposed by Allain et al. [2] and by Nelson and his co-workers [5–7,14]. It is also shown that each relaxation process neglected in Section 4 leads to additional effects, at very long time and for low temperature, in the ERFs related to the heat-absorption process: such effects are similar to those detected, e.g. in [2,6,11] and analysed in [2,29];
- Section 7 summarises our results.

2 The phenomenological equations

2.1 Introduction

The expression of the generalised Navier-Stokes equations necessary to describe the dynamics of a supercooled molecular liquid formed of axially symmetric molecules was proposed in [22] and proved in [23,24] in the case where the time window necessary to describe the experiment is sufficiently short for neglecting the energy conservation problem. This generalisation goes as follows.

Let $\hat{u}$ be the unit vector (characterised by the polar angles ϑ and φ) defining the direction of the axis of the molecule and let $P(\vartheta, \varphi, \vec{r}, t)$ be the probability density of finding $\hat{u}$ in that direction at time t, in the vicinity of $\vec{r}$. One can introduce the set of orientational variables, $Q_{ij}(\vec{r}, t)$, defined by

$$Q_{ij}(\vec{r}, t) = \int \sin\theta \, d\vartheta \, d\varphi P(\vartheta, \varphi, \vec{r}, t) \; C_{ij}\left(\hat{u}(\vartheta, \varphi)\right), \quad (2.1)$$

with

$$C_{ij}(\hat{u}) = \hat{u}_i \hat{u}_j - \frac{1}{3}\delta_{ij}. \quad (2.2)$$

By construction, this orientational density has the form of a symmetrical traceless tensor, $\bar{\bar{Q}}(\vec{r}, t)$. It was shown in [24] that the linearised Navier-Stokes equations necessary for the description of the Brillouin spectra in the GHz region are the two usual conservation laws

$$\delta\dot{\rho}(\vec{r}, t) + \mathrm{div}\,\vec{J}(\vec{r}, t) = 0, \quad (2.3)$$

$$\dot{\vec{J}}(\vec{r}, t) = \mathrm{div}\,\bar{\bar{\sigma}}(\vec{r}, t), \quad (2.4)$$

where ρ is the mass density and $\delta\rho$ is its fluctuation, $\vec{J}$ is the mass current density, and $\bar{\bar{\sigma}}$ is the stress tensor. The latter is expressed, in terms of other variables of the problem, as

$$\bar{\bar{\sigma}} = (-\delta P + \eta_b \otimes \mathrm{div}\,\vec{v})\bar{\bar{I}} + \eta_s \otimes \bar{\bar{\tau}} - \mu \otimes \dot{\bar{\bar{Q}}}. \quad (2.5)$$

In equation (2.4), $\bar{\bar{I}}$ is the unit tensor.

$\vec{J}$ is related to $\vec{v}$ through

$$\vec{J} = \rho_m \vec{v}, \quad (2.6)$$

where ρ_m is the mean mass density and $\vec{v}$ is the linear velocity of the molecules.

$\bar{\bar{\tau}}$ is the strain rate, traceless, second rank tensor

$$\tau_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\mathrm{div}\,\vec{v}\delta_{ij}. \quad (2.7)$$

$\delta P(\vec{r}, t)$ is the local pressure change, which is related to $\delta\rho(\vec{r}, t)$ by

$$\delta P(\vec{r}, t) = c_a^2 \delta\rho(\vec{r}, t), \quad (2.8a)$$

where c_a is the adiabatic sound velocity.

η_b, η_s and μ are, respectively, the bulk and shear viscosities, and the rotation-translation coupling relaxation functions, the symbol $\otimes$ standing for a convolution product in time: e.g., $\eta_b \otimes \mathrm{div}\,\vec{v}$ stands for

$$\left(\eta_b \otimes \mathrm{div}\,\vec{v}\right)(\vec{r}, t) \equiv \int_0^t \eta_b(t-s)\mathrm{div}\,\vec{v}(\vec{r}, s) ds. \quad (2.8b)$$

An additional equation of motion has to be written for $\bar{\bar{Q}}(\vec{r}, t)$ which reads [24]

$$\ddot{\bar{\bar{Q}}} = -\omega_R^2 \bar{\bar{Q}} - \Gamma' \otimes \dot{\bar{\bar{Q}}} + \Lambda' \mu \otimes \bar{\bar{\tau}}, \quad (2.9)$$

where:

- Γ' is the orientational relaxation function;
- ω_R is the libration frequency of the axial molecules;
- Λ' is the rotation-translation coupling constant, a quantity that takes into accounts the fact that ρ and $\bar{\bar{Q}}$ have different dimensions. It was also shown in [24] that, if one defines the Laplace-Transform of $f(t)$ by

  $$LT\left[f(t)\right](\omega) = i \int_0^\infty dt f(t) \exp(-i\omega t), \quad (2.10)$$

  the imaginary parts of $\Gamma'(\omega)$, $\eta_b(\omega)$, and $\eta_s(\omega)$, Laplace-Transforms, respectively, of $\Gamma'(t)$, $\eta_b(t)$, and $\eta_s(t)$, are positive for all real frequencies, which implies in particular that their $t = 0$ value is always positive.

Equations (2.5, 2.9) are the necessary ingredients describing the long wavelength dynamics of a supercooled molecular liquid when one simply imposes the two constraints of conservation of mass (Eq. (2.2)) and of linear momentum (Eq. (2.3)).

As a HD-TG experiment involves a time interval long enough for the local temperature of the fluid to possibly vary, the conservation of energy has also to be taken into account. An equation which explicitly involves the local temperature must be added to the preceding set. Furthermore, equations (2.5, 2.9) describe the dynamics of a closed system while, in a HD-TG experiment, one measures the response of the system subjected to an external perturbation: source terms have to be added to those equations. Most of the remaining part of this section is devoted to generalising this set of equations: in Section 2.2 we shall build up the generalised Navier-Stokes equations for a supercooled molecular fluid of axially symmetric molecules while the source terms will be added in Section 2.3; the different polarisations of the two pumps that are necessary to obtain the maximum information from these experiments will be discussed in Section 2.4.

2.2 The generalised Navier-Stokes equations

As was already the case with the phenomenological derivation of equations (2.5, 2.9) performed in [22], two different problems have to be considered: one is the writing of a set of equations which conserves mass, linear momentum and energy in a molecular fluid formed of anisotropic molecules, without consideration of retardation effects; the second is the introduction of these retardation effects. We treat those two problems in turn.

If one ignores retardation effects, equation (2.5) simply reads[2]

$$\bar{\bar{\sigma}} = (-\delta P + \widehat{\eta}_b \mathrm{div}\, \vec{v})\bar{\bar{I}} + \widehat{\eta}_s \bar{\bar{\tau}} - \widehat{\mu}\dot{\bar{\bar{Q}}}. \tag{2.11}$$

As long as the temperature fluctuations could be neglected, δP could simply be expressed as

$$\delta P = \left.\frac{\partial P}{\partial \rho}\right)_T \delta\rho = c_i^2 \delta\rho, \tag{2.12}$$

where c_i is the isothermal sound velocity[3]. When the thermal fluctuations, $\delta T(\vec{r}, t)$, also need to be considered, the preceding equation has to be generalised to

$$\delta P = \left.\frac{\partial P}{\partial \rho}\right)_T \delta\rho + \left.\frac{\partial P}{\partial T}\right)_\rho \delta T \equiv c_i^2 \delta\rho + \rho_m \widehat{\beta} \delta T, \tag{2.13}$$

where $\widehat{\beta}$, with the same notation as above, is the tension (also called thermal pressure) coefficient. The expression for the stress tensor then reads

$$\bar{\bar{\sigma}} = \left(-c_i^2 \delta\rho - \rho_m \widehat{\beta} \delta T + \widehat{\eta}_b \mathrm{div}\, \vec{v}\right) \bar{\bar{I}} + \widehat{\eta}_s \bar{\bar{\tau}} - \widehat{\mu}\dot{\bar{\bar{Q}}}. \tag{2.14}$$

Let us now consider equation (2.9) without retardation effects,

$$\ddot{\bar{\bar{Q}}} = -\omega_R^2 \bar{\bar{Q}} - \widehat{\Gamma'} \dot{\bar{\bar{Q}}} + \Lambda' \widehat{\mu} \bar{\bar{\tau}}. \tag{2.15}$$

As $\bar{\bar{Q}}$ is a second rank, symmetrical, traceless tensor, each term of equation (2.15) must be of the same form. The only traceless tensor involving temperature contains, at least, a second derivative in space. It can be shown to be negligible for the long wavelength dynamics considered here so that no term involving temperature needs being included in equation (2.15).

Finally, for the same reason, an expression linear in $\bar{\bar{Q}}$ cannot enter into the equation of conservation of energy, so that the latter must keep its usual form [30]

$$\widehat{C}_V \dot{T} - T_m \widehat{\beta} \dot{\rho} - \lambda \Delta T = 0, \tag{2.16}$$

where $\widehat{C}_V$ is the specific heat per unit volume at constant volume, T_m is the equilibrium temperature of the liquid, and λ the heat diffusion coefficient.

The introduction of retarded effects in [22] was based on purely phenomenological arguments. It was claimed that these effects had to be introduced on all the terms corresponding to friction. This led us to propose the use of equations (2.5, 2.9) that have since been rigorously demonstrated [24].

Introducing memory functions in equation (2.16) by the same argument as in [22] yields:

$$C_V \otimes \dot{T} - T_m \beta \otimes \dot{\rho} - \lambda \Delta T = 0 \tag{2.17}$$

which introduces retardation effects in the specific heat[4] at constant volume, $C_V(t)$, and in the tension coefficient[5], $\beta(t)$, with relaxation functions that smoothly tend to zero when $t \to \infty$ (cf. [27]). We must stress that the physics behind those two retardation effects is different from that leading to the relaxation functions considered in the preceding paragraph; their modelling will be briefly discussed at the end of Section 4.1 and in Appendix D. Such a form of $\beta(t)$ also implies that equation (2.14) should be transformed into

$$\bar{\bar{\sigma}} = (-c_i^2 \delta\rho - \rho_m \beta \otimes \delta T + \eta_b \otimes \mathrm{div}\, \vec{v})\bar{\bar{I}} + \eta_s \otimes \bar{\bar{\tau}} - \mu \otimes \dot{\bar{\bar{Q}}}. \tag{2.18}$$

The proposed set of generalised Navier-Stokes equations pertinent to the present problem is thus equations (2.3, 2.4, 2.9, 2.17, 2.18).

2.3 The Navier-Stokes equations with external sources

In order to derive, in Section 3 and in Appendix C, the algebraic expressions of the different responses that can be recorded in a TG-experiment when the signal is detected by density and orientation modulations of the dielectric tensor, it is convenient to introduce the sources in as general a form as possible. These sources are defined by the interaction of the exciting electric fields of the pumps with the material and they correspond to several effects that we discuss in this section. The experimental geometry we consider here is the typical one used in previous works (see e.g. [11]). It is defined in Figure 1.

The two coherent sources propagate with wavevectors $\vec{q}_1$ and $\vec{q}_2$ forming a small angle θ. We define the directions $\hat{x}$ and $\hat{z}$ to be the external and internal bisectors of these two wavevectors, $\hat{y}$ being perpendicular to the plane Π formed by $\hat{x}$ and $\hat{z}$. If $q_0 = |\vec{q}_1| = |\vec{q}_2|$, the electric field associated with the two pumps can be written

$$\vec{E}_1(\vec{r}, t) = E_1 \hat{e}^1 \exp\left(i(q_0 z - \omega t)\right) \exp\left(i q_0 x\right) g_0(t), \tag{2.19a}$$

$$\vec{E}_2(\vec{r}, t) = E_2 \hat{e}^2 \exp\left(i(q_0 z - \omega t)\right) \exp\left(-i q_0 x\right) g_0(t), \tag{2.19b}$$

where $g_0(t)$ is an envelope function whose duration is of the order of a few picoseconds. The total electric field to which the sample is subjected is

$$\vec{E}_{int}(\vec{r}, t) = \vec{E}_1(\vec{r}, t) + \vec{E}_2(\vec{r}, t). \tag{2.19c}$$

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[2] We make use, here, of the notation $\widehat{\eta}_b$, $\widehat{\mu}$, etc. to stress that those quantities have the dimension of the time integral of the corresponding relaxation functions.

[3] Note that the isothermal sound velocity, c_i, appears here and not the adiabatic sound velocity, c_a, as was the case in equation (2.8). The reason for this difference has been discussed at the end of Section 4 of [24], and we shall come back to that point in Section 4.1.

[4] Equation (2.17) is a correct generalisation of equation (2.16) as long as the thermal fluctuations can be neglected (see [27]).

[5] The heat diffusion coefficient, λ, which is related to a heat flow, depends on mechanisms that should not be affected by the structural relaxation processes [27].

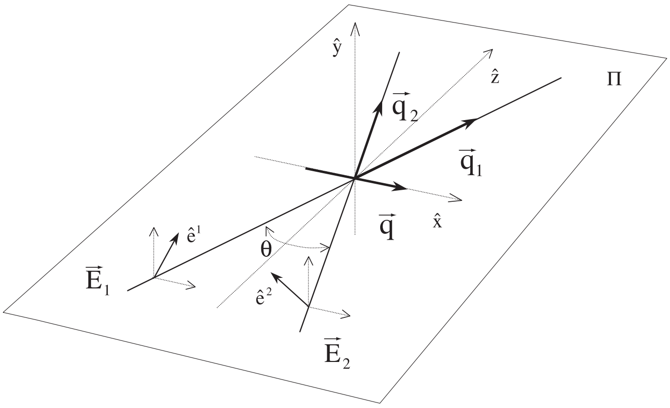

Fig. 1. Geometry of a TG-experiment. The incident vectors, $\vec{q}_1$ and $\vec{q}_2$, as well as the directions of the polarisation vectors, $\hat{e}^1$ and $\hat{e}^2$, and those of $\hat{x}$, $\hat{y}$ and $\hat{z}$ are shown.

Its interaction with the supercooled liquid gives rise to three different physical effects. Each acts as a source that has to be added to one of the equations (2.9, 2.17) or (2.18). Though some of them have already been described in [5] and references therein, and in [14], we repeat the whole argument in order to introduce these three sources within a unified language and in their full generality.

Let us first introduce the density of local electromagnetic energy, which is proportional to

$$U(\vec{r},t) = \overline{\mathrm{Re}\left(\vec{E}_{int}(\vec{r},t)\right)\cdot\mathrm{Re}\left(\vec{E}_{int}(\vec{r},t)\right)}, \qquad (2.20)$$

where the bar symbol indicates averaging over one period. Then, $U(\vec{r},t)$ is easily expressed as

$$U(\vec{r},t) = \frac{1}{2}\left[E_1^2 + E_2^2 + 2E_1E_2\left(\hat{e}^1\cdot\hat{e}^2\right)\cos(qx)\right]g_0^2(t), \qquad (2.21a)$$

where $\vec{q} = \vec{q}_1 - \vec{q}_2 = 2q_0\hat{x} \equiv q\hat{x}$. $U(\vec{r},t)$ is the sum of two terms. One corresponds to a uniform energy density, of no interest with respect to the problem we treat here and that will be discarded in the rest of the paper. The second,

$$U^g(\vec{r},t) = E_1E_2\left(\hat{e}^1\cdot\hat{e}^2\right)\cos(qx)g_0^2(t), \qquad (2.21b)$$

exhibits a periodic spatial dependence with wavevector $\vec{q}$.

Two of the three interactions of $\vec{E}_{int}(\vec{r},t)$ with the liquid are given in term of $U^g(\vec{r},t)$. The first one is the energy absorption by the liquid. As this absorption is very weak, the amount of energy absorbed per unit length along the $\hat{z}$ direction is uniform. This energy, absorbed by overtones or combinations of intramolecular vibrations, decays into thermal energy on a picosecond time scale. The rate of local heat absorption is thus proportional to the energy density and we write it in the form

$$\Sigma_{heat} = 2HU^g(\vec{r},t), \qquad (2.22)$$

where H, the heat-absorption coefficient, is a positive constant that depends on the molecular species and on the laser frequency. This heat acts as an external source that needs to be added to the r.h.s. of equation (2.17) for the energy balance to be satisfied

$$C_V\otimes\dot{T} - T_m\beta\otimes\dot{\rho} - \lambda\Delta T = 2HU^g. \qquad (2.23)$$

We shall later on refer to the term proportional to H in the response functions, $R_{ij,kl}(t)$ (to be defined in Sect. 3), as the heat mechanism.

The second effect to be considered is the optical analogue of the electrostrictive effect, that results from the interaction of $\vec{E}_{int}(\vec{r},t)$ with the relative susceptibility of the liquid at optical frequency, $\chi\bar{\bar{I}}$. At every point, $\vec{E}_{int}(\vec{r},t)$ creates a potential

$$V_{pot}(\vec{r},t) = -\frac{\varepsilon_0}{2}\chi\,U(\vec{r},t), \qquad (2.24a)$$

where ε_0 is the vacuum polarisability. This potential varies in space owing to $U^g(\vec{r},t)$. The liquid tends to minimise its energy with respect to this potential by building up a density modulation with the same wavevector and this potential leads to a contribution to the pressure (see Appendix A) that can be written

$$-2KU^g(\vec{r},t). \qquad (2.24b)$$

We show in Appendix A (Eq. (A.6)) that, when the deviations from equilibrium of the relative dielectric tensor are expressed by equation (3.2), K, the electrostrictive coefficient, is simply proportional to $a = \left.\frac{\partial\chi}{\partial\rho}\right)_T$. The proportionality factor is positive as is also, in general, this derivative. As the pressure contributes to $\bar{\bar{\sigma}}$ with a negative sign, the optical electrostrictive effect modifies equation (2.18) into

$$\bar{\bar{\sigma}} = (-c_i^2\delta\rho - \rho_m\beta\otimes\delta T + \eta_b\otimes\mathrm{div}\,\vec{v})\bar{\bar{I}} + \eta_s\otimes\bar{\bar{\tau}} - \mu\otimes\dot{\bar{\bar{Q}}} + 2KU^g\bar{\bar{I}}. \qquad (2.24c)$$

The third interaction of $\vec{E}_{int}(\vec{r},t)$ with the liquid is the Optical Kerr Effect (OKE). The r.h.s. of equation (2.9) can be seen as the formal derivative of a non-equilibrium free-energy density with respect to $\bar{\bar{Q}}$ for the torque and with respect to $\dot{\bar{\bar{Q}}}$ for the two dissipative terms in $\bar{\bar{\tau}}$ and in $\dot{\bar{\bar{Q}}}$. The interaction of $\vec{E}_{int}(\vec{r},t)$ with the anisotropic part of the molecular polarisability adds a term to the free energy density that can be written

$$\Sigma_{\mathrm{OKE}} = -2F\vec{E}\cdot\bar{\bar{Q}}\cdot\vec{E}. \qquad (2.25)$$

where F is the OKE coefficient. The torque tensor related to this additional free-energy density reads

$$-\frac{\partial\Sigma_{\mathrm{OKE}}}{\partial Q_{ij}} = 2F\left[\overline{\mathrm{Re}\left(E_{int}(\vec{r},t)_i\right)\mathrm{Re}\left(E_{int}(\vec{r},t)_j\right)} - \frac{\delta_{ij}}{3}U(\vec{r},t)\right] \equiv 2F\left(\bar{\bar{T}}\right)_{ij}, \qquad (2.26)$$

where the second factor in the square bracket originates from the fact that the l.h.s. acts as a torque on a traceless tensor so that it must also be a traceless tensor. As was the case for equation (2.21a), equation (2.26) contains a term $T^{u}_{ij}(\vec{r},t)$, uniform throughout the liquid, and a term $T^{g}_{ij}(\vec{r},t)$ that has the form of a grating and which is readily expressed as

$$T^{g}_{ij}(\vec{r},t) = \frac{E_1 E_2}{2}\cos(qx) g_0^2(t) \times \left[\hat{e}^1_i \hat{e}^2_j + \hat{e}^2_i \hat{e}^1_j - \frac{2}{3}\delta_{ij}\left(\hat{e}^1 . \hat{e}^2\right)\right] \equiv \left(\bar{\bar{T}}^{g}\right)_{ij}, \quad (2.27)$$

where $\hat{e}^1_i$ (respectively $\hat{e}^2_j$) is the ith (respectively jth) component of $\hat{e}^1$ (respectively $\hat{e}^2$). Equation (2.9) has thus to be modified into

$$\ddot{\bar{\bar{Q}}} = -\omega_0^2 \bar{\bar{Q}} - \Gamma' \otimes \dot{\bar{\bar{Q}}} + \Lambda' \mu \otimes \bar{\bar{\tau}} + 2F\bar{\bar{T}}^{g}. \quad (2.28)$$

Owing to the spatial dependence of $\bar{\bar{T}}^{g}(\vec{r},t)$, the latter induces a periodic orientational grating that launches phonons through the rotation-translation relaxation function (see Sects. 3 and 4).

In Appendix A, we show that the anisotropic part of the relative molecular polarisability tensor, b, which enters into the expression of the deviation of the relative dielectric tensor from equilibrium, equation (3.2), can be related to the OKE coefficient F in a similar way as $\left.\frac{\partial\chi}{\partial\rho}\right)_T$ is related to the electrostrictive coefficient K.

2.4 Discussion of the role of the sources

In the preceding section, we have used the most general form for the amplitude and the polarisation of $\vec{E}_1$ and $\vec{E}_2$. In fact, we only need to find how many different polarisations and amplitudes are necessary to obtain all the information contained in a HD-TG experiment. First, equations (2.21b, 2.27) show that the sources only depend on the product E_1E_2: as no information is gained by varying the relative amplitude of the two fields, we put, for simplicity, $E_1 = E_2 = E$ for the rest of the paper. The only remaining variables are then the polarisation vectors.

Since the three equations (2.23, 2.24c, 2.28) are linear, we are left with the problem of decomposing the sources into irreducible elements, a weighted sum of which will represent any configuration of the polarisation vectors. Because $\vec{q}_1$ and $\vec{q}_2$ are nearly parallel to $\hat{z}$, the projection of $\hat{e}^1$ and $\hat{e}^2$ on that direction can be neglected and one can write $U^{g}(\vec{r},t)$ and $T^{g}_{ij}(\vec{r},t)$ under the approximate form

$$U^{g}(\vec{r},t) = E^2 \cos(qx) g_0^2(t)\left[\hat{e}^1_x \hat{e}^2_x + \hat{e}^1_y \hat{e}^2_y\right], \quad (2.29)$$

$$T^{g}_{ij}(\vec{r},t) = E^2 \cos(qx) g_0^2(t)\left[\hat{e}^1_x \hat{e}^2_x C_{ij}(\hat{x}) + \hat{e}^1_y \hat{e}^2_y C_{ij}(\hat{y}) + \frac{\left(\hat{e}^1_x \hat{e}^2_y + \hat{e}^1_y \hat{e}^2_x\right)}{2}\left(\delta_{ix}\delta_{jy} + \delta_{iy}\delta_{jx}\right)\right]. \quad (2.30)$$

Equations (2.29, 2.30) make it clear that the effect of two pumps with arbitrary polarisation vectors can be decomposed into the sum of three independent elements. One is $\hat{e}^1_x \hat{e}^2_x$, and this corresponds to the two pumps polarised along $\hat{x}$, i.e. in the scattering plane. The second element is $\hat{e}^1_y \hat{e}^2_y$, where the two pumps are polarised along $\hat{y}$ i.e. perpendicular to the scattering plane. The last one is $\hat{e}^1_x \hat{e}^2_y + \hat{e}^1_y \hat{e}^2_x$ and it corresponds, for instance, to one pump polarised along $\hat{x}$ and the second along $\hat{y}$. We shall thus only need to consider these three independent configurations in the following sections.

3 The transient grating response

3.1 Introduction

We calculate the different response functions that can be measured in a TG experiment with heterodyne detection (see e.g. [11]) by selecting the polarisation of pumps, probe and detected beams (see e.g. [12]).

In such an experiment, the different sources introduced in Section 2 are expressed via two modulations, of equal amplitudes and respective wavevectors $\vec{q}$ and $-\vec{q}$, of U^{g} and $\bar{\bar{T}}^{g}$. Within the general linear response formalism, the $\vec{q}$ modulation (with electric fields $E_1\hat{e}^1$ and $E_2\hat{e}^2$) acting at time $t = 0$, generates at time t a similar modulation of the ij component of the dielectric tensor, $\delta\varepsilon_{ij}$, linearly related to the electric fields of the two pumps through

$$\delta\varepsilon_{ij}(\vec{q},t) = R_{ij,kl}(\vec{q},t) E_1 E_2 \frac{\hat{e}^1_k \hat{e}^2_l + \hat{e}^2_k \hat{e}^1_l}{2}, \quad (3.1a)$$

where a sum over repeated Cartesian indices is implied. An identical expression holds for $-\vec{q}$. The previous expression also implies the impulsive limit for the excitation (i.e. the square of the envelope function, $g_0^2(t)$, introduced in equations (2.19), is identified with a delta function) and the Cartesian indices refer here to the axes defined in Figure 1.

As recalled in Appendix B, for $\vec{q}$ parallel to $\hat{x}$, and for a spatially local approximation of the dielectric function, $R_{ij,kl}(\vec{q},t)$, the TG dielectric response function for wavevector $\vec{q}$, has seven independent elements, namely,

$$\begin{aligned} R_{xx,xx}(\vec{q},t),\ R_{yy,yy}(\vec{q},t) &= R_{zz,zz}(\vec{q},t),\\ R_{yy,zz}(\vec{q},t) &= R_{zz,yy}(\vec{q},t),\\ R_{xx,yy}(\vec{q},t) &= R_{xx,zz}(\vec{q},t),\\ R_{yy,xx}(\vec{q},t) &= R_{zz,xx}(\vec{q},t),\\ R_{xy,xy}(\vec{q},t) &= R_{xz,xz}(\vec{q},t),\ R_{yz,yz}(\vec{q},t). \end{aligned} \quad (3.1b)$$

Since $\hat{e}^1$ and $\hat{e}^2$ have no component parallel to $\hat{z}$, only the first six elements appearing in equation (3.1b) can be launched by the pump beams. Furthermore, conventionally, (see, e.g., [11,12]), the probe beam also propagates in the Π plane of Figure 1 with a wavevector nearly parallel to $\hat{z}$ so that the same is true for the diffracted beam. Their polarisation vectors (corresponding respectively to the indices i and j for the probe and diffracted beams) have thus, again, no z component. Consequently, only the five elements of equation (3.1b) not containing a z index can be detected and each can be detected independently from the others. Indeed, with the usual light scattering terminology, since an index x (respectively y) can be associated with the H (respectively V) polarisation of the corresponding field, the five independent elements can be obtained by using the (*HH, HH*), (*VV, VV*), (*HH, VV*), (*VV, HH*) and (*HV, HV*) configurations for the two pumps, probe and diffracted beams, respectively, i.e. with four "parallel polarisation" and one "perpendicular polarisation" of these beams.

As previously discussed [25], symmetry considerations require that the fluctuations of the relative dielectric tensor only related to density and/or orientational thermal fluctuations should be written, in leading order, as

$$\delta\bar{\bar{\varepsilon}}(\vec{r},t) = a\delta\rho(\vec{r},t)\bar{\bar{I}} + b\bar{\bar{Q}}(\vec{r},t). \tag{3.2}$$

We consistently use the same expression when $\delta\rho(\vec{r},t)$ and $\bar{\bar{Q}}(\vec{r},t)$ are modulations created by the sources. As already indicated in Section 2.3, the coefficient a equals the quantity $\left.\frac{\partial\chi}{\partial\rho}\right)_T$ introduced below equation (2.24b), while b is the anisotropic part of the relative polarisability per molecule.

Equation (3.2) opens the route to calculate the different response functions listed in equation (3.1b) using the generalised Navier-Stokes equations with the source terms included. We first explain why equation (3.2) and the different sources give rise to different response functions, depending on the polarisation of the different beams.

Since heat absorption and optical electrostriction, which are isotropic, exist only for "parallel polarisation" of the pumps, they only induce modulations of diagonal tensors, which couple to longitudinal modes but not to transverse ones. They thus lead to a density grating and to a non-zero value of Q_{xx}: $\delta\varepsilon_{xx}$ has a non-zero Q_{xx} contribution. Furthermore, since $\bar{\bar{Q}}$ is a traceless tensor, a non-zero value of Q_{xx} leads to a non-zero value for Q_{yy}: $\delta\varepsilon_{yy}$ also has a molecular orientation contribution, with a sign opposite to that entering into $\delta\varepsilon_{xx}$. Thus, each point of the grating exhibits optical anisotropy.

The third source, the orientational torque, is different as it can couple to transverse as well as to longitudinal modes. For parallel polarisation of the pumps, non-zero values of Q_{xx} and Q_{yy} are generated. Via the rotation-translation coupling mechanism, this non-zero Q_{xx} element is also the source of a longitudinal mode but, as the elements of $\bar{\bar{C}}$ depend on the polarisation of the pumps, the four elements $R_{ii,jj}(\vec{q},t)$ are not identical. For crossed polarisation of the pumps, the sole source is the orientational torque that only induces non-zero values of Q_{xy} and τ_{xy}. A transverse mode is generated. There is no density modulation and only Q_{xy} contributes to the local dielectric tensor: $\delta\bar{\bar{\varepsilon}}$ has only non-zero off diagonal elements. The calculation of $R_{xy,xy}(\vec{q},t)$ is simpler than for the parallel cases and it will be performed in Appendix C.

3.2 Calculation of $\mathbf{R_{yy,yy}(\vec{q},t)}$

We compute, in this section, $\delta\varepsilon_{yy}(\vec{q},t)$ when the polarisation of the two pumps is perpendicular to the scattering plane. The calculation is easily performed using Laplace-Transform techniques (see Eq. (2.10)). The functions we are interested in are the modulations of the mass density, $\delta\rho(\vec{r},t)$, of the local temperature, $\delta T(\vec{r},t)$, and of some components of $\bar{\bar{Q}}(\vec{r},t)$ as well as their Fourier-Transforms. Furthermore, since we deal with a stimulated experiment, we assume that the modulations generated by the external sources are much more important than the corresponding spontaneous fluctuations: the initial values of all those quantities will be taken equal to zero. Finally, as the pumps are polarised along $\hat{y}$, the two components of $\bar{\bar{C}}$ entering into the calculation take the values $C_{xx} = -1/3$ and $C_{yy} = 2/3$.

Equations (2.3, 2.4) may be grouped into

$$-\delta\ddot{\rho}(\vec{r},t) = \operatorname{div}\operatorname{div}\bar{\bar{\sigma}}(\vec{r},t), \tag{3.3a}$$

which, with the use of a Fourier-Laplace Transform, reads

$$\omega^2\delta\rho(\vec{q},\omega) = -q^2\sigma_{xx}(\vec{q},\omega). \tag{3.3b}$$

This last equation implies that, in equation (2.24c), one needs to calculate $\dot{Q}_{xx}(\vec{r},t)$ as well as $\tau_{xx}(\vec{r},t)$, while the computation of $\delta\varepsilon_{yy}(\vec{r},t)$ requires also the knowledge of $Q_{yy}(\vec{r},t)$ and $\tau_{yy}(\vec{r},t)$. As the sources only launch longitudinal modes of wavevectors $\pm\vec{q}$, ($\vec{v} \parallel \vec{q}$), one has

$$\tau_{xx}(\vec{r},t) = \frac{4}{3}\operatorname{div}\vec{v}(\vec{r},t) = -\frac{4}{3}\frac{\delta\dot{\rho}(\vec{r},t)}{\rho_m}, \tag{3.4a}$$

$$\tau_{yy}(\vec{r},t) = -\frac{2}{3}\operatorname{div}\vec{v}(\vec{r},t) = \frac{2}{3}\frac{\delta\dot{\rho}(\vec{r},t)}{\rho_m}. \tag{3.4b}$$

Similarly, for the orientational variable, equation (2.28) yields

$$Q_{xx}(\vec{q},\omega) = -\frac{4}{3}\frac{\Lambda'}{\rho_m}r(\omega)\delta\rho(\vec{q},\omega) - \frac{i}{3}\frac{FE^2}{D(\omega)}, \tag{3.5a}$$

$$Q_{yy}(\vec{q},\omega) = \frac{2}{3}\frac{\Lambda'}{\rho_m}r(\omega)\delta\rho(\vec{q},\omega) + \frac{2i}{3}\frac{FE^2}{D(\omega)}, \tag{3.5b}$$

with

$$D(\omega) = \omega_R^2 + \omega\Gamma'(\omega) - \omega^2, \tag{3.6a}$$

$$r(\omega) = \omega\mu(\omega)\left[D(\omega)\right]^{-1}, \tag{3.6b}$$

where $\mu(\omega)$ and $\Gamma'(\omega)$ are the Laplace-Transforms of the memory function $\mu(t)$ and $\Gamma'(t)$. The r.h.s. of equation (3.6b) implies that $r(\omega)$ characterises the rotation-translation coupling.

Finally, with similar notations, the Fourier-Laplace Transform of the heat equation, equation (2.23), reads

$$\left(\omega C_V(\omega) + \lambda q^2\right)\delta T(\vec{q},\omega) = T_m\omega\beta(\omega)\delta\rho(\vec{q},\omega) + iHE^2. \tag{3.7}$$

Inserting equations (3.5a, 3.7) into the Fourier-Laplace Transform of the xx component of equation (2.24c) yields, with the help of equation (3.4a),

$$\begin{aligned}\sigma_{xx}(\vec{q},\omega) = \\ &-\left[c_i^2 + \rho_m^{-1}\omega\eta_L(\omega) - \frac{iT_m\rho_m\omega\beta^2(\omega)}{\omega C_V(\omega)+\lambda q^2}\right]\delta\rho(\vec{q},\omega) \\ &+\left[-\frac{\rho_m\beta(\omega)H}{\omega C_V(\omega)+\lambda q^2} + i\left(K+\frac{F}{3}r(\omega)\right)\right]E^2, \qquad (3.8)\end{aligned}$$

where we have defined the longitudinal viscosity, $\eta_L(\omega)$, by

$$\eta_L(\omega) = \eta_b(\omega) + \frac{4}{3}\eta_T(\omega), \qquad (3.9a)$$

and the transverse viscosity, $\eta_T(\omega)$, by

$$\eta_T(\omega) = \eta_s(\omega) - \frac{\Lambda'}{\omega}D(\omega)r^2(\omega). \qquad (3.9b)$$

Substituting equation (3.8) into equation (3.3b), one obtains

$$\begin{aligned}\delta\rho(\vec{q},\omega) = -i\Bigg[\Bigg(&i\frac{\rho_m\beta(\omega)}{\lambda}\frac{H}{1+i\omega\tau_h(q,\omega)} \\ &+q^2\left(K+\frac{F}{3}r(\omega)\right)\Bigg)E^2\Bigg]P'_L(\vec{q},\omega), \qquad (3.10)\end{aligned}$$

with

$$P'_L(\vec{q},\omega) = \left[\omega^2 - q^2\left(c_i^2 + \rho_m^{-1}\omega\eta_L(\omega) + g(q,\omega)\right)\right]^{-1}, \qquad (3.11)$$

$$g(q,\omega) = -i\rho_m T_m\frac{\beta^2(\omega)}{C_V(\omega)}\frac{i\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}, \qquad (3.12)$$

$$\tau_h(q,\omega) = -i\frac{C_V(\omega)}{\lambda q^2}. \qquad (3.13)$$

$\tau_h(q,\omega)$ has the dimension of a time, namely the heat-diffusion time for a grating with wavevector $\vec{q}$. $P'_L(\vec{q},\omega)$ is the full phonon propagator; it generalises the usual adiabatic longitudinal phonon propagator, (see [24,25] and Eq. (4.4)) by introducing through $g(q,\omega)$ the heat-diffusion process and by modifying the adiabatic sound velocity, c_a, into the isothermal one, c_i.

Equations (3.10) can be inserted into equation (3.5b) to obtain $Q_{yy}(\vec{q},\omega)$. With the help of $\delta\varepsilon_{yy}(\vec{r},t)$, equation (3.2), one finally obtains

$$\delta\varepsilon_{yy}(\vec{q},t) = E^2R_{yy,yy}(\vec{q},t) = E^2LT^{-1}\left[R_{yy,yy}(\vec{q},\omega)\right], \qquad (3.14a)$$

where, by definition[6]

$$LT^{-1}\left[A(\omega)\right] = \frac{2}{\pi}\int_0^\infty \mathrm{Im}\left[A(\omega)\right]\cos(\omega t)d\omega, \qquad (3.14b)$$

while

$$\begin{aligned}R_{yy,yy}(\vec{q},\omega) = \frac{2i}{3}\frac{bF}{D(\omega)} - i\left[a + \frac{2}{3}\frac{\Lambda'}{\rho_m}br(\omega)\right]P'_L(\vec{q},\omega) \\ \times\left[i\frac{\rho_m\beta(\omega)}{\lambda}\frac{H}{1+i\omega\tau_h(q,\omega)} + q^2\left(K+F\frac{r(\omega)}{3}\right)\right]. \\ (3.14c)\end{aligned}$$

3.3 Calculation of $\mathbf{R_{xx,yy}(\vec{q},t)}$, $\mathbf{R_{xx,xx}(\vec{q},t)}$ and $\mathbf{R_{yy,xx}(\vec{q},t)}$

We calculate now the three other elements of the response function that can be measured when selecting "parallel polarisation" of the pumps. To derive $R_{xx,yy}(\vec{q},t)$, we need to evaluate $\delta\varepsilon_{xx}(\vec{q},\omega)$ with $\hat{y}$ polarised pumps, a computation quite similar to the previous one except for the use of $Q_{xx}(\vec{q},\omega)$, equation (3.5a), instead of $Q_{yy}(\vec{q},\omega)$. To obtain $R_{xx,xx}(\vec{q},t)$ and $R_{yy,xx}(\vec{q},t)$, we need to evaluate $\delta\varepsilon_{xx}(\vec{q},\omega)$ and $\delta\varepsilon_{yy}(\vec{q},\omega)$, respectively, with $\hat{x}$ polarised pumps. The two components of $\bar{\bar{C}}$ which enter into the calculation are then $C_{xx} = 2/3$ and $C_{yy} = -1/3$.

The four $R_{ii,jj}(\vec{q},t)$ can then be compressed into a single formula. Defining $\varepsilon_p = 1$, ($\varepsilon_p = -1$) for the probe and diffracted beams polarised along $\hat{y}$ ($\hat{x}$) and $\varepsilon_{ex} = 1$, ($\varepsilon_{ex} = -1$) for the pumps (excitation mechanism) polarised along $\hat{y}$ ($\hat{x}$), the four response functions can be expressed as

$$R_{ii,jj}(\vec{q},t) = LT^{-1}\left[R_{ii,jj}(\vec{q},\omega)\right], \qquad (3.15)$$

with

$$R_{ii,jj}(\vec{q},\omega) = R^{(1)}_{ii,jj}(\omega) + R^{(2)}_{ii,jj}(\vec{q},\omega), \qquad (3.16)$$

$$R^{(1)}_{ii,jj}(\omega) = b\frac{iF}{2}\frac{(1+3\varepsilon_p\varepsilon_{ex})}{3}D^{-1}(\omega), \qquad (3.17a)$$

$$R^{(2)}_{ii,jj}(\vec{q},\omega) = i\left[a + \frac{\Lambda'}{\rho_m}b\frac{(3\varepsilon_p-1)}{3}r(\omega)\right]P'_L(\vec{q},\omega)A(\vec{q},\omega), \qquad (3.17b)$$

$$\begin{aligned}A(\vec{q},\omega) = -\Bigg[&i\frac{\rho_m\beta(\omega)}{\lambda}\frac{H}{1+i\omega\tau_h(q,\omega)} \\ &+q^2\left(K+\frac{F}{2}\frac{(3\varepsilon_{ex}-1)}{3}r(\omega)\right)\Bigg]. \qquad (3.17c)\end{aligned}$$

$R^{(1)}_{ii,jj}(\omega)$ is the pure orientational dynamics of the molecules, independent of the wavevector, which can also be measured in an OKE experiment. Therefore, we define

$$R_{\mathrm{OKE}}(t) = LT^{-1}[iD^{-1}(\omega)] \qquad (3.18a)$$

as the elementary response function, generated by the torque source, detected by the local mean orientation of the molecules and which does not depend on the wavevector.

Similarly, $R^{(2)}_{ii,jj}(\vec{q},t)$ corresponds to longitudinal modes launched by the three sources (whence the appearance of H, K and F in Eq. (3.17c)) and detected through

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[6] Since our convention of the Laplace-Transform has an additional imaginary i term in the exponent, the cosine transform of the imaginary part of $A(\omega)$ can easily be numerically performed.

density (term in a) and orientation (term in b) modulations. In order to ease the further analysis of $R_{ii,jj}(\vec{q},t)$, it is convenient to separate it into the weighted sum of seven "elementary response functions" (ERFs), one of them being $R_{\mathrm{OKE}}(t)$. Each of them is labelled according to a given excitation mechanism (electrostriction, K, torque, F, or heat absorption, H) and to the modulation (density, $\delta\rho$, or orientation tensor, $\bar{\bar{Q}}$) that produces the dielectric variation. Their generic name, ERF, originates from the fact that they depend neither on the five coefficients H, K, F, a, and b, nor on the polarisation of the experiment.

Let us thus define the six remaining ERFs which, contrary to $R_{\mathrm{OKE}}(t)$, all depend on the wavevector.

$$R_{dens-ther}(\vec{q},t) = LT^{-1}\left[\frac{\beta(\omega)P'_L(\vec{q},\omega)}{[1+i\omega\tau_h(q,\omega)]}\right] \tag{3.18b}$$

is the ERF that originates from the heat absorption with a density-modulation detection mechanism (term in aH of (Eqs. (3.17)). This response is usually referred to as the ISTS response function [4]; similarly,

$$R_{or-ther}(\vec{q},t) = LT^{-1}\left[\frac{\beta(\omega)r(\omega)P'_L(\vec{q},\omega)}{[1+i\omega\tau_h(q,\omega)]}\right] \tag{3.18c}$$

originates from the heat absorption, the detection mechanism being a net local molecular orientation modulation (term in bH). Next,

$$R_{dens-dens}(\vec{q},t) = LT^{-1}\left[-iP'_L(\vec{q},\omega)\right] \tag{3.18d}$$

is the ERF that corresponds to the action of the optical electrostriction (density modulation) detected by a density modulation (term in aK). It is usually called the ISBS response function [3]. Similarly,

$$R_{or-dens}(\vec{q},t) = LT^{-1}\left[-ir(\omega)P'_L(\vec{q},\omega)\right] \tag{3.18e}$$

is the ERF that originates from the same density modulation and which is detected by a net local molecular orientation (term in bK). Owing to their identical analytical form

$$R_{dens-or}(\vec{q},t) = R_{or-dens}(\vec{q},t), \tag{3.18f}$$

where $R_{dens-or}(\vec{q},t)$ is the ERF generated by the torque source and detected by a density modulation (term in aF). Finally,

$$R_{or-or}(\vec{q},t) = LT^{-1}\left[-ir(\omega)P'_L(\vec{q},\omega)r(\omega)\right] \tag{3.18g}$$

is the second ERF generated by the torque source and detected by a net local molecular orientation but, contrary to equation (3.18a), it involves a longitudinal mode (term in bF of Eq. (3.17c)). Let us stress that these last two ERFs, equations (3.18f, 3.18g), originate from the $Fr(\omega)$ term of equation (3.17c) and correspond to longitudinal modes launched by the OKE through the orientation-translation coupling.

Also, equations (3.17) show that the four $R_{ii,jj}(\vec{q},t)$ functions are all different. In particular, $R^{(2)}_{xx,yy}(\vec{q},t) \neq R^{(2)}_{yy,xx}(\vec{q},t)$: there is no symmetry between the pumps and the detection mechanism. In fact, we shall point out in Section 4 that some symmetry can be identified in equations (3.17) because of equation (A.16), which relates F, K, a, and b (see Appendix A).

With the help of these ERFs, $R_{ii,jj}(\vec{q},t)$ can be expressed as

$$R_{ii,jj}(\vec{q},t) = R^{(1)}_{ii,jj}(t) + R^{(2)}_{ii,jj}(\vec{q},t), \tag{3.19a}$$

with

$$R^{(1)}_{ii,jj}(t) = b\frac{F}{2}\left(\frac{1+3\varepsilon_p\varepsilon_{ex}}{3}\right)R_{\mathrm{OKE}}(t), \tag{3.19b}$$

and

$$\begin{aligned} R^{(2)}_{ii,jj}(\vec{q},t) &= \frac{\rho_m}{\lambda}\,a\,H\,R_{dens-ther}(\vec{q},t) \\ &+\frac{\Lambda'}{\lambda}\,b\,H\,\frac{3\varepsilon_p-1}{3}\,R_{or-ther}(\vec{q},t) + q^2\Bigg(a\,K\,R_{dens-dens}(\vec{q},t) \\ &\quad+\frac{\Lambda'}{\rho_m}\,b\,K\,\frac{3\varepsilon_p-1}{3}\,R_{or-dens}(\vec{q},t)\Bigg) \\ &\quad+q^2\Bigg(a\frac{F}{2}\frac{3\varepsilon_{ex}-1}{3}\;R_{dens-or}(\vec{q},t) \\ &+\frac{\Lambda'}{\rho_m}\,b\frac{F}{2}\frac{3\varepsilon_{ex}-1}{3}\,\frac{3\varepsilon_p-1}{3}\;R_{or-or}(\vec{q},t)\Bigg). \end{aligned} \tag{3.19c}$$

4 Discussion — Study of the elementary response functions

4.1 Preliminary remarks

The purpose of the present section is to link the expressions obtained in Section 3 for $R_{ii,jj}(\vec{q},t)$ with results obtained in [24,25] in order to achieve two goals. One is the study of the time evolution of the different ERFs. The second is the separation of $R_{ii,jj}(\vec{q},t)$ into the sum of two functions. One, that we shall call the "generalised ISBS" response function, is the contribution of the electrostriction and the OKE sources to $R_{ii,jj}(\vec{q},t)$. We shall relate it, through the Fluctuation-Dissipation theorem, to Brillouin spectra discussed in [25]. The other function, the "generalised ISTS" response function, originates from the heat absorption. It has no equivalent in the Brillouin spectra and contains information on $\eta_L(t)$ and $\mu(t)$ in the $10-10^4$ ns time scale, as we shall discuss in Section 4.4.

The relation between the six distinct ERFs, equations (3.18), and quantities computed in [25] requires a preliminary discussion because these last quantities have not been derived with the same set of Navier-Stokes equations: [25] deals with a Brillouin-scattering experiment, the frequency domain of which is small enough to ignore the energy conservation problem. The set of equations used in [25] is thus equations (2.5, 2.9) in conjunction with equation (3.2). For the same scattering geometry as used in Figure 1 ($\hat{q}_2$ and $\hat{q}_1$ being now the directions of the incident and scattered beams), one obtains using those equations that, for instance, for a y polarisation of the two beams ($\hat{e}_1 \parallel \hat{e}_2 \parallel \hat{y}$), the scattered intensity is proportional to

$$I_{yy}(\vec{q},\omega) = I_{yy}^{(1)}(\omega) + I_{yy}^{(2)}(\vec{q},\omega), \tag{4.1}$$

with

$$I_{yy}^{(1)}(\omega) = \frac{\mathrm{Im}}{\omega} b^2 \left(1 - \frac{\omega_R^2}{D(\omega)}\right) \langle \left|Q_{yy}^0\right|^2 \rangle, \tag{4.2}$$

$$I_{yy}^{(2)}(\vec{q},\omega) = \frac{1}{\omega}\mathrm{Im}\left\{a^2 + q^2 c_i^2 \left[a + \frac{2\Lambda'}{3\rho_m} br(\omega)\right]\right. \\ \left. \times P_L(\vec{q},\omega)\left[a + \frac{2\Lambda'}{3\rho_m} br(\omega)\right]\right\} \langle \left|\delta\rho^0\right|^2 \rangle \tag{4.3}$$

where

$$P_L(\vec{q},\omega) = \left[\omega^2 - q^2\left(c_a^2 + \rho_m^{-1}\omega\tilde{\eta}_L(\omega)\right)\right]^{-1}. \tag{4.4}$$

In these expressions:

- $\langle \left|Q_{yy}^0\right|^2 \rangle$ is the thermal average of $(Q_{yy}(t))^2$;
- $\langle \left|\delta\rho^0\right|^2 \rangle$ is the corresponding quantity for the density fluctuations of the liquid, and the two quantities are related by

$$\langle \left|Q_{yy}^0\right|^2 \rangle = \frac{4\Lambda'}{3\rho_m}\frac{c_i^2}{\omega_R^2}\langle \left|\delta\rho^0\right|^2 \rangle; \tag{4.5}$$

- c_a and c_i are the adiabatic and the isothermal sound velocities[7], respectively (see Eqs. (2.8, 2.12));
- $\tilde{\eta}_L(\omega)$ is a renormalised longitudinal viscosity (see Eqs. (4.9) below);
- $P_L(\vec{q},\omega)$ is the adiabatic phonon propagator and its relation with $P_L'(\vec{q},\omega)$ will be discussed at the end of this section.

The comparison between equations (3.15–3.17) for $\varepsilon_p = \varepsilon_{ex} = 1$ and equations (4.1–4.3) reveals a great similarity in their structure. In both cases, there exists a first term, $R_{yy,yy}^{(1)}(\omega)$ or $I_{yy}^{(1)}(\omega)$, independent of the wavevector, which corresponds to the orientational dynamics of the molecules uncoupled to the longitudinal phonons. The second terms, $R_{yy,yy}^{(2)}(\vec{q},\omega)$ and $I_{yy}^{(2)}(\vec{q},\omega)$, have a similar structure[8]: both are the products of three factors. The first is the same for the two expressions: in a light-scattering experiment, one detects the fluctuations of the dielectric tensor through the same mechanism as the one that diffracts the probe beam in equation (3.17c). The second factor is a phonon propagator, the form of which differs in the two expressions (compare Eqs. (3.11, 4.4)). The identification of these two propagators in a very large frequency range is a prerequisite to the rest of this Section that will be summarised below and discussed in Appendix E. The main difference between $R_{yy,yy}^{(2)}(\vec{q},\omega)$ and $I_{yy}^{(2)}(\vec{q},\omega)$ is in their last factor: the sources corresponding to a light-scattering experiment are only the density and orientational fluctuations (whence the appearance of terms in a and in b in the last factor of $I_{yy}^{(2)}(\vec{q},\omega)$) instead of being the three sources explicitly mentioned in equation (3.17c).

We show in Appendix E that $P_L'(\vec{q},\omega)$ can be identified with $P_L(\vec{q},\omega)$ for frequencies such that $\omega\tau_h(q,\omega) \geq 1$. This identification requires first to analyse $C_V(\omega)$ and $\beta(\omega)$. We argue in Appendix D, in agreement with [27], that

$$C_V(\omega) = iC_V^{th} - i\omega\delta C_V(\omega), \tag{4.6a}$$

$$\beta(\omega) = i\beta^{th} - i\omega\delta\beta(\omega), \tag{4.6b}$$

where C_V^{th} and β^{th} are the thermodynamic values of the specific heat at constant volume and of the tension coefficient, i.e. the time integral of $C_V(t)$ and $\beta(t)$. $\delta C_V(t)$ and $\delta\beta(t)$ have the usual properties of time correlation functions. This implies, in particular, that the $\omega \to \infty$ limit of $\omega\delta C_V(\omega)$ (resp. $\omega\delta\beta(\omega)$) is real. Furthermore, one has

$$0 < \lim_{\omega\to\infty}\left[\omega\delta C_V(\omega)\right] < C_V^{th}, \tag{4.7}$$

so that $\mathrm{Im}(C_V(\omega = \infty))$ is a positive quantity. A relation similar to equation (4.7) has no a priori reason to hold for the tension coefficient though this is frequently the case and the physical meaning of equations (4.6, 4.7) will be briefly discussed in Appendix D. Appendix E shows that, as long as $\omega\tau_h(q,\omega) \gg 1$, $P_L'(\vec{q},\omega)$ can be identified with $P_L(\vec{q},\omega)$ provided that one relates in equations (4.4, 3.11), c_a^2 to c_i^2 through

$$c_a^2 = c_i^2 + \rho_m T_m \frac{\left(\beta^{th}\right)^2}{C_V^{th}} \equiv \gamma c_i^2, \tag{4.8a}$$

with:

$$\gamma = \frac{C_P^{th}}{C_V^{th}}, \tag{4.8b}$$

which is the usual thermodynamical result [30], C_p^{th} being the specific heat at constant pressure. Similarly, this identification necessitates that $\eta_L(\omega)$ be modified into a renormalised longitudinal viscosity, $\tilde{\eta}_L(\omega)$, with

$$\tilde{\eta}_L(\omega) = \tilde{\eta}_b(\omega) + \frac{4}{3}\eta_T(\omega), \tag{4.9a}$$

$$\rho_m^{-1}\omega\tilde{\eta}_b(\omega) = \rho_m^{-1}\omega\eta_b(\omega) - i\rho_m T_m\left(\frac{\beta^2(\omega)}{C_V(\omega)} - \frac{\beta^2(0)}{C_V(0)}\right). \tag{4.9b}$$

Having performed this identification, we also approximate, up to Section 6.3, $-i\beta(\omega)$ by β^{th} in equations (3.18b, 3.18c), and $-iC_V(\omega)$ by C_V^{th} in equation (3.13). This last approximation implies that the heat

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[7] Since the energy conservation problem was ignored in [25], there was no difference between c_a and c_i and the loose expression "relaxed velocity, c", was used in that paper for those two quantities. When translating results obtained in [25] into the present language, the results of [27] imply that c has to be replaced by c_i at every place in the equations we shall use here, except in the phonon propagator where the adiabatic sound velocity, c_a, appears. All the formulae imported from [25] in the present section have been transformed according to that rule.

[8] Except for a $\delta(\omega)$ contribution in equation (4.3), of no importance at this stage of the discussion.

diffusion time, $\tau_h(q,\omega)$, is no longer frequency dependent. For convenience, we shall simply write it as τ_h. Within such limitations and approximations, we can use the results obtained in [25] on the auto and cross correlation functions of $\delta\rho(\vec{q},\omega)$ and $Q_{ii}(\vec{q},\omega)$ to study the time evolution of the seven different ERFs defined in equations (3.18). This will be done for $R_{\mathrm{OKE}}(t)$ in Section 4.2, for the ERFs involving only the density and the torque sources in Section 4.3, and for those involving the heat source in Section 4.4. Those studies will be partly simplified by the use of relationships that can be derived between some of them. Section 4.5 will finally be devoted to a more global analysis of $R_{ii,jj}(\vec{q},t)$, as explained at the beginning of this section.

The neglect of $\delta C_V(\omega)$ and $\delta\beta(\omega)$, and of the influence of $\omega\tau_h(q,\omega)$ on the phonon propagator, is unjustified for very low frequencies, in particular at low temperature i.e. for long relaxation times. We shall return briefly to this point in Section 6.3.

4.2 Time evolution of $\mathbf{R_{OKE}(t)}$

It was shown in [25] that the dynamics of a diagonal element of the orientational variable contains a part uncoupled from the density fluctuations. This uncoupled dynamics can be expressed (see Eqs. (24, 25) of [25]) as

$$Q_{yy}(\vec{q},\omega)=\frac{1}{\omega}\left(1-\frac{\omega_R^2}{D(\omega)}\right)Q^0_{yy}(\vec{q}), \tag{4.10}$$

where we have used for $Q_{yy}(\vec{q},t=0)$ the general notation

$$f^0\equiv f(t=0). \tag{4.11a}$$

Equation (4.10) yields

$$LT\left[\langle Q_{yy}(\vec{q},t)Q^0_{yy}(\vec{q})^*\rangle\right](\omega)=\frac{1}{\omega}\left(1-\frac{\omega_R^2}{D(\omega)}\right)\langle\left|Q^0_{yy}(\vec{q})\right|^2\rangle, \tag{4.12a}$$

while, by definition

$$\langle\left|Q^0_{yy}(\vec{q})\right|^2\rangle=\langle Q_{yy}(\vec{q},t)Q^0_{yy}(\vec{q})^*>_{t=0}. \tag{4.12b}$$

Our definition of the Laplace Transform implies that

$$LT\left[\dot{f}(t)\right](\omega)=i\left(\omega f(\omega)-f^0\right). \tag{4.12c}$$

Thus, with $f(t)=\langle Q_{yy}(\vec{q},t)Q^0_{yy}(\vec{q})^*\rangle$, equation (4.12a) yields

$$LT\left[\frac{d}{dt}\langle Q_{yy}(\vec{q},t)Q^0_{yy}(\vec{q})^*\rangle\right](\omega)=-\frac{i\omega_R^2}{D(\omega)}\langle\left|Q^0_{yy}(\vec{q})\right|^2\rangle, \tag{4.13a}$$

or, equivalently,

$$R_{\mathrm{OKE}}(t)=-\frac{1}{\omega_R^2}\frac{d}{dt}\frac{\langle Q_{yy}(\vec{q},t)Q^0_{yy}(\vec{q})^*\rangle}{\langle\left|Q^0_{yy}(\vec{q})\right|^2}, \tag{4.13b}$$

where the $q\to 0$ limit can be taken in the r.h.s. of this last equation because the l.h.s. does not depend on $\vec{q}$. Let us remark that, as $D(\omega)$ does not depend on this wavevector, we could have taken already this $q\to 0$ limit in equation (4.10). We have preferred to keep this superfluous dependence up to equation (4.13b) because this form will be useful in Section 4.5.

$R_{\mathrm{OKE}}(t)$ is the strictly orientational response function of the anisotropic molecules to a strong orienting electric field, i.e. it is the thermal mean value of some orientational variable at time t if the latter has been perturbed from equilibrium at time $t=0$. Equation (4.13b) simply expresses the fact that the Fluctuation-Dissipation relation holds for that variable. This remark, used in conjunction with the analytic form of $R_{\mathrm{OKE}}(t)$, equation (3.18a), totally explains the shape and the temperature evolution of that ERF. At short times, $\omega_R t\le\pi/2$, $R_{\mathrm{OKE}}(t)$ behaves as $\frac{1}{\omega_R}\sin(\omega_R t)$: the signal is positive and reaches its maximum in the vicinity of $\omega_R t=\pi/2$. Conversely, for longer times, the correlation function has a monotonic decay, characterised by the rotational relaxation time, τ_R. In this time window, $R_{\mathrm{OKE}}(t)$ has amplitude that decreases as τ_R^{-1} because of the time derivative appearing in equation (4.13b).

This time and temperature evolution of $R_{\mathrm{OKE}}(t)$ is exemplified in Figure 2 that has been computed with the help of equation (3.18a). $D(\omega)$ is given by equation (3.6a) and we express $\Gamma'(\omega)$ according to a model of the rotational dynamics used in [23]:

$$\Gamma'(\omega)=\frac{\Gamma_0^2}{\omega}\left[1-\left(\frac{1}{1+i\omega\tau_R}\right)^{\beta}\right]+i\nu_0. \tag{4.14}$$

In this model, Γ_0, ω_R, ν_0, and β are assumed to be temperature independent, and are given values $\omega_R=\Gamma_0=2\pi$ THz, $\nu_0=10\pi$ THz, while $\beta=0.7$. The temperature evolution is taken into account through τ_R, which varies by factors 10^2 from 10^{-1} ns to 10^5 ns.

The results are represented in Figure 2 on a log-log scale. After a linear increase independent of τ_R, $R_{\mathrm{OKE}}(t)$ passes through a maximum around 10^{-3} ns and then decreases. The α-relaxation regime, represented, in the frequency space, by the bracketed term of equation (4.14), appears as the plateau followed by an abrupt decrease visible for every value of τ_R. We have verified that the corresponding part of the response function follows the "time-temperature" superposition scaling characteristic of the OKE response [31]: once multiplied by τ_R and plotted on a t/τ_R scale, the rescaled α-relaxation parts of the response functions perfectly superpose each other, for all temperatures (values of τ_R). The part of $R_{\mathrm{OKE}}(t)$ accessible to a TG-experiment begins in the vicinity of 1 ns: at the highest temperatures, this time window corresponds to the α-relaxation regime, and such a regime does not seem to have been recorded in any TG-experiment performed with parallel polarisation of the pumps. At lower temperatures, the signal amplitude decreases so much that it cannot be detected.

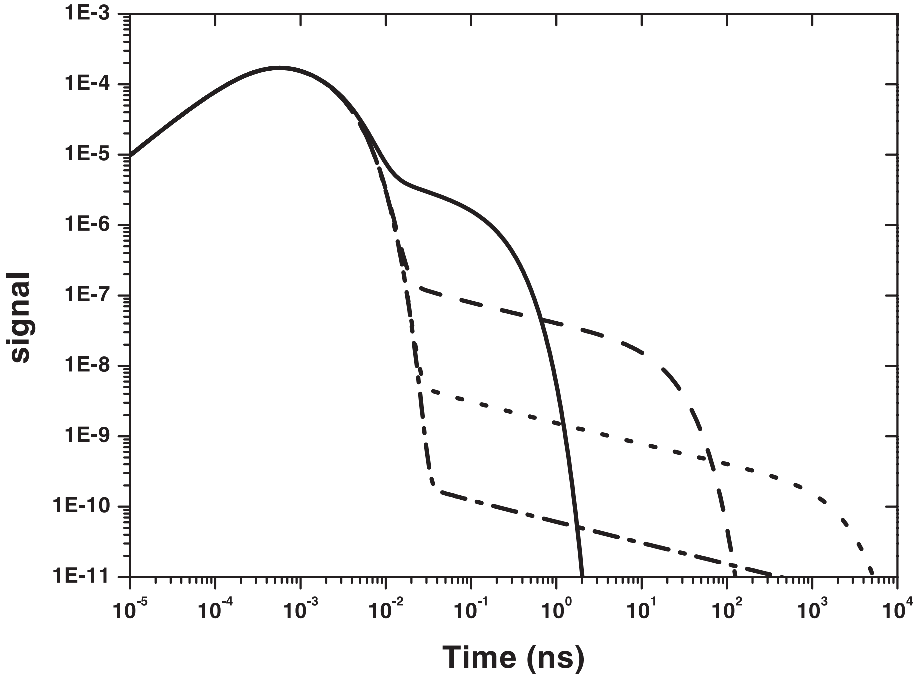


Fig. 2. $R_{\mathrm{OKE}}(t)$ vs. time on a log-log scale. $R_{\mathrm{OKE}}(t)$ is shown for values of the α-relaxation time of the orientational function, τ_R, equal to 10^{-1} ns (——), 10 ns (– – –), 10^3 ns (· · · · ·), and 10^5 ns (– · – · –).

4.3 Time evolution of $\mathbf{R_{dens-dens}(\vec{q},t)}$, $\mathbf{R_{or-dens}(\vec{q},t)}$, $\mathbf{R_{dens-or}(\vec{q},t)}$ and $\mathbf{R_{or-or}(\vec{q},t)}$

We now study the ERFs contained in equations (3.19) related to the electrostrictive and OKE sources. We start with $R_{dens-dens}(\vec{q},t)$, which is the inverse Laplace-Transform of $-iP_L(\vec{q},\omega)$. According to equation (29a) of [25], one has

$$\frac{1}{\omega}\left[1+q^2c_i^2P_L(\vec{q},\omega)\right]\langle\left|\delta\rho^0(\vec{q})\right|^2\rangle = LT\left[\langle\delta\rho(\vec{q},t)\delta\rho^0(\vec{q})^*\rangle\right](\omega), \quad (4.15)$$

where the imaginary part of the l.h.s. of this equation is the a^2 contribution to $I_{yy}^{(2)}(\vec{q},\omega)$, equation (4.3), and where, in the long wavelength limit considered here, the $q=0$ limit of $\langle\left|\delta\rho^0(\vec{q})\right|^2\rangle$ can be taken. Using equation (4.12c), one easily obtains

$$R_{dens-dens}(\vec{q},t) = \frac{-1}{q^2c_i^2}\frac{d}{dt}\frac{\langle\delta\rho(\vec{q},t)\delta\rho^0(\vec{q})^*\rangle}{\langle\left|\delta\rho^0\right|^2\rangle}. \quad (4.16)$$

This equation has the expected form: $R_{dens-dens}(\vec{q},t)$, which is the thermal mean value of the density modulation at time t created by another density modulation at time $t=0$ is proportional to the time derivative of the corresponding correlation function, with a negative pre-factor.

Equation (4.16) provides an easy way of understanding the time and temperature variation of $R_{dens-dens}(\vec{q},t)$. The density-density correlation function describes the time evolution of a longitudinal phonon with effective frequency $\nu_B=\omega_B/2\pi$, wavevector q and decay constant Γ. The decay of this phonon is mostly governed by τ_{anh}, which slowly varies with temperature and is proportional to q^{-2}. This is not true in the region where $\omega_B\tau_L\approx 1$, in which case the phonon is strongly damped by the structural relaxation. Thus, in complete similarity with the case of $R_{\mathrm{OKE}}(t)$, at short times ($\omega_Bt\le 1$), $R_{dens-dens}(\vec{q},t)$ will increase as $\frac{1}{\omega_B}\sin(\omega_Bt)$. At later times, it will decay as an attenuated sinusoidal function, whose decay time is close to τ_{anh} for most temperatures. The role of τ_L will be hardly detectable except for $\omega_B\tau_L\approx 1$. When $\tau_L\gg\tau_{anh}$, though there exists a long time decay governed by τ_L, the latter will not be visible. For $t\approx\tau_L$, $R_{dens-dens}(\vec{q},t)$ has already so much decayed under the influence of τ_{anh} that this ERF is hardly measurable; a change in its decay rate cannot be detected.

This discussion agrees with the elementary response functions shown in Figure 3. They have been computed with the help of equation (3.18d) through the same technique as for $R_{\mathrm{OKE}}(t)$. We have chosen values for the parameters entering $P_L(\vec{q},\omega)$ which could represent approximately a m-toluidine signal for $q=0.6\ \mu\mathrm{m}^{-1}$. We have written

$$\frac{\omega\tilde{\eta}_L(\omega)}{\rho_m} = \Delta^2\left[1-\left(\frac{1}{1+i\omega\tau_L}\right)^{\beta_L}\right]+i\gamma, \quad (4.17)$$

with $q\Delta=2\pi$ GHz, $q^2\gamma=0.2\pi$ GHz and $\beta_L=0.7$ and have taken $qc_a=1.2\times 2\pi$ GHz. The temperature variation is taken into account by the sole variation of τ_L, which we change by factors 10^2 from 10^{-2} ns to 10^4 ns. The predicted variations are clearly visible and, in particular, the signal is always limited in time by the anharmonic decay, except for $\tau_L=1$ ns, when the longitudinal relaxation

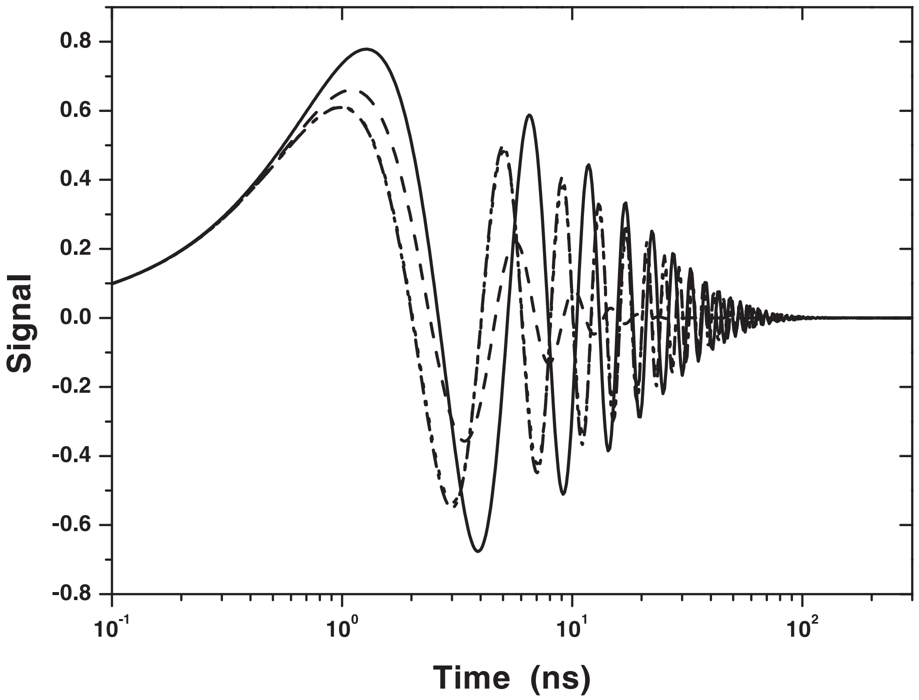


Fig. 3. $R_{dens-dens}(\vec{q},t)$ vs. time on a semi-log scale. $R_{dens-dens}(\vec{q},t)$ is shown for values of the α-relaxation time of the longitudinal viscosity, τ_L, equal to 10^{-2} ns (——), 1 ns (– – –), 10^{2} ns (· · · · ·), and 10^{4} ns (– · – · –). Note that, on that scale, the last two curves cannot be distinguished.

time is responsible for the much stronger damping visible in the figure.

To study the time evolution and analyse the information that can be extracted from $R_{or-dens}(\vec{q},t)$, it is convenient to relate that ERF to $R_{dens-dens}(\vec{q},t)$. Let us first remark that, taking into account the definition of $r(\omega)$, equation (3.6b), one can write

$$-ir(\omega)P_L(\vec{q},\omega) = (-i)\left[\frac{i\omega_R^2}{D(\omega)}\right]\left[\frac{-i\omega\mu(\omega)}{\omega_R^2}P_L(\vec{q},\omega)\right] \approx -\frac{i\omega\mu(\omega)}{\omega_R^2}P_L(\vec{q},\omega). \qquad (4.18)$$

The approximation indicated in equation (4.18) means that the frequency dependence of $D(\omega)$ may be neglected. Indeed, the term in the middle of that equation corresponds, in the time domain, to the convolution product of $R_{\mathrm{OKE}}(t)$ with the inverse Laplace-Transform of the r.h.s. of that equation. As the duration of the part of $R_{\mathrm{OKE}}(t)$ that has a non-negligible amplitude is of the order of a few picoseconds while the signal of the r.h.s. extends over hundreds of nanoseconds, this neglect is perfectly legitimate. Furthermore, one can write

$$\frac{\omega\mu(\omega)}{\omega_R^2}\left[-iP_L(\vec{q},\omega)\right] = \frac{\mu^0}{\omega_R^2}\left[-iP_L(\vec{q},\omega)\right] + (-i)\left[i\frac{\omega\mu(\omega)-\mu^0}{\omega_R^2}\right]\left[-iP_L(\vec{q},\omega)\right], \qquad (4.19a)$$

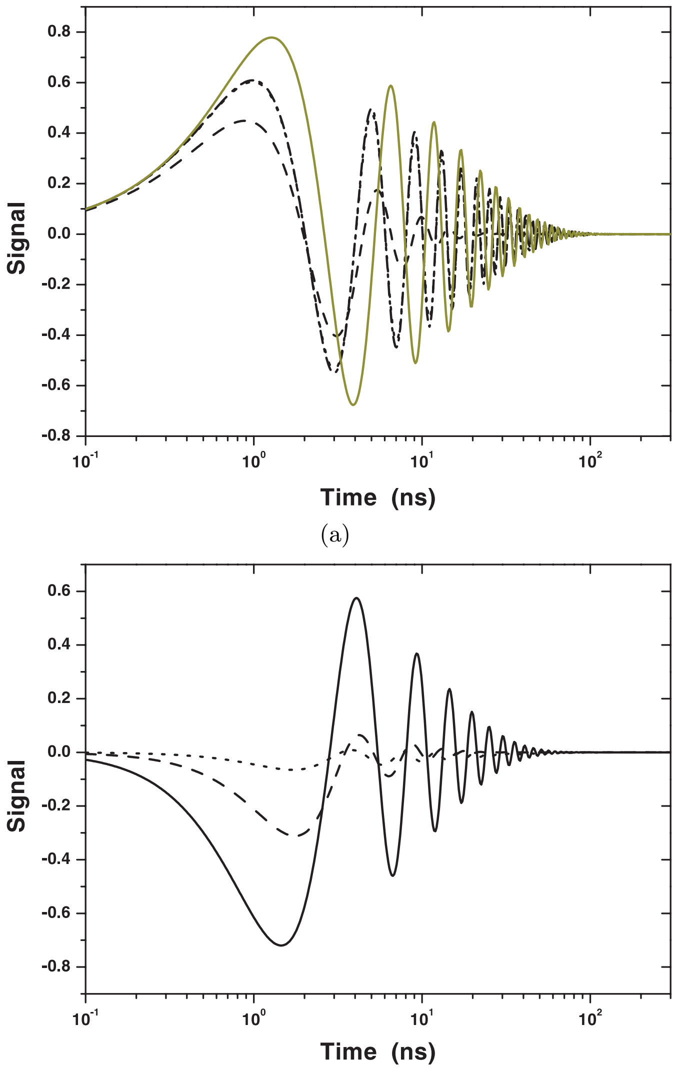
which implies, in the time domain,

$$R_{or-dens}(\vec{q},t) = \frac{\mu^0}{\omega_R^2}R_{dens-dens}(\vec{q},t) + \frac{\dot{\mu}(t)}{\omega_R^2}\otimes R_{dens-dens}(\vec{q},t). \qquad (4.19b)$$

The r.h.s. of equation (4.19b) is the sum of $R_{dens-dens}(\vec{q},t)$ (up to a μ^0/ω_R^2 factor) and of its convolution with $\dot{\mu}(t)/\omega_R^2$. For short relaxation times, it is easily shown that the second term of equation (4.19b) largely cancels the first term. For longer relaxation times, this second term is negligible with respect to the first one because $\dot{\mu}(t)$ is proportional to τ_μ^{-1}, the inverse of the rotation–translation relaxation time. In summary, $R_{or-dens}(\vec{q},t)$ has a shape quite similar to $R_{dens-dens}(\vec{q},t)$, except for very short values of τ_μ. This is illustrated in Figure 4a where we have computed the r.h.s. of equation (3.18e) taking for $\frac{\omega\mu(\omega)}{\omega_R^2}$ a form similar to equation (4.17)

$$\frac{\omega\mu(\omega)}{\omega_R^2} = \mu^0\left[1-\left(\frac{1}{1+i\omega\tau_\mu}\right)^{\beta_\mu}\right]. \qquad (4.19c)$$

We have taken $\beta_\mu = \beta_L = 0.7$ and chosen $\tau_\mu = 3\tau_L$ whatever the temperature, a constant ratio suggested again by m-toluidine HD-TG experiments [13]. In order to make clear that $R_{or-dens}(\vec{q},t)$ brings very little novel information, Figure 4b represents only the second term of the r.h.s. of equation (4.19b) computed for $\tau_L = 10^{-1}$ ns,



(a)

(b)

Fig. 4. (a) $R_{or-dens}(\vec{q},t)$ vs. time on a semi-log scale. $R_{or-dens}(\vec{q},t)$ is computed for values of the α-relaxation time of the rotation-translation coupling function, τ_μ, equal to $3\tau_L$ with the same values of τ_L as in Figure 3. Note that, on that scale, the curves corresponding to the two largest values of τ_L cannot be distinguished. (b) $R_{or-dens}(\vec{q},t) - \frac{\mu_0}{\omega_R^2} R_{dens-dens}(\vec{q},t)$ vs. time on a semi-log scale for the same ratio $\tau_\mu\tau_L$ as in Figure 4a and for $\tau_L = 10^{-1}$ ns (——), 1 ns (− − −), and 10 ns (· · · · ·). The difference decreases with increasing values of τ_L and also decreases as $R_{or-dens}(\vec{q},t)$ for increasing time.

1 ns and 10 ns. This second term is important only for $\tau_L = 10^{-1}$ ns and it is completely negligible for $\tau_L \geq 10$ ns.

The study of the two other elementary response functions, $R_{dens-or}(\vec{q},t)$ and $R_{or-or}(\vec{q},t)$, goes along similar lines. Firstly, $R_{dens-or}(\vec{q},t)$ is identical to $R_{or-dens}(\vec{q},t)$, equation (3.18f). Also, the time evolution $R_{or-or}(\vec{q},t)$ is easily derived from that of $R_{dens-dens}(\vec{q},t)$ by applying twice to $R_{or-or}(\vec{q},t)$ the technique that led to equation (4.19b):

$$\begin{aligned}R_{or-or}(\vec{q},t) \approx \left(\frac{\mu^0}{\omega_R^2}\right)^2 R_{dens-dens}(\vec{q},t) \\ + 2\frac{\mu^0}{\omega_R^2}\frac{\dot{\mu}(t)}{\omega_R^2} \otimes R_{dens-dens}(\vec{q},t) \\ + \frac{\dot{\mu}(t)}{\omega_R^2} \otimes \frac{\dot{\mu}(t)}{\omega_R^2} \otimes R_{dens-dens}(\vec{q},t). \qquad (4.20)\end{aligned}$$

This equation and the discussion performed below equation (4.19b) shows that also $R_{or-or}(\vec{q},t)$ has the same time extent as $R_{dens-dens}(\vec{q},t)$ and it will differ from it only at short times and for small values of τ_μ.

The study performed in Section 4.2 and here already allows us to understand that the five ERFs discussed up to now do not bring much information that could not be derived from other optical techniques. $R_{\mathrm{OKE}}(t)$ can be measured in an OKE experiment or could be obtained by a Laplace-Transform of the central peak that appears in a Brillouin-scattering experiment. The four other elementary response functions are related to each other through appropriate convolution products of $R_{dens-dens}(\vec{q},t)$ with the time derivative of the rotation-translation coupling function, $\mu(t)$, and they do not differ much from each other. Furthermore, $R_{dens-dens}(\vec{q},t)$ is proportional to the time derivative of the density-density correlation function, which is an essential ingredient of the polarised Brillouin spectrum. Thus, none of these four response functions can contain much more information than this spectrum. We shall return to this problem in Section 4.5 and show that, in fact, the contribution of those five ERFs to any $R_{ii,jj}(\vec{q},t)$ is just the inverse Laplace-Transform of some light scattering spectrum.

4.4 Time evolution of $\mathbf{R_{dens-ther}(\vec{q},t)}$ and $\mathbf{R_{or-ther}(\vec{q},t)}$

These last two response functions differ from the preceding ones because they cannot be expressed solely through terms that enter into the expression of a polarised Brillouin-scattering experiment. This explains why, in particular, $R_{dens-ther}(\vec{q},t)$, the ISTS response function, brings information on the α-relaxation time of the longitudinal viscosity for values not accessible with the previous technique. The time and temperature evolution of $R_{dens-ther}(\vec{q},t)$ has been discussed in detail in [6] and partly summarised in the Introduction.

In principle, we should thus simply discuss the new information contained in $R_{or-ther}(\vec{q},t)$. Yet, in order to be complete, we perform the study of those two response functions in a language largely similar to the one used in the two previous sections.

Neglecting the frequency dependence of $\beta(\omega)$ and $C_V(\omega)$ (see end of Sect. 4.1), one easily obtains

$$R_{dens-ther}(\vec{q},t) = -\frac{\beta^{th}}{\tau_h} \exp\left(-t/\tau_h\right) \otimes R_{dens-dens}(\vec{q},t). \qquad (4.21a)$$

This expression, and its alternate form,

$$R_{dens-ther}(\vec{q},\omega) = i\frac{\beta^{th}}{1+i\omega\tau_h}P_L(\vec{q},\omega), \qquad (4.21b)$$

are convenient to explain the time and temperature evolution of $R_{dens-dens}(\vec{q},t)$.

First, the short time behaviour of equation (4.21a) goes as $\beta^{th}\frac{\cos\omega_B t-1}{\omega_B^2}$, up to terms in $(t/\tau_h)^2$ or $(\Gamma t)^2$, as can be directly checked from the convolution product of an exponential with $\frac{\exp(-\Gamma t)\sin\omega_B t}{\omega_B}$ (a reasonable approximation for $R_{dens-dens}(\vec{q},t)$ at short times), and this expression is valid as long as $\omega_B t \leq 1$. $R_{dens-dens}(\vec{q},t)$ has thus a sign opposite to that of β^{th}, as could have been anticipated. Indeed, β^{th} is related to α^{th}, the thermodynamic limit of the thermal expansion coefficient at constant pressure by

$$\beta^{th} = c_i^2\alpha^{th}. \qquad (4.21c)$$

For positive α^{th}, an increase of temperature results in a decrease of the density while electrostriction corresponds to its increase.

Equation (4.21b) explains the long time behaviour of $R_{dens-ther}(\vec{q},t)$. Let us first generalise equation (4.17) to

$$\frac{\omega\tilde{\eta}_L(\omega)}{\rho_m} = \Delta^2\left[1-f(\omega\tau_L)\right], \qquad (4.22)$$

where $f(\omega\tau_L=0)=1$, while $\lim_{\omega\to\infty}\left[f(\omega\tau_L)\right]=0$. For frequencies such that $\omega\tau_h \gg \omega\tau_L \gg 1$, $P_L(\vec{q},\omega)$ reduces to

$$P_L(\vec{q},\omega) \approx -\frac{1}{(\omega_B^\infty)^2}\left[1+\left(\frac{q\Delta}{\omega_B^\infty}\right)^2 f(\omega\tau_L)\right], \qquad (4.23a)$$

with

$$(\omega_B^\infty)^2 = q^2\left[c_a^2+\Delta^2\right]. \qquad (4.23b)$$

If one neglects the second term of equation (4.23a), (very long time behaviour), $R_{dens-ther}(\vec{q},\omega)$, equation (4.21b), only depends on ω through its first factor which represents the thermal decay of the grating. As long as one neglects the frequency dependence of $\beta(\omega)$ and $C_V(\omega)$, the very long time part of $R_{dens-ther}(\vec{q},t)$ does not carry any information on a structural relaxation process.

The second term of the r.h.s. of equation (4.23a) explains the appearance of the longitudinal relaxation time in $R_{dens-ther}(\vec{q},t)$ at intermediate times ($\omega\tau_L \approx 1$). Its introduction into equation (4.21b) leads to direct information on the structural relaxation time for $t \approx \tau_L < \tau_h$. Indeed, one can verify that if, for instance, $[1-f(\omega\tau_L)]$ has the form of a Cole-Davidson function (cf. Eq. (4.19c)), the $f(\omega\tau_L)$ part of equation (4.23a) can be approximately represented by a stretched exponential with a positive prefactor, in agreement with the experimental results. The α-relaxation of the density-density correlation function is directly visible in that part of $R_{dens-ther}(\vec{q},t)$. The three characteristics of the time evolution of $R_{dens-ther}(\vec{q},t)$ which make this ERF fundamental in the study of supercooled liquids are thus easily explained. Let us nevertheless remark that our discussion of this long time behaviour has been based on the approximation $\omega\tau_h(q,\omega) \gg 1$. This yielded a definition of τ_h, equation (3.13), in which $-iC_V(\omega)$ is approximated by C_V^{th}. Such an approximation is clearly inconsistent with the frequency regime ($\omega\tau_h \approx 1$) just discussed. We shall show, in Section 6.3, that a more consistent treatment of this regime simply results in redefining τ_h through C_P^{th}, the thermodynamic limit of the specific heat at constant pressure, instead of C_V^{th}, in agreement with [27,32].

Let us finally discuss the new information introduced by $R_{or-ther}(\vec{q},t)$. From a formal point of view, one finds, in analogy with equation (4.21a),

$$R_{or-ther}(\vec{q},t) = -\frac{\beta^{th}}{\tau_h}\exp\left(-t/\tau_h\right)\otimes R_{or-dens}(\vec{q},t). \qquad (4.24a)$$

Yet, this result is not particularly useful. It is more interesting to use the same technique as for the study of $R_{or-dens}(\vec{q},t)$, cf. equation (4.19b), to obtain

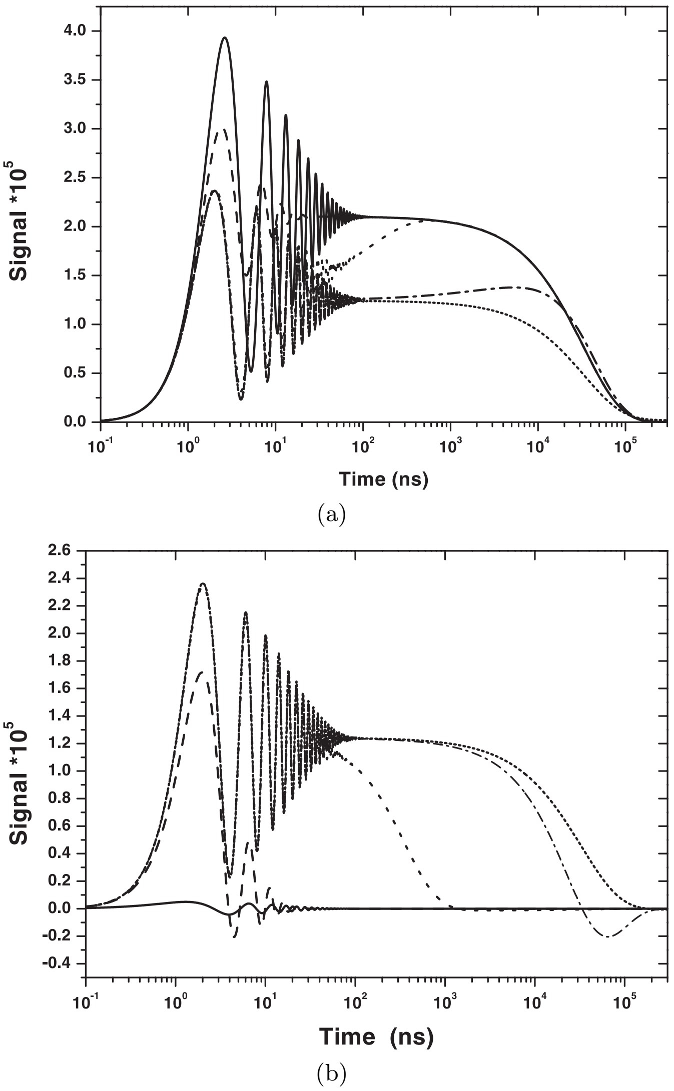
$$R_{or-ther}(\vec{q},t) = \frac{\mu^0}{\omega_R^2}R_{dens-ther}(\vec{q},t) + \frac{\dot{\mu}(t)}{\omega_R^2}\otimes R_{dens-ther}(\vec{q},t). \qquad (4.24b)$$

An analytical discussion of equation (4.24b) shows that, as long as $\omega_B\tau_\mu \ll 1$, its two terms nearly cancel, as was already the case for $R_{or-dens}(\vec{q},t)$. Conversely, for $\omega_B\tau_\mu \gg 1$, the analytic forms of $R_{or-dens}(\vec{q},t)$ and $R_{or-ther}(\vec{q},t)$ are quite different because $R_{dens-dens}(\vec{q},t)$ tends rapidly to zero for long times while $R_{dens-ther}(\vec{q},t)$ remains approximately constant and finite for $\tau_{anh} < t < \tau_h$. Then, approximating $R_{dens-dens}(\vec{q},t)$ by that constant, the convolution product in equation (4.24b) yields

$$R_{or-ther}(\vec{q},t) \approx \frac{\mu(t)}{\omega_R^2}R_{dens-ther}(\vec{q},t). \qquad (4.24c)$$

This equation shows that, for $\tau_{anh} < t < \tau_h$ and $\omega_B\tau_\mu \gg 1$, which are the conditions to extract information on the α-relaxation time of $\tilde{\eta}_L(t)$ from $R_{dens-ther}(\vec{q},t)$, the α-relaxation time of $\mu(t)$ can similarly be extracted from $R_{or-ther}(\vec{q},t)$.

Our analysis of the time evolution of these two ERFs agrees with the functions shown in Figures 5a and 5b. They have been calculated with the same fixed and varying parameters as for Figures 3 and 4a, choosing $\tau_h = 33$ μs, a value of τ_h typical of m-toluidine for $q = 0.6$ μm^{-1}. Nevertheless, in order to ease the comparison with the familiar results presented, e.g. in [6], we have plotted the opposite of $R_{dens-ther}(\vec{q},t)$ and $R_{or-ther}(\vec{q},t)$. Figure 5a represents $R_{dens-ther}(\vec{q},t)$: the three features discussed above are clearly visible and the increase of the function in the $10-10^4$ ns window for $\tau_L = 10^2$ ns and $\tau_L = 10^4$ ns has already been discussed in the Introduction. Figure 5b represents $R_{or-ther}(\vec{q},t)$, computed with $\mu^0 = \omega_R^2$. It shows the weakness of the $R_{or-ther}(\vec{q},t)$ response function for $\tau_\mu = 3\times10^{-1}$ ns and also that this ERF decreases as $\mu(t)$ for larger values of τ_μ, the decrease becoming slightly more complex than predicted by equation (4.24c) when $\tau_\mu \approx \tau_h$.



(a)

(b)

Fig. 5. (a) $R_{dens-ther}(\vec{q},t)$ vs. time on a semi-log scale. $R_{dens-ther}(\vec{q},t)$ is computed for a value of the heat-diffusion time, τ_h, equal to 33 μs and values of the α-relaxation time, τ_L, of the longitudinal viscosity, equal to 10^{-2} ns (——), 1 ns (– – –), 10^2 ns (· · · · ·), 10^4 ns (– · – · –), and 10^6 ns (·····). Note the strong damping of the acoustic phonon for $\tau_L = 1$ ns, i.e. when $\omega_B\tau_L \approx 1$. (b) $R_{or-ther}(\vec{q},t)$ vs. time on a semi-log scale. $R_{or-ther}(\vec{q},t)$ is computed for the same values of τ_h and τ_L as in (a), and for the same ratio $\tau_\mu\tau_L = 3$ as in Figure 4. Note the difference between (a) and (b) at long time.

4.5 Comparison between the HD-TG response functions and polarised light scattering results

Up to now, we have studied separately the seven ERFs but we have not made use of the general expression, equations (3.19). A more global and physically meaningful analysis of $R_{ii,jj}(\vec{q},t)$ can be performed when using simultaneously some results derived in Sections 4.1–4.3 and the relation, equation (A.16), between K, F, a and b derived in Appendix A. This equation reads

$$\frac{\rho_m}{\Lambda'}\frac{F}{2b} = \frac{K}{a} = S, \qquad (4.25)$$

where S is a positive parameter. Equations (3.19) can thus be transformed into

$$R_{ii,jj}(\vec{q},t) = R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t) + R^{\mathrm{ISTS}}_{ii,jj}(\vec{q},t), \qquad (4.26a)$$

with

$$\begin{aligned} R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t) = S\Bigg[&\left(\frac{\rho_m}{\lambda}\right)\frac{\Lambda'}{\rho_m}b^2\frac{1+3\varepsilon_{ex}\varepsilon_p}{3}\,R_{\mathrm{OKE}}(t)\\ &+q^2\left(a^2\,R_{dens-dens}(\vec{q},t)+\frac{\Lambda'}{\rho_m}ab\,\left(\frac{3\varepsilon_p-1}{3}\,R_{or-dens}(\vec{q},t)\right.\right.\\ &\left.\left.+\frac{3\varepsilon_{ex}-1}{3}\,R_{dens-or}(\vec{q},t)\right)\right)+q^2\,\left(\frac{\Lambda' b}{\rho_m}\right)^2\\ &\times\frac{3\varepsilon_p-1}{3}\,\frac{3\varepsilon_{ex}-1}{3}R_{or-or}(\vec{q},t)\Bigg]. \qquad (4.26b)\end{aligned}$$

We call $R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t)$ the "generalised ISBS" response function because, for isotropic molecules (b equal to zero), this function is simply proportional to $R_{dens-dens}(\vec{q},t)$, which is the ISBS response function originally introduced in [5,6]. Similarly

$$\begin{aligned} R^{\mathrm{ISTS}}_{ii,jj}(\vec{q},t) &= \frac{\rho_m}{\lambda}H\\ &\times\left[aR_{dens-ther}(\vec{q},t)+\frac{\Lambda' b}{\rho_m}\frac{3\varepsilon_p-1}{3}R_{or-ther}(\vec{q},t)\right], \qquad (4.26c)\end{aligned}$$

and we call $R^{\mathrm{ISTS}}_{ii,jj}(\vec{q},t)$ the "generalised ISTS" response function because, for b and/or $r(\omega)$ equal to zero, this function is simply proportional to $R_{dens-ther}(\vec{q},t)$, which is the ISTS response function first introduced in the same two papers.

Let us analyse now $R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t)$. First, because of the equality of $R_{or-dens}(\vec{q},t)$ and $R_{dens-or}(\vec{q},t)$, $R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t)$ is symmetrical in the interchange of i and j (i.e. of ε_p and ε_{ex}). There exist only three distinct response functions of this type: $R^{\mathrm{ISBS}}_{xx,xx}(\vec{q},t)$, $R^{\mathrm{ISBS}}_{xx,yy}(\vec{q},t) = R^{\mathrm{ISBS}}_{yy,xx}(\vec{q},t)$, and $R^{\mathrm{ISBS}}_{yy,yy}(\vec{q},t)$. It is the $R^{\mathrm{ISTS}}_{ii,jj}(\vec{q},t)$ contribution to $R_{ii,jj}(\vec{q},t)$ which breaks the symmetry between i and j in the total response function.

Second, we can relate directly $R^{\mathrm{ISBS}}_{yy,yy}(\vec{q},t)$ to $I_{yy}(\vec{q},t)$ by making use of equations (4.13b, 4.16) and of similar relations that we shall now prove. To start with, equation (32) of [25] can be expressed, in the notations of the present paper as

$$\begin{aligned} LT\left[\langle Q_{yy}(\vec{q},t)\delta\rho^0(\vec{q})^*\rangle\right](\omega) &=\\ &\frac{2}{3}\frac{\Lambda'}{\rho_m}q^2c_i^2\frac{r(\omega)}{\omega}P_L(\vec{q},\omega)\langle\left|\delta\rho^0\right|^2\rangle, \qquad (4.27)\end{aligned}$$

so that, as symmetry reasons impose that $\left\langle Q^0_{yy}(\vec{q})\delta\rho^0(\vec{q})^*\right\rangle$ is of order q^2, one obtains

$$R_{or-dens}(\vec{q},t) = \frac{-3}{2}\frac{\rho_m}{\Lambda'}\frac{1}{q^2c_i^2}\frac{d}{dt}\frac{\langle Q_{yy}(\vec{q},t)\delta\rho^0(\vec{q})^*\rangle}{\langle|\delta\rho^0|^2\rangle}. \tag{4.28}$$

Up to some algebraic factors, equation (4.28) is, as equation (4.16), a rather trivial result. $R_{or-dens}(\vec{q},t)$ being, by definition, an orientational response function to a density modulation at time $t=0$, it must be proportional to the time derivative of the correlation function of some diagonal component of the molecular orientation tensor with the density. Furthermore, owing to the time-reversal symmetry of that correlation function, one can also write

$$R_{dens-or}(\vec{q},t) = \frac{-3}{2}\frac{\rho_m}{\Lambda'}\frac{1}{q^2c_i^2}\frac{d}{dt}\frac{\left\langle\delta\rho(\vec{q},t)Q^0_{yy}(\vec{q})^*\right\rangle}{\left\langle|\delta\rho^0|^2\right\rangle}. \tag{4.29}$$

Finally, equation (33) of [25] can be written in the form

$$LT\left[\langle Q_{yy}(\vec{q},t)Q^0_{yy}(\vec{q})^*\rangle\right](\omega) = \left[\frac{1}{\omega}\left(1-\frac{\omega_R^2}{D(\omega)}\right)\right.$$
$$\left.+\frac{\Lambda'}{3\rho_m}q^2\omega_R^2\frac{r^2(\omega)}{\omega}P_L(\vec{q},\omega)\right]\langle|Q^0_{yy}|^2\rangle. \tag{4.30}$$

The second term in the r.h.s. corresponds to phonons launched and detected, in a Brillouin-scattering experiment, by the orientational fluctuations while the first term is the corresponding central peak. With the help of the expression of the Laplace-Transform of the derivative of a function, equation (4.11b), and of equation (4.5), the preceding equation can be transformed into

$$R_{\text{OKE}}(t)+\frac{\Lambda'}{\rho_m}\frac{q^2}{3}R_{or-or}(\vec{q},t) =$$
$$-\frac{3}{4}\frac{\rho_m}{\Lambda'}\frac{1}{c_i^2}\frac{d}{dt}\frac{\left\langle Q_{yy}(\vec{q},t)Q^0_{yy}(\vec{q})^*\right\rangle}{\left\langle|\delta\rho^0|^2\right\rangle}. \tag{4.31}$$

As expected, $R_{or-or}(\vec{q},t)$ is proportional to one part of the time derivative of the auto-correlation function of the orientational variable, while $R_{\text{OKE}}(t)$ is another part of it.

We can now group together the results relating the five ERFs entering $R^{\text{ISBS}}_{yy,yy}(\vec{q},t)$ with the time derivative of the corresponding correlation functions. An easy calculation involving equations (4.16, 4.28, 4.29, 4.31) and the definition of $\delta\bar{\bar{\varepsilon}}$, equation (3.2), yields

$$R^{\text{ISBS}}_{yy,yy}(\vec{q},t) = \frac{-S}{c_i^2}\frac{d}{dt}\frac{\left\langle\delta\varepsilon_{yy}(\vec{q},t)\delta\varepsilon^0_{yy}(\vec{q})^*\right\rangle}{\left\langle|\delta\rho^0|^2\right\rangle}. \tag{4.32}$$

Noting that $I_{yy}(\vec{q},\omega)$ is given by

$$I_{yy}(\vec{q},\omega) = \text{Im}\left(LT\left[\left\langle\delta\varepsilon_{yy}(\vec{q},t)\delta\varepsilon^0_{yy}(\vec{q})^*\right\rangle\right](\omega)\right), \tag{4.33}$$

one sees that $R^{\text{ISBS}}_{yy,yy}(\vec{q},t)$ contains the same information as $I_{yy}(\vec{q},\omega)$.

Equation (4.33) can be extended to the other values of i and j, as can be shown by using other results of [24,25] (see also [27]). In its general form, the preceding equation reads

$$R^{\text{ISBS}}_{ii,jj}(\vec{q},t) = \frac{-S}{c_i^2}\frac{d}{dt}\frac{\left\langle\delta\varepsilon_{ii}(\vec{q},t)\delta\varepsilon^0_{jj}(\vec{q})^*\right\rangle}{\left\langle|\delta\rho^0|^2\right\rangle}. \tag{4.34}$$

This equation generalises a result that was implicit in [5,6]. When the anisotropy of the molecules can be neglected ($b=0$), $R^{\text{ISBS}}_{ii,jj}(\vec{q},t)$ reduces to the density-density response function which, by nature, is related to the density-density correlation function by the Fluctuation-Dissipation theorem. As, in previous works on supercooled liquids, the same $b=0$ approximation was made for the dielectric fluctuations, $\left\langle\delta\varepsilon_{ii}(\vec{q},t)\delta\varepsilon^0_{jj}(\vec{q})^*\right\rangle$ was proportional to $\left\langle\delta\rho(\vec{q},t)\delta\rho^0(\vec{q})^*\right\rangle$ and did not depend on the values of the indices i or j. In this simple case, equation (4.34) is a trivial statement but it already suggests that the ISBS response function contains the same information as the corresponding Brillouin spectrum. Its general form, equation (4.34), generalises this statement to the case of anisotropic molecules. Indeed, in that case, there exist three independent Brillouin spectra that involve longitudinal phonons. They are labelled respectively $I_{VV}(\vec{q},\omega)\equiv I_{yy}(\vec{q},\omega)$, $I_{HH}(\vec{q},\omega)$ (see, e.g. [24]) which is a weighted sum of $I_{xx}(\vec{q},\omega)$ and $I_{yy}(\vec{q},\omega)$, and a third spectrum, proportional to

$$\text{Im}\left(LT\left[\left\langle\delta\varepsilon_{xx}(\vec{q},t)\delta\varepsilon^0_{yy}(\vec{q})^*\right\rangle\right](\omega)\right). \tag{4.35}$$

The latter can be extracted from spectra measured in a geometry intermediate between the VV and the HH ones [33]. Equation (4.34) indicates that the information contained in the three distinct "generalised ISBS" response functions is identical to that present in these three Brillouin spectra: they are related by the same Fluctuation-Dissipation theorem.

The "generalised ISTS" response function contains unique information on $\tilde{\eta}_L(t)$ and $\mu(t)$ in the 10–10^4 ns range but it does not lead to as rich an analysis as for $R^{\text{ISBS}}_{ii,jj}(\vec{q},t)$. With the help of equations (4.16, 4.21a, 4.24a, 4.29) and of results in [25], $R^{\text{ISTS}}_{ii,jj}(\vec{q},t)$ can be transformed into

$$R^{\text{ISTS}}_{ii,jj}(\vec{q},t) = \frac{\rho_m}{\lambda}\frac{\beta^{th}}{q^2c_i^2}H\frac{1}{\tau_h}$$
$$\times\exp\left(-{}^{t}\!/_{\tau_h}\right)\otimes\frac{d}{dt}\frac{\left\langle\delta\varepsilon_{ii}(\vec{q},t)\delta\rho^0(\vec{q})*\right\rangle}{\left\langle|\delta\rho^0|^2\right\rangle}. \tag{4.36}$$

$R^{\text{ISTS}}_{ii,jj}(\vec{q},t)$ is the convolution product of $\exp(-t/\tau_h)$, characteristic of the irreversible heat diffusion process, with the derivative of a correlation function describing part of the liquid dynamics. This convolution product breaks the symmetry between i and j, as the latter does not appears in the r.h.s. of equation (4.36). It is also the reason for obtaining from this "generalised ISTS" response function, information not accessible by Brillouin-scattering.

To conclude this section, let us point out that heat diffusion and temperature modulation should not be confused. One can generalise [27] the model for dielectric fluctuations by including also temperature fluctuations (see [34] where such an addition is necessary to explain HD-TG experiments in supercooled water):

$$\delta\bar{\bar{\varepsilon}}(\vec{r},t) = a\delta\rho(\vec{r},t)\bar{\bar{I}} + b\bar{\bar{Q}}(\vec{r},t) + c\delta T(\vec{r},t)\bar{\bar{I}}. \qquad (4.37)$$

This leads to a more involved form of $R_{ii,jj}(\vec{q},t)$, containing also terms related to the temperature modulation. However, $R_{ii,jj}(\vec{q},t)$ will still contain a $R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t)$ part, that will verify equation (4.34) and hence fulfil the Fluctuation-Dissipation theorem, and a $R^{\mathrm{ISTS}}_{ii,jj}(\vec{q},t)$ part. Similarly to equation (4.36), the latter will again characterise the irreversible heat diffusion process, and will not satisfy that theorem.

5 Determination of the elementary response functions

We have shown in the preceding section that $R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t)$ contains the same information as some Brillouin spectra so that these response functions could, in principle, be computed from such spectra, then subtracted from $R_{ii,jj}(\vec{q},t)$ to obtain the two distinct $R^{\mathrm{ISTS}}_{ii,jj}(\vec{q},t)$. In practice, such a method is inapplicable because of the numerical uncertainties introduced by performing a Laplace-Transform on an experimental spectrum as well as by the limited frequency range spanned by a typical Brillouin spectrum. It would thus be interesting to obtain directly the six distinct ERFs from the polarised HD-TG experiments. This is unfortunately impossible because there are only four different[9] $R_{ii,jj}(\vec{q},t)$ available to determine those six unknown functions. One can simplify the problem slightly by grouping together in equation (3.19c) the two ERFs $R_{dens-ther}(\vec{q},t)$ and $R_{dens-dens}(\vec{q},t)$ that are independent of the value of ε_p and ε_{ex}. Introducing

$$R_{dens-iso}(\vec{q},t) = R_{dens-ther}(\vec{q},t) + a\frac{\lambda q^2}{\rho_m}\frac{S}{H}R_{dens-dens}(\vec{q},t) \qquad (5.1)$$

(where we have made use, as will be done in the remaining of this section, of equation (4.25) to eliminate K), we are still left with five unknown functions in equation (3.19c), $R_{dens-iso}(\vec{q},t)$ replacing $R_{dens-ther}(\vec{q},t)$ and $R_{dens-dens}(\vec{q},t)$ being eliminated, while we can only perform four independent measurements. One obtains, for instance,

$$2b^2\frac{\Lambda'}{\rho_m}SR_{\mathrm{OKE}}(t) = 2\left(R_{yy,yy}(\vec{q},t) - R_{yy,xx}(\vec{q},t)\right) + \left(R_{xx,yy}(\vec{q},t) - R_{xx,xx}(\vec{q},t)\right) - 6ab\frac{\Lambda'}{\rho_m}q^2 SR_{or-dens}(\vec{q},t), \qquad (5.2)$$

a formula which is at odds with equation (23e) of [14] for a reason we shall discuss in Section 6. Nevertheless, there are two routes that may be used to obtain individually the ERFs. One is applicable when the relative weight of the different sources (S and H), or detection mechanisms (a and b) are sufficiently different to neglect one compared to the other. The other route takes advantage of the short duration of $R_{\mathrm{OKE}}(t)$ with respect to the other response functions. Let us discuss in turn these two possibilities.

5.1 The order of magnitude aspect — The isotropic and anisotropic spectra

For a given wavevector, the relative intensities of the different terms entering into equations (3.19b, 3.19c) depend on two ratios, $\frac{H}{S}\frac{\rho_m\beta^{th}}{\lambda a}$ and $\frac{b\Lambda'\mu^0}{a\rho_m\omega_R^2}$. The first describes the relative importance of the heat absorption with respect to the two other sources and may be varied by changing the frequency of the pumps. The second ratio depends basically on b/a, the ratio between the two scattering efficiencies, and on μ^0/ω_R^2, a molecular quantity totally fixed by the shape of the molecule and by the inter-molecular interactions. Four different approximations may be considered.

- If $\frac{H}{S}\frac{\rho_m\beta^{th}}{\lambda a} \ll 1$, the heat absorption process is negligible: one can simply measure the different elements of $R^{\mathrm{ISBS}}_{ii,jj}(\vec{q},t)$ and the HD-TG response functions are just Laplace-Transforms of Brillouin-scattering experiments. Yet, we are left here with only three independent measurements ($R_{xx,yy}(\vec{q},t) = R_{yy,xx}(\vec{q},t)$) so that the independent determination of the four elementary response functions is still not possible in principle.
- If $\frac{H}{S}\frac{\rho_m\beta^{th}}{\lambda a} \approx 1$ but $\frac{b\Lambda'\mu^0}{a\rho_m\omega_R^2} \ll 1$, the molecular aspect of the liquid does not show up: only $R_{dens-iso}(\vec{q},t)$ has a non-negligible value and the four possible $R_{ii,jj}(\vec{q},t)$ response functions are identical. This seems to be the case for o-terphenyl studied in [11], where the authors have been able to disentangle the ISBS response function from the ISTS one by a careful analysis of their data.
- If $\frac{H}{S}\frac{\rho_m\beta^{th}}{\lambda a} \gg 1$ while $\frac{b\Lambda'\mu^0}{a\rho_m\omega_R^2} \ll 1$, the situation is even simpler. The heat absorption dominates, there is neither rotation-translation coupling nor "generalised ISBS" contribution. One only measures $R_{dens-ther}(\vec{q},t)$, whatever the signal recorded.
- Finally, if $\frac{H}{S}\frac{\rho_m\beta^{th}}{\lambda a} \gg 1$ but if the second ratio is large enough, the "generalised ISBS" contribution is still negligible but polarisation effects of the pumps can

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[9] The measurement of $R_{xy,xy}(\vec{q},t)$ gives no additional information (see Appendix C) as it is a weighted sum of $R_{\mathrm{OKE}}(t)$ and of another elementary response function related to a transverse phonon and not to a longitudinal one.

be obtained on $R^{\mathrm{ISTS}}_{ii,jj}(\vec{q},t)$: one detects linear combinations of the two elementary response functions, $R_{dens-ther}(\vec{q},t)$ and $R_{or-ther}(\vec{q},t)$. This seems to be the case of salol [14] and of m-toluidine [12,13]. In such cases, one can access to two terms proportional, respectively, to $R_{dens-ther}(\vec{q},t)$ and to $R_{or-ther}(\vec{q},t)$ through the two combinations, $R_{iso}(\vec{q},t)$ and $R_{aniso}(\vec{q},t)$, defined as

$$\begin{aligned} R_{iso}(\vec{q},t) &= \frac{1}{3}\left[2R_{yy,jj}(\vec{q},t) + R_{xx,jj}(\vec{q},t)\right] \\ &= \frac{a\rho_m H}{\lambda} R_{dens-ther}(\vec{q},t), \qquad (5.3) \\ R_{aniso}(\vec{q},t) &= \frac{1}{2}\left[R_{yy,jj}(\vec{q},t) - R_{xx,jj}(\vec{q},t)\right] \\ &= \frac{b\Lambda' H}{\lambda} R_{or-ther}(\vec{q},t). \qquad (5.4) \end{aligned}$$

The ratio of their amplitude gives directly the value of $\frac{b\Lambda'\mu^0}{a\rho_m\omega_R^2}$. These results, corrected of minor typos, are those that have been already presented in [12,13].

5.2 The time separation method

The other possible technique to access the elementary response functions is to make use of the results of Figure 2 or of experimental results on OKE such as [31,35] to argue that $R_{\mathrm{OKE}}(t)$ becomes negligible at the time when the five other signals of equations (3.19c) become visible. For such times and with such a neglect, one easily derives the following formulae

$$\begin{aligned} \left(b\frac{\Lambda'}{\rho_m}\right)^2 q^2 S R_{or-or}(\vec{q},t) &= \frac{1}{4}\left[\left(R_{yy,yy}(\vec{q},t) - R_{yy,xx}(\vec{q},t)\right)\right. \\ &\quad \left. - \left(R_{xx,yy}(\vec{q},t) - R_{xx,xx}(\vec{q},t)\right)\right], \qquad (5.5) \\ ab\frac{\Lambda'}{\rho_m} q^2 S R_{dens-or}(\vec{q},t) &= \frac{1}{6}\left[2\left(R_{yy,yy}(\vec{q},t) - R_{yy,xx}(\vec{q},t)\right)\right. \\ &\quad \left. + \left(R_{xx,yy}(\vec{q},t) - R_{xx,xx}(\vec{q},t)\right)\right], \qquad (5.6) \\ \frac{b\Lambda'}{\lambda} H R_{or-ther}(\vec{q},t) &= \frac{1}{2}\left[R_{yy,xx}(\vec{q},t) - R_{xx,yy}(\vec{q},t)\right], \qquad (5.7) \\ \frac{a\rho_m}{\lambda} H R_{dens-iso}(\vec{q},t) &= \frac{1}{9}\left[4R_{yy,yy}(\vec{q},t) + 2R_{yy,xx}(\vec{q},t)\right. \\ &\quad \left. + 2R_{xx,yy}(\vec{q},t) + R_{xx,xx}(\vec{q},t)\right]. \qquad (5.8) \end{aligned}$$

Three of the five elementary response functions can thus be obtained separately and equation (5.4) is just a special case of equation (5.7) valid when the response functions do not depend on the index j. The same is true for equations (4.3, 4.8) but it is now $R_{dens-iso}(\vec{q},t)$, instead of its first term, $R_{dens-ther}(\vec{q},t)$, that is obtained because S is no longer negligible.

6 Relationship with previous work and practical discussion

6.1 Introduction

As recalled in Section 1, the study of supercooled liquids by TG-techniques has a long history. Independently of the seminal work of Allain et al. [2], Yan, Cheng, and Nelson [5] proposed in 1988 a set of equations describing the instantaneous interaction of a supercooled liquid with the two pumps and its later temporal evolution. The next important contribution was a more precise analysis of the solution of these equations by Yang and Nelson [6]. Finally the existence of polarisation effects in a HD-TG experiment on salol led Glorieux et al. to extend somewhat the preceding set of equations [14]. In Section 6.2, we shall summarise and discuss these previous approaches in the language of the present paper.

The study of $R_{dens-ther}(\vec{q},t)$, the ISTS response function, as identified in [8,11] in the time domain, was performed following a formula proposed in [8]. Yet, its application revealed an anomaly of the heat diffusion time at low temperature for which a possible explanation has recently been proposed [29] in the language of out-of-equilibrium thermodynamics. In Section 6.3, we reanalyse this problem with the help of the exact expression of $R_{dens-ther}(\vec{q},t)$ given in equation (3.18b). Arguing that, except for a very small temperature domain, the anomaly arises from the terms we dropped, or the approximation we made in Section 4, we shall reintroduce the missing terms in turn and show that their neglect is presumably at the origin of this apparent anomaly.

6.2 Comparison with other work

All the papers analysing TG-experiments performed on supercooled liquids published before 2002 ignored their molecular nature: there was no variable equivalent to $\bar{\bar{Q}}$, and thus no equation equivalent to equation (2.28). Allain et al. [2], who ignored electrostriction, analysed in essence their experiments with the help of two equations which read, with the present notation

$$\bar{\bar{\sigma}} = \left[-c_i^2\delta\rho + \eta_L \otimes \mathrm{div}\,\vec{v} - \rho_m\beta \otimes \delta T\right]\bar{\bar{I}}, \qquad (6.1a)$$

$$C_V \otimes \dot{T} - T_m\beta \otimes \dot{\rho} - \lambda\Delta T = 2HU^g, \qquad (6.1b)$$

but they only looked for the long time behaviour, $t \approx \tau_h$, of their solution. In fact, they obtained those equations in the frequency domain, considering, on the one hand, their infinite frequency limit and introducing, on the other hand, the relaxation processes through the coupling of the density and temperature modulations to a very large number of additional variables, ξ_i, supposed to exhibit a relaxational dynamics. Indeed, using forms equivalent to equation (4.22), they first expressed equations (4.6a, 4.6b) in the form

$$\begin{aligned} C_V(\omega) &= i\left[C_V^{th} - \delta C_V\left[1 - f_C(\omega\tau_C)\right]\right] \\ &\equiv i\left[C_V^{\infty} + \delta C_V f_C(\omega\tau_C)\right], \end{aligned} \tag{6.2a}$$

$$\beta(\omega) = i\left[\beta^{th} - \delta\beta\left[1 - f_\beta(\omega\tau_\beta)\right]\right] \equiv i\left[\beta^{\infty} + \delta\beta f_\beta(\omega\tau_\beta)\right], \tag{6.2b}$$

$f_C(\omega\tau_C)$ and $f_\beta(\omega\tau_\beta)$ having the same low and high frequency limits as $f(\omega\tau_L)$ in equation (4.22). The set of equations used in [2] was[10]

$$\bar{\bar{\sigma}} = -\left[\left(c_i^2 + \Delta^2\right)\delta\rho + \rho_m\beta^{\infty}\delta T + \rho_m\sum_i A_i X_i \xi_i\right]\bar{\bar{I}}, \tag{6.3a}$$

$$\begin{aligned} -T_m\left(\beta^{\infty}\dot{\rho} + \sigma_\rho\delta\rho\right) + C_V^{\infty}\dot{T} + \sigma_T\delta T - \lambda\Delta\delta T \\ -T_m\sum_i A_i Y_i \tau_i^{-1}\xi_i = 2HU^g, \end{aligned} \tag{6.3b}$$

$$\tau_i^{-1}\left(X_i\delta\rho - Y_i\delta T + \xi_i\right) + \dot{\xi}_i = 0, \tag{6.3c}$$

with

$$\sigma_T = T_m\sum_i A_i Y_i^2\tau_i^{-1};\quad \sigma_\rho = \sum_i A_i X_i Y_i \tau_i^{-1}, \tag{6.4a}$$

the ratio between the different relaxation times, τ_i, being independent of temperature. Taking the Laplace-Transforms of equations (6.3), the elimination of the set of variables ξ_i led, when transformed back in the time domain to equations (6.1a, 6.1b) while, in particular,

$$\delta C_V f_C(\omega\tau_C) = T_m\sum_i \frac{A_i Y_i^2}{1 + i\omega\tau_i}, \tag{6.4b}$$

$$\delta\beta f_\beta(\omega\tau_\beta) = \sum_i \frac{A_i X_i Y_i}{1 + i\omega\tau_i}. \tag{6.4c}$$

Conversely, in the later works that ignored $\bar{\bar{Q}}$, the experiments were described with the help of equations that can be expressed as

$$\bar{\bar{\sigma}} = \left[-c_i^2\delta\rho + \tilde{\eta}_L \otimes \operatorname{div}\vec{v} - \beta^{th}\rho_m\delta T + 2KU^g\right]\bar{\bar{I}}, \tag{6.5a}$$

$$C_V^{th}\dot{T} - T_m\beta^{th}\dot{\rho} - \lambda\Delta T = 2HU^g. \tag{6.5b}$$

These equations ignore retardation effects except for the longitudinal viscosity[11]. The existence of the two distinct response functions, the ISBS, corresponding to the electrostrictive effect, and the ISTS response due to the heat absorption, were already recognised in [5]. Nevertheless, up to 1995, the analysis of the recorded signal remained limited to its oscillatory part, which was described as an ISBS response function:

$$R_{dens-dens}(\vec{q},t) = \frac{\exp\left(-\mathit{\Gamma} t\right)\sin\omega_B t}{\omega_B}. \tag{6.6}$$

At each temperature, information on $\tilde{\eta}_L(\omega)$ was obtained by varying the scattering angle and extracting $\tilde{\eta}_L(\omega_B)$ from the fit parameters $\mathit{\Gamma}$ and ω_B.

Yang and Nelson [6,8] made an important break through by proposing an analytical expression for the ISTS response function that was able, inter alia, to explain the long time behaviour of the signal

$$\begin{aligned} R_{dens-ther}(\vec{q},t) \approx A\left(\exp\left(-t/\tau_{h-fit}\right) - \exp\left(-\mathit{\Gamma} t\right)\cos\omega_B t\right) \\ + B\left(\exp\left(-t/\tau_{h-fit}\right) - \exp\left(-\left(t/\tau_L\right)^{\beta}\right)\right), \end{aligned} \tag{6.7}$$

$\mathit{\Gamma}$ and ω_B being parameters common to equations (6.6, 6.7). This expression was obtained as an "ad hoc" generalisation [8] of the exact ISTS solution of equations (6.5a, 6.5b) when $\tilde{\eta}_L(t)$ is a Debye-relaxation function. In that case, $\beta = 1$ while τ_{h-fit}, τ_L, $\mathit{\Gamma}$ and ω_B are analytical functions of the parameters entering into these two equations[12]. The generalisation to $\beta \neq 1$ was performed to link the long time behaviour of $R_{dens-ther}(\vec{q},t)$ to the structural relaxation of the liquid, the seven parameters of equation (6.7) becoming fit parameters. In this last case, their physical interpretation is not always obvious, as we shall see in Section 6.3 when discussing the relation between τ_{h-fit} and τ_h.

The difference between response functions measured with different polarisations in salol [14,15] led the authors of these two papers to introduce a rotation-translation coupling. This was obtained by simply enlarging the set of equations (6.5a, 6.5b), adding a third equation partly similar to equation (2.28). This equation reads [14], in an unspecified Markov approximation

$$\dot{S}_{flow} + \frac{S_{flow}}{\tau_\mu} - \gamma\tau_{xx} = 0. \tag{6.8}$$

It couples an orientational variable, called $\mathrm{S}_{flow}(\mathrm{t})$ and taken to be scalar, to the divergence of the molecular mean velocity, i.e. to the xx component of the strain rate tensor $\bar{\bar{\tau}}$ in the HD-TG geometry of Figure 1. Equation (6.8) misses, in particular, a torque source (see Eq. (2.28)). Also, a $\dot{S}_{flow}(t)$ (or $S_{flow}(t)$) counterpart of the $\gamma\tau_{xx}$ term of equation (6.8) was not added to equation (6.5a). The response functions of [14] that should compare to our equations (3.17) are thus incomplete. In particular, they do not depend on the polarisation of the pumps. Also, in the absence of a torque source, the $R_{\mathrm{OKE}}(t)$ term, explicitly mentioned in [14] as a part of their response functions, has an unclear origin.

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[10] Equations (6.3) are here corrected from some minor errors appearing in [2] which do not affect their general philosophy.

[11] Retardation on the tension coefficient and on the specific heat was, in fact, formally introduced in [5] but it was not taken into account when studying the solutions of these equations.

[12] Equation (6.7) was already proposed in [36] but with no justification or analysis of its time dependence.

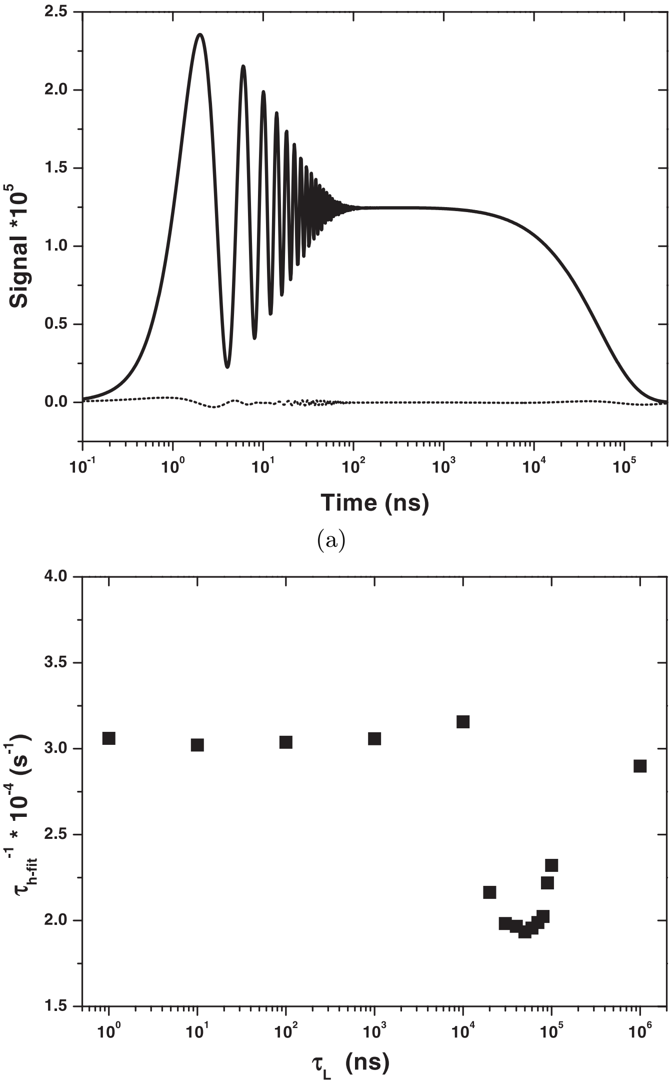
6.3 The low temperature heat-diffusion time problem

With the exception of [13], all the TG-experiments have been analysed so far by directly fitting $R_{dens-ther}(\vec{q},t)$ and $R_{dens-dens}(\vec{q},t)$ to, respectively, equations (6.6, 6.7). In the original spirit of [6], equation (6.7) was only valid for $\tau_{anh} < \tau_L < \tau_h$ but, already in [8], this formula was used to fit response functions even for temperatures at which $\tau_L \geq \tau_h$. Performing such fits, it has been found that:

- as long as $\tau_L \ll \tau_h$, the fit parameter τ_{h-fit} is, as anticipated, very little temperature dependent (for instance $\frac{1}{\tau_{h-fit}} \frac{d\tau_{h-fit}}{dT} \cong 2 \times 10^{-4}$ K^{-1} in [11]), while, at each temperature, $\left(\tau_{h-fit} q^2\right)^{-1}$ is independent of q, in agreement with equation (3.13) when the frequency dependence of $C_V(\omega)$ can be neglected;
- when lowering the temperature beyond that limit, $\left(\tau_{h-fit} q^2\right)^{-1}$ has a dip [11] of the order of 30% when τ_L is in the vicinity of τ_{h-fit}, i.e. in a temperature interval of a few degrees. Conversely [8,11], at lower temperature, one observes a steady increase of the same quantity above its high temperature value, this increase being of the order of 30% in the limited range of temperature (10–20 K) where the measurements can be considered as reliable. Those two opposite effects when $\tau_L \approx \tau_h$ and $\tau_L \gg \tau_h$ had been, in fact, already noticed in [2] where the authors also fit the long time behaviour of $R_{dens-ther}(\vec{q},t)$ in the time domain.

The origin of the dip is, very likely, a fitting artefact: when $\tau_L \approx \tau_{h-fit}$, this parameters has not its anticipated physical meaning. This is easily shown by fitting with equation (6.7) different response functions computed with the same fixed parameters as for Figure 5a (in particular $\tau_h = 3.3 \times 10^4$ ns) and for various values of τ_L. We varied τ_L by factors 10 from $\tau_L = 1$ ns to $\tau_L = 10^6$ ns and, in order to study in detail the region $\tau_L \approx \tau_h$, we also used the values $\tau_L = n \times 10^4$ ns, where n is an integer ranging from 1 to 10. All the fits were quite satisfactory in the sense that the difference signals (fit function minus the input function) were nearly equal to zero, as exemplified in Figure 6a, drawn for the worse case, $\tau_L = 4 \times 10^4$ ns. Nevertheless, as shown in Figure 6b, the values of τ_{h-fit}^{-1} exhibit, in the vicinity of $\tau_L = \tau_h$, a dip quite similar to that found in [6] while they are equal to τ_h when $\tau_L \ll \tau_h$ (high temperature case).

Yet, τ_{h-fit} returns to its high temperature value for larger values of τ_L. The reported increase must thus originates from physical effects we neglected in Section 4, i.e. either the frequency dependence of $C_V(\omega)$ and $\beta(\omega)$, or the neglect of the last term of equation (E.5) which corresponds to the change, in the phonon propagator, from the high frequency adiabatic propagation to the very low frequency isothermal one. A complete discussion of those effects is out of place in the present paper and we shall only sketch its main aspects.



(a)

(b)

Fig. 6. (a) Fit of $R_{dens-ther}(\vec{q},t)$ (—) for the same parameters as in Figure 5a and $\tau_L = 4$ ns, by the approximate formula (Eq. (6.7)). Though this value corresponds to the worse reliability factor of all the fits performed, see (b), the fit function and $R_{dens-ther}(\vec{q},t)$ cannot be distinguished on that scale. The difference between the fit function and $R_{dens-ther}(\vec{q},t)$ is represented as $(\cdots\cdot)$. (b) Values of τ_{h-fit}^{-1} vs. τ_L obtained by fitting $R_{dens-ther}(\vec{q},t)$ by equation (6.7) when the latter has been computed with $\tau_h^{-1} = 3 \times 10^4$ ns and the values of τ_L given in abscissa. Note the strong apparent dip of τ_{h-fit}^{-1} when $\tau_L \approx \tau_h$.

The frequency dependence of $C_V(\omega)$ and $\beta(\omega)$ was already introduced under a simple form in equations (6.2a, 6.2b) and, for simplicity, we shall assume that $\tau_C = \tau_\beta = \tau_L$.

Let us start with the role of $C_V(\omega)$, which is, possibly, the most important effect. Its influence on $R_{dens-ther}(\vec{q},t)$ for $t \approx \tau_h$ may be obtained by performing an analysis of this ERF similar to the one performed in Section 4.4 but which includes the role of $\delta C_V(\omega)$

$$R_{dens-ther}(\vec{q},\omega) \approx \frac{-i}{q^2\left[c_i^2 + \Delta^2\left[1 - f(\omega\tau_L)\right]\right]} \frac{\beta^{th}}{1 + \omega C_V(\omega)(\lambda q^2)^{-1}}. \quad (6.9)$$

For both the $\tau_L \ll \tau_h$ and the $\tau_L \gg \tau_h$ regimes, the phonon propagator does not influence the frequency dependence of $R_{dens-ther}(\vec{q},\omega)$ when $\omega\tau_h \approx 1$. In this frequency domain, expressing $C_V(\omega)$ through the two forms indicated in equation (6.2a), one easily obtains that:

- when $\tau_L \ll \tau_h$, $\delta C_V\left[1 - f_C(\omega\tau_C)\right]$ is negligible, $C_V(\omega) \approx iC_V^{th}$ and the decay of $R_{dens-ther}(\vec{q},t)$ is governed by
$$\tau_h^0 = C_V^{th}\left(\lambda q^2\right)^{-1}; \quad (6.10a)$$
- conversely, when $\tau_L \gg \tau_h$, $f_C(\omega\tau_L) \ll 1$, $C_V(\omega) \approx i\left[C_V^{th} - \delta C_V\right]$ and the decay time decreases to
$$\tau_h^\infty = C_V^\infty\left(\lambda q^2\right)^{-1}. \quad (6.10b)$$

The corresponding decrease of the decay time may be important because, at low temperature, $\delta C_V/C_V^{th}$ may reach values as large as 0.5 [37,38].

The results quoted in equations (6.10) are still partly incorrect because, τ_h^0 and τ_h^∞ should not be expressed through C_V^{th} and δC_V but rather through C_P^{th} and δC_P, the corresponding quantities at constant pressure, as well as through γ^∞ (see below). This is because the identification we performed at the beginning of Section 4 between $P_L'(\vec{q},\omega)$ and $P_L(\vec{q},\omega)$ was based on the hypothesis $\omega\tau_h(q,\omega) \gg 1$, which is inconsistent with the long time regime discussed here. In this regime, the analysis of $R_{dens-ther}(\vec{q},t)$ must be performed using $P_L'(\vec{q},\omega)$. This will result in a renormalisation of τ_h^0 and another renormalisation of τ_h^∞, the $\tau_L \approx \tau_h$ region being probably characterised by a small decrease in the renormalisation factor.

To discuss this point, it is unnecessary to explicitly introduce the frequency dependence of τ_h. Thus, we simply write $g(q,\omega)$, equation (3.12), as

$$\begin{aligned} g(q,\omega) &= -i\rho_m T_m \frac{\beta^2(\omega)}{C_V(\omega)} \frac{i\omega\tau_h}{1 + i\omega\tau_h} \\ &\equiv c_i^2\left(\gamma(\omega) - 1\right)\frac{i\omega\tau_h}{1 + i\omega\tau_h}, \end{aligned} \quad (6.11)$$

where $\gamma(\omega = 0)$ is the ratio γ introduced in equation (4.8b). Representing here $\omega\rho_m^{-1}\eta_L(\omega)$ rather than $\omega\rho_m^{-1}\tilde{\eta}_L(\omega)$ by equation (4.22), and neglecting the frequency dependence of $\beta(\omega)$ in equation (2.18b), one easily obtains

$$R_{dens-ther}(\vec{q},\omega) \approx \frac{-i\beta^{th}}{q^2\left[\left\{c_i^2 + \Delta^2\left[1 - f(\omega\tau_L)\right]\right\}(1 + i\omega\tau_h) + c_i^2\left(\gamma(\omega) - 1\right)i\omega\tau_h\right]}. \quad (6.12)$$

This expression of $R_{dens-ther}(\vec{q},\omega)$ can once again be approximated in the $\omega\tau_h \approx 1$ domain in both the $\tau_L \ll \tau_h$ and the $\tau_L \gg \tau_h$ cases:

- when $\tau_L \ll \tau_h$, an easy calculation yields
$$R_{dens-ther}(\vec{q},\omega) \approx \frac{-i\beta^{th}}{q^2 c_i^2} \frac{1}{1 + i\omega\gamma\tau_h^0}, \quad (6.13a)$$
$\gamma(\omega)$ taking its $\omega = 0$ value. In this case, the effective diffusion time is
$$\tau_h'^0 = \gamma\tau_h^0 = \gamma C_V^{th}\left(\lambda q^2\right)^{-1}, \quad (6.14a)$$
while, following equation (4.8b), $\gamma C_V^{th} = C_P^{th}$: the thermal diffusion is thus governed by C_P^{th}, in agreement with [27,32];
- when $\tau_L \gg \tau_h$, a similar calculation leads to
$$R_{dens-ther}(\vec{q},\omega) \approx \frac{-i\beta^{th}}{q^2\left(c_i^2 + \Delta^2\right)} \frac{1}{1 + i\omega\tau_h^\infty \dfrac{c_i^2\gamma(\omega \to \infty) + \Delta^2}{c_i^2 + \Delta^2}}, \quad (6.13b)$$
whence
$$\tau_h'^\infty = \tau_h^\infty\left(\gamma^\infty - \frac{\Delta^2(\gamma^\infty - 1)}{c_i^2 + \Delta^2}\right), \quad (6.14b)$$
where we have used the renormalised value of the heat-diffusion time (cf. Eq. (6.10b)) for this time regime, and made explicit the renormalisation factor that applies to that case. If γ does not depend on frequency, one finds that the renormalisation of τ_h^∞ is smaller than that of τ_h^0, so that taking proper account of equation (3.12) would result, not only in the renormalisation from the specific heat at constant volume to that at constant pressure, but also in a larger ratio between the effective heat-diffusion times at high and low temperatures. Even if γ is frequency dependent, as $\gamma^\infty - 1$ is a small positive number, the role of equation (6.14b) if one neglects the frequency dependence of $\tau_h(q,\omega)$ is much less important than the frequency dependence of the specific heat.

Finally, the frequency dependence of $\beta(\omega)$ adds a convolution product of $R_{dens-ther}(\vec{q},t)$, as studied above, with $\beta(t)$. Writing equation (6.2b) as

$$\beta(\omega) = i\beta^\infty\left[1 + \frac{\delta\beta}{\beta^\infty} f_\beta(\omega\tau_L)\right], \quad (6.15)$$

the frequency dependence of $\beta(\omega)$ plays a role equivalent to the r.h.s. of equation (4.23a), a factor which explained the appearance of the structural relaxation in the long time part of $R_{dens-ther}(\vec{q},t)$. $\beta(\omega)$ introduces an additional channel for coupling this relaxation to the thermal decay. This channel may be important in the $t \approx \tau_h$ regime when $\tau_h < \tau_L$ because the coefficient $\delta\beta/\beta^\infty$ may be of order unity. Disentangling the effects of $C_V(\omega)$, $\beta(\omega)$, and

$\eta_L(\omega)$ in $R_{dens-ther}(\vec{q},t)$ may thus be an uneasy task in this $t \approx \tau_h$ regime.

Let us finally remark that the long time behaviour of $R_{dens-ther}(\vec{q},t)$ of glycerol has been recently reanalysed, after [2], by some of the present authors (A.T and R.T.) and co-authors in [29]. They used an approximate form of equations (6.3) in which the dynamics of $\delta\rho$ was ignored, i.e. the approximation $\bar{\bar{\sigma}} = 0\bar{\bar{I}}$ was made in equation (6.3a) while the coefficients of $\delta\rho$ and $\dot{\rho}$ were taken equal to zero in equations (6.3b, 6.3c). Furthermore, in order to take partly into account the results of equations (6.14), C_V^{∞} was replaced by C_P^{∞} in equation (6.3b). Similarly to the calculation that led from equations (6.3) to equations (6.1), one obtains

$$R_{dens-ther}(\vec{q},\omega) \approx \frac{-i\beta^{\infty}}{(\omega_B^{\infty})^2} \frac{\left[1 + \dfrac{\delta\beta}{\beta^{\infty}} f(\omega\tau_L)\right]}{1 + i\omega\tau_h^{\infty}\left[1 + \dfrac{\tau_h^0 - \tau_h^{\infty}}{\tau_h^{\infty}} f(\omega\tau_L)\right]}, \qquad (6.16)$$

where here $f_{\beta}(\omega\tau_{\beta}) = f_C(\omega\tau_C) = f(\omega\tau_L)$ because, in equations (6.3), Y_i was taken to be proportional to X_i whatever i. Good fits were obtained for that long time part, which suggests that the frequency dependence of both $\beta(\omega)$ and $C_V(\omega)$ plays a role in glycerol.

7 Summary

The present paper has presented a consistent phenomenological approach to HD-TG experiments performed at small scattering angles in molecular supercooled liquids formed of linear molecules[13].

In Section 2, we have proposed a set of generalised Navier-Stokes equations which take into account, simultaneously:

- the molecular character of the liquid, whence the addition to the usual set of equations of an additional equation describing the dynamics of $\bar{\bar{Q}}$, a symmetrical traceless tensor that represents the mean local anisotropy of the molecular orientation;
- the existence of a rotation-translation coupling mechanism for these molecules, which couples the strain rate to $\dot{\bar{\bar{Q}}}$ through the rotation-translation coupling function μ(t);
- the viscoelastic nature of the liquid, which leads to the introduction of various relaxation processes in these generalised Navier-Stokes equations.

Furthermore, in each of those equations, a single source term describes the interaction of the pumps with the liquid when only density and orientation modulations contribute to the variation of the dielectric tensor[14].

Let $R_{ij,kl}(\vec{q},t)$ be the TG dielectric response function (see Eq. (3.1a)) measured in such an experiment at time t after an impulse with wavevector $\vec{q}$ has been given to the liquid by the sources at time $t = 0$, i and j being indices describing, respectively, the polarisation of the probe and diffracted beams, while k and l describe the polarisation of the two pumps. We have shown that only six such response functions exist that are analytically distinct, and that particular choices for the polarisation of the pumps, probe, and diffracted beams allow to detect separately five of them; Section 3 and Appendix C have been devoted to the computation of the these five response functions. In the rest of the paper, we have concentrated on the four response functions that have the specific form $R_{ii,jj}(\vec{q},t)$, the directions i (or j) being either parallel to the longitudinal phonon, (direction $\hat{x}$) or perpendicular to the scattering plane (direction $\hat{y}$) (see Fig. 1)). The four different $R_{ii,jj}(\vec{q},t)$ have the form of weighted sums of two terms.

The first term corresponds to the direct orientation of the molecules by the electric torque owing to the coupling of the pumps to the anisotropic part of the molecular polarisability tensor. This signal could also have been measured in an Optical Kerr Effect (OKE) experiment so that we have named this response function $R_{\mathrm{OKE}}(t)$.

The second term is the product of three factors in the frequency space:

- one is the detection mechanism, (see Eq. (3.2)), which appears as the sum of density (label "dens") and molecular orientation (label "or") modulations;
- the second factor is the propagator of the longitudinal phonon launched by the three sources;
- the third factor represents the sum of the interaction of the three sources with the liquid: thermal absorption (label "ther"), density change (label "dens") due to the electrostrictive effect at optical frequencies, and orientation of the molecules (label "or") due to the torque effect, the heat diffusion mechanism appearing with the thermal absorption.

This second term can thus be split into a weighted sum of six "elementary response functions", in short ERFs, each being specified by two labels, the first one describing the detection mechanism, and the second the corresponding source. Thus those ERFs will be called, for instance, $R_{or-ther}(\vec{q},t)$, or $R_{dens-or}(\vec{q},t)$.

Section 4 has been totally devoted to the study of $R_{\mathrm{OKE}}(t)$ and, within a certain approximation discussed in its first section, of the six other ERFs: their time evolution, the relations between some of them and Brillouin-scattering spectra have been successively studied. In particular, we have shown that:

(a) any ERF containing a label "or" can be deduced from the corresponding ERF containing, at the same place, the label "dens" by a convolution product of the latter ERF with $\dot{\mu}(t)$ (cf., e.g., Eqs. (4.19b, 4.24b)). This implies that the total information contained in these six ERFs is concentrated, in fact in $R_{dens-dens}(\vec{q},t)$, frequently called the ISBS signal, $R_{dens-ther}(\vec{q},t)$, the ISTS signal, and in $\mu(t)$, the rotation-translation coupling relaxation function;

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[13] We expect our results to be very little modified for molecules having a higher anisotropy.

[14] Other source terms would have to be added if the variation of the dielectric tensor would also depend, e.g., on the temperature modulation [27].

(b) $R_{dens-dens}(\vec{q},t)$ can be expressed as the time derivative of the density-density correlation function of the liquid;

(c) $R_{dens-ther}(\vec{q},t)$ can be expressed as the convolution product of $R_{dens-dens}(\vec{q},t)$ with the relaxation function describing the thermal diffusion process (see Eqs. (4.21a, 4.21b)). We have also shown that this special analytic form allows obtaining information on the phonon and rotation-translation coupling relaxation times on a time scale that extends up to some 10 μs;

(d) for the four possible couples i and j, the weighted sum of the five ERFs entering the corresponding $R_{ii,jj}(\vec{q},t)$, and not involving the label "ther", is proportional to the time derivative of the correlation function of the diagonal elements of the dielectric function which have the same indices (see Eqs. (4.33, 4.34)). We have called this sum the generalised ISBS response function. Its existence has two consequences. On the one hand, as the Laplace-Transform of those correlation functions corresponds to Brillouin spectra that can be recorded using appropriate scattering geometries, those spectra and the generalised ISBS response function contain exactly the same information. On the other hand, despite the absence of symmetry between the sources (indices j) and the detection mechanism (indices i), the corresponding part of the response function is symmetrical in those two sets of indices, a totally non-trivial result;

(e) conversely, the part of $R_{ii,jj}(\vec{q},t)$ involving the label "ther", that we have called the generalised ISTS response function, is not symmetrical in i and j: the heat-absorption process breaks the symmetry between the pumps and the detection mechanism.

Because $R_{\mathrm{OKE}}(t)$ has a much shorter duration than the other ERFs, we have shown, in Section 5, that, in the most general case, three other ERFs, as well as a weighted sum of the ISTS and the ISBS signals, can be individually measured through definite linear combinations of the different $R_{ii,jj}(\vec{q},t)$. The results are even simpler if either the ISTS signal, or the ISBS signal, overweighs the other.

A short part of Section 6 has been devoted to a comparison between the present approach and former studies of TG-experiments performed on (molecular) supercooled liquids. In the rest of that section, we have discussed what happens to $R_{dens-dens}(\vec{q},t)$ at very long time and low temperature, when the supercooled liquid becomes already quite viscous. We have shown that various relaxation processes and some effects that have been neglected in Section 4 may be involved in the decrease of the effective heat-diffusion time. Such effects have been experimentally observed [2,8,11,29] when the structural relaxation time becomes longer than this diffusion time.

Our study has shown that different effects play a role in the shape of the polarised HD-TG signal of a supercooled molecular liquid. It is important to study this signal as the inverse Laplace-Transform of $R_{ii,jj}(\vec{q},\omega)$ to obtain a physically meaningful interpretation of its time evolution.

Polarisation is necessary to detect the difference between $R_{dens-ther}(\vec{q},t)$ and $R_{or-ther}(\vec{q},t)$, i.e. between the isotropic and anisotropic parts of the generalised ISTS signal. Their simultaneous study gives unique information on the longitudinal relaxation function and on the rotation-translation coupling function for $\tau_{anh} < \tau_L < \tau_h$.

Conversely, the two signals have the same shape for $\tau_L \approx \tau_h$ and for $\tau_L > \tau_h$. In these regions, it is the interplay between the heat-diffusion process and the relaxation processes related to the longitudinal relaxation, the specific heat, and the tension coefficient that governs the shape of the signal. It will be necessary to study this signal over a very large time interval (i.e. even for $t \ll \tau_h$), and a large temperature region (i.e. even for $\tau_L \ll \tau_h$) to disentangle effects that can compete one against the others.

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Appendix A

We compute here the proportionality factor between the coefficient K that characterises the electrostrictive effect at optical frequencies, equation (2.24), and the coefficient a entering the dielectric tensor fluctuations, equation (3.2). We also compute the equivalent relation between the coefficient F characterising the torque produced by the electric field of the pumps and the anisotropic part of the molecular polarisability, the coefficient b of the same equation. This will result in a very simple relationship between K, F, a and b. We obtain these results by:

- first, directly relating the action of the pumps, supposed to act permanently ($g_0(t)$ = constant) on a transparent liquid (no heat absorption) to their physical consequences: building up of a permanent periodic density-modulation, $\delta\rho^0(\vec{r})$, or of a permanent orientation-modulation, $\bar{\bar{Q}}^0(\vec{r})$;
- second, obtaining the same result using either equation (2.24c) or equation (2.28).

The comparison between the results of the two techniques yields the proportionality coefficients, and finally, a simple relation, equation (A.16), between these four coefficients, Λ', and ρ_m.

Before starting this calculation, let us point out that equation (3.2) corresponds to the separation of the polarisability fluctuations of the liquid into two parts: an electronic part, that corresponds to the change of the refractive index and which, eventually, leads to density modulations and an orientational part. In a static electrostrictive experiment, the liquid minimises its energy with respect to the two mechanisms but one cannot separate their relative contribution. TG-experiments necessitate this separation both for the detection mechanism and for the sources. This is why we discuss in Section A.1 an electrostrictive experiment that involves only the electronic contribution while Section A.2 is devoted to the similar orientation effect.

A.1 Relationship between a and K

Let χ be the relative susceptibility of the liquid at optical frequencies. $\vec{E}_{int}(\vec{r})$ creates in the whole liquid a periodic, permanent, energy density equal to[15]

$$V_{pot}(\vec{r}) = -\frac{\varepsilon_0}{2}E^2\chi\cos qx, \tag{A.1}$$

where χ is a function of the mass density, $\rho(\vec{r})$. $V_{pot}(\vec{r})$ generates, in turn, a density fluctuation, $\delta\rho(\vec{r})$, with the same period, which further decreases the liquid energy. This energy-density change reads

$$\delta V_{pot}(\vec{r}) = -\frac{\varepsilon_0}{2}E^2\rho_m \left.\frac{\partial\chi}{\partial\rho}\right)_T \cos qx\frac{\delta\rho(x)}{\rho_m}. \tag{A.2}$$

As a relative density change is the opposite of a local deformation of the liquid ($\frac{\delta\rho(x)}{\rho_m} = -\frac{dU(x)}{dx}$, where $U(x)$ is the mean displacement of the molecules in the liquid), $\delta\rho(\vec{r})$ also increases the local elastic energy density

$$\delta V_{elas}(\vec{r}) = \frac{\rho_m}{2}c_i^2\left(\frac{dU(x)}{dx}\right)^2 = \frac{\rho_m}{2}c_i^2\left(\frac{\delta\rho(x)}{\rho_m}\right)^2. \tag{A.3}$$

Minimising, at every point, $\delta V_{pot}(\vec{r}) + \delta V_{elas}(\vec{r})$ with respect to $\frac{\delta\rho(x)}{\rho_m}$ yields the equilibrium value, $\delta\rho^0(x)$

$$c_i^2\delta\rho^0(x) = \frac{\varepsilon_0}{2}E^2\rho_m \left.\frac{\partial\chi}{\partial\rho}\right)_T \cos qx. \tag{A.4}$$

The same result can be obtained from equation (2.24c). In the permanent regime, there is no thermal modulation, $\delta T(\vec{r}) = 0$, and the two time derivatives, $\vec{v}$ and $\dot{\bar{\bar{Q}}}$, are also equal to zero. As the permanent situation corresponds to the absence of stress in the liquid, this equation reads

$$c_i^2\delta\rho^0(x) - 2KE^2\cos qx = 0. \tag{A.5}$$

Identifying equation (A.4) with equation (A.5) leads, with the help of the definition $a = \left.\frac{\partial\chi}{\partial\rho}\right)_T$, to

$$\frac{K}{a} = \frac{\varepsilon_0}{4}\rho_m. \tag{A.6}$$

A.2 Relationship between b and F

In a real liquid, the orientational isotropy is an equilibrium situation that results from the thermal agitation and that will eventually be reached whatever is the initial orientational probability distribution. Conversely, the model represented by equation (2.9) implies the existence of an instantaneous restoring force characterised by the libration frequency $\omega_R/2\pi$, ω_R^{-1} being very short with respect to any other characteristic time of the problem, in particular the period of the longitudinal phonons. The short time dynamics of the supercooled liquid can be obtained by describing it as an isotropic orientational glass with fixed mean orientation for each molecule. This orientation can be perturbed by the molecular libration motion and it is also modified by the coupling of the anisotropic part of its polarisability tensor to $\vec{E}_{int}(\vec{r})$.

To obtain the relation between F and b, it is sufficient to consider one particular $\vec{E}_{int}(\vec{r})$. We choose it to result from fields $\vec{E}_1$ and $\vec{E}_2$ parallel to $\hat{y}$ so that

$$T_{ij}^g(\vec{r}) = E^2C_{ij}(\hat{y})\cos qx, \tag{A.7}$$

and $\hat{y}$ will also be the polar axis that defines the variable ϑ of the molecular orientation.

With the definition of b given in equation (3.2), the energy density at point $\vec{r}$, for molecules with orientation ϑ, φ (orientational probability $\frac{\sin\vartheta d\vartheta d\varphi}{4\pi}$) produced by the polarisation anisotropy of those molecules by $\vec{E}_{int}(\vec{r})$ is

$$V_{orient}(\vec{r},\vartheta) = -\frac{\varepsilon_0}{2}E^2nb\left(\cos^2\vartheta - \frac{1}{3}\right)\cos qx, \tag{A.8}$$

where n is the number density of the liquid. V_{orient} plays for the molecular orientation the same role as V_{pot} for the mass density in equation (A.1). The molecules tend to reorient by some amount $\delta\vartheta$ to minimise their energy with respect to V_{orient}. Simultaneously, this change of orientation increases their energy in their vibrational potential. The equilibrium value, $\delta\vartheta^0(x,\vartheta)$, of the orientational change generates an anisotropic orientational probability, thus a non-zero value, $\bar{\bar{Q}}^0(x)$, of $\bar{\bar{Q}}(x)$, that we now compute.

The change in $V_{orient}(\vec{r},\vartheta)$ due to $\delta\vartheta(x,\vartheta)$ is

$$\delta V_{orient}(\vec{r},\vartheta) = \varepsilon_0E^2n\,b\cos\vartheta\sin\vartheta\cos qx\,\delta\vartheta(x,\theta), \tag{A.9}$$

while the departure from their preferred orientation corresponds to an increase of energy density

$$\delta V_{libr}(\vec{r},\theta) = \frac{nI}{2}\omega_R^2\delta\vartheta^2(x,\vartheta), \tag{A.10}$$

where I is the moment of inertia of the molecule around an axis perpendicular to its symmetry axis and passing through its centre of mass. The equilibrium value, $\delta\vartheta^0(x,\theta)$, is obtained from the minimisation of $\delta V_{orient}(\vec{r},\theta) + \delta V_{libr}(\vec{r},\theta)$, which yields

$$\delta\vartheta^0(x,\vartheta) = -\frac{\varepsilon_0E^2b}{I}\omega_R^2\cos\vartheta\sin\vartheta\cos qx \equiv h^0(\vartheta,x). \tag{A.11}$$

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[15] In view of the discussion performed in Section 2.4, we chose E_1 and E_2 to be equal to E, the two fields having identical polarisation.

All the molecules with initial orientation ϑ, φ have their orientation changed into $\vartheta + h^0(\vartheta, x), \varphi$, and the local mean value, $F(x)$, of a function $F(\vartheta, \varphi, x)$ with this modified orientational probability is

$$F(x) = \frac{1}{4\pi}\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\vartheta F\left(\vartheta + h^0(\vartheta, x), \varphi\right) d\vartheta. \tag{A.12}$$

By definition, the tensor $\bar{\bar{Q}}(x)$ is the local mean value of $n\bar{\bar{C}}(\vartheta, \varphi, x)$. Expanding equation (A.12) up to first order in $h^0(\vartheta, x)$ and taking for F the six components of $C_{ij}(\hat{u})$, one obtains

$$\bar{\bar{Q}}^0(x) = \frac{\varepsilon_0 E^2}{2}\frac{4}{5}\frac{nb}{I}\omega_R^2 \bar{\bar{C}}(\hat{y})\cos qx. \tag{A.13}$$

It was shown in equation (31b) of [23] that $\Lambda' = \frac{2}{5}\frac{n}{I}$. The preceding equation can thus be expressed as

$$\omega_R^2 \bar{\bar{Q}}^0(x) = \frac{2\Lambda'}{\rho_m}\frac{\varepsilon_0}{2}\rho_m b E^2 \bar{\bar{C}}(\hat{y})\cos qx. \tag{A.14a}$$

The value of $\omega_R^2 \bar{\bar{Q}}^0(x)$ can also be obtained from a direct use of equation (2.28) in the permanent regime

$$\omega_R^2 \bar{\bar{Q}}^0(x) = 2FE^2 \bar{\bar{C}}(\hat{y})\cos qx. \tag{A.14b}$$

Identification of equation (A.14a) with equation (A.14b) leads to

$$\frac{\rho_m}{\Lambda'}\frac{F}{2b} = \frac{\varepsilon_0}{4}\rho_m. \tag{A.15}$$

Comparing equations (A.6, A.15), one finally obtains a relation between K, F, a, and b

$$\frac{K}{a} = \frac{\rho_m}{\Lambda'}\frac{F}{2b} = \frac{\varepsilon_0}{4}\rho_m = S. \tag{A.16}$$

Appendix B

In a liquid, in absence of non-local effects at the macroscopic level, and in the limit of zero absorption, the dielectric function which relates the electric displacement field, $\vec{D}(\vec{r}, t)$, to the electric macroscopic field, $\vec{E}(\vec{r}, t)$, is a local quantity

$$\vec{D}(\vec{r}, t) = \varepsilon_0 \int_{-\infty}^{t} dt' \int d\vec{r}\,' \bar{\bar{\varepsilon}}(\vec{r}\,', t')\vec{E}(\vec{r}\,', t')\delta(\vec{r} - \vec{r}\,')\delta(t - t'), \tag{B.1}$$

where $\bar{\bar{\varepsilon}}(\vec{r}, t)$ is a symmetrical tensor. At equilibrium, the spatio-temporal translational invariance of the liquid imposes that $\bar{\bar{\varepsilon}}(\vec{r}, t)$ depends neither on $\vec{r}$, nor on t

$$\bar{\bar{\varepsilon}}(\vec{r}, t) = \bar{\bar{\varepsilon}}_m, \tag{B.2}$$

while rotational invariance implies that $\bar{\bar{\varepsilon}}_m$ is an isotropic tensor

$$\bar{\bar{\varepsilon}}_m = \varepsilon_m \bar{\bar{I}}. \tag{B.3}$$

When the liquid is perturbed by a time and space varying fluctuation characterised by the wavevector $\vec{q}$, $\bar{\bar{\varepsilon}}(\vec{r}, t)$ looses its translational symmetry along the direction $\hat{q}$ and in time but it keeps its rotational symmetry around $\hat{q}$. When the Fourier-Transform of $\bar{\bar{\varepsilon}}(\vec{r}, t)$, $\bar{\bar{\varepsilon}}(\vec{q}, t)$, is expressed as a response function, equation (3.1a), the elements $R_{ij,kl}(\vec{q}, t)$ of the response function are symmetrical in i and j, by definition of $\bar{\bar{\varepsilon}}(\vec{r}, t)$, and in k and l by construction. There are thus only 6 (ij) and 6 (kl) couples and thus, at most, 36 different elements of this tensor. But $R_{ij,kl}(\vec{q}, t)$ has a D_∞ symmetry along $\hat{q}$ because of the remaining rotational symmetry around this direction and of the additional symmetry of the source in $\vec{q}$ and $-\vec{q}$. More precisely, if the axes of the system are defined as in Figure 1, there are only 12 non zero elements, among which only 7 are different, as indicated in equation (3.1b), because this symmetry imposes that each index must appear an even number of times and that the $\hat{y}$ and $\hat{z}$ directions are equivalent but are different of the $\hat{x}$ direction.

Appendix C

The calculation of $R_{xy,xy}(\vec{q}, \omega)$ is simple because the sole source is the torque on the molecules, the last term of equation (2.30). There is no temperature modulation and one must only consider equations (2.5, 2.28). Taking $\vec{E}_1 = E\hat{x}$ and $\vec{E}_2 = E\hat{y}$, one easily obtains from equations (2.4, 2.5, 2.7)

$$\omega\rho_m v_y(\vec{q}, \omega) = -q\sigma_{xy}(\vec{q}, \omega), \tag{C.1}$$

$$\tau_{xy}(\vec{q}, t) = -iqv_y(\vec{q}, t), \tag{C.2}$$

$$\sigma_{xy}(\vec{q}, \omega) = -\left[q\eta_s(\omega)v_y(\vec{q}, \omega) + \omega\mu(\omega)Q_{xy}(\vec{q}, \omega)\right], \tag{C.3}$$

while equation (2.28) yields

$$Q_{xy}(\vec{q}, \omega) = -q\Lambda' r(\omega)v_y(\vec{q}, \omega) + i\frac{FE^2}{2D(\omega)}. \tag{C.4}$$

Solving equations (C.1, C.3) for $v_y(\vec{q}, \omega)$ and injecting the result into equation (C.4) gives

$$Q_{xy}(\vec{q}, \omega) = \frac{iFE^2}{2}\left[D^{-1}(\omega) - \Lambda'\frac{q^2}{\rho_m}r(\omega)P_T(\vec{q}, \omega)\right], \tag{C.5a}$$

where

$$P_T(\vec{q}, \omega) = \left[\omega^2 - q^2\rho_m^{-1}\omega\eta_T(\omega)\right]^{-1} \tag{C.5b}$$

is the propagator of a transverse phonon with wave vector q (cf. Eq. (37b) of [23]). One thus obtains, in complete analogy with the parallel polarisation case,

$$R_{xy,xy}(\vec{q}, \omega) = R^{(1)}_{xy,xy}(\omega) + R^{(2)}_{xy,xy}(\vec{q}, \omega), \tag{C.6}$$

$$R^{(1)}_{xy,xy}(\omega) = ibD^{-1}(\omega)F, \tag{C.7a}$$

$$R^{(2)}_{xy,xy}(\vec{q}, \omega) = -\frac{i\Lambda' b}{\rho_m}r(\omega)P_T(q, \omega)q^2 Fr(\omega). \tag{C.7b}$$

Thus, $R_{xy,xy}(\vec{q}, t)$ contains two ERFs. One is $R_{\mathrm{OKE}}(t)$, as in the polarised experiments. The second has a structure similar to $R_{or-or}(\vec{q}, t)$ but it involves a transverse phonon instead of longitudinal one.

Appendix D

We discuss here the form of $C_V(\omega)$ and $\beta(\omega)$. As has been proposed by Götze and Latz [39] (see also Franosch et al. [32]) there are two contributions to the specific heat at constant volume. One is instantaneous and corresponds to the degrees of freedom that define the local temperature (such as the thermal motions of the centres of mass): a change in temperature corresponds to an immediate transfer of heat to the liquid. In a second step, the internal degrees of freedom exchange energy with the heat bath to modify the liquid structure: this takes place on the time scale of the structural relaxation. To maintain the temperature at its new set value, extra energy has to be given to the liquid at later times. If $\delta C_V(\mathrm{t})$ is a positive decreasing function whose limit equals zero for infinite time, the opposite of its derivative is also always positive with a zero limit for infinite time. One can thus write

$$C_V(t) = C_V^\infty \delta(t) - \delta \dot{C}_V(t), \tag{D.1}$$

where C_V^∞ is a positive quantity. One has by definition

$$C_V^{th} \equiv \int_0^\infty C_V(t)dt = C_V^\infty + \delta C_V(t=0). \tag{D.2}$$

Using equations (4.11a, 4.12c), the Laplace-Transform of equation (D.1) reads

$$C_V(\omega) = iC_V^\infty - i\left(\omega\delta C_V(\omega) - \delta C_V^0\right) = iC_V^{th} - i\omega\delta C_V(\omega), \tag{D.3a}$$

with

$$C_V^{th} = C_V^\infty + \delta C_V^0. \tag{D.3b}$$

This general form of equation (D.3a) agrees with the measurements of the frequency dependence of the specific heat, as performed in different supercooled liquids, where values of $\lim_{\omega\to\infty}[\omega\delta C_V(\omega)]$ of the order of $C_V^{th}/2$ have been reported [37,38] in the vicinity of the liquid-glass transition. Unfortunately, such measurements correspond to values of the α-relaxation times longer than 10^{-4} s and are not technically feasible for the shorter relaxation times of interest here. Conversely, theoretical considerations and numerical calculations predict [40] an important decrease of $\lim_{\omega\to\infty}[\omega\delta C_V(\omega)]$ with increasing temperature while C_V^{th} changes very little. Indeed, in a normal liquid, the disorder is completely taken into account by the normal degrees of freedom. No extra energy has to be taken into account, contrary to the case of a supercooled liquid.

A similar analysis can be made for $\beta(\omega)$, leading to a functional form similar to equation (D.3a). Yet, the signs of β^{th} and $\delta\beta(t)$ cannot be predicted from a priori considerations. A hint for these quantities can be obtained if we assume that the relation, valid for normal liquids,

$$\beta = c_i^2\alpha, \tag{D.4a}$$

where α is the isobaric thermal expansion coefficient, still approximately holds when structural relaxation is present

$$\beta(t) = c_i^2\alpha(t). \tag{D.4b}$$

Though there is no general rule (water below 4 °C is, in that respect, a well-known counter example), α^{th} and $\delta\alpha(t)$ are usually positive.

Appendix E

The decomposition of $g(q,\omega)$, equation (3.12), into a form that allows to pass from the full phonon propagator, $P_L'(\vec{q},\omega)$, to the usual phonon propagator in the adiabatic limit, $P_L(\vec{q},\omega)$, is conveniently performed in two steps. The first one consists in ignoring the frequency dependence of $C_V(\omega)$ and $\beta(\omega)$, which reduces them to iC_V^{th} and $i\beta^{th}$, respectively. The classical decomposition of $\bar{g}(q,\omega)$, the corresponding form of $g(q,\omega)$, is described, e.g., in [30]

$$\begin{aligned}\bar{g}(q,\omega) &= \rho_m T_m \frac{\left(\beta^{th}\right)^2}{C_V^{th}}\left[1 - \frac{1}{1+i\omega\tau_h(q)}\right]\\ &= g_0 - \rho_m T_m \frac{\left(\beta^{th}\right)^2}{C_V^{th}}\frac{1}{1+i\omega\tau_h(q)},\end{aligned} \tag{E.1a}$$

with

$$\tau_h(q) = \frac{C_V^{th}}{\lambda q^2}. \tag{E.1b}$$

For $\omega\tau_h(q) \gg 1$, the Brillouin-scattering domain, the r.h.s. of equation (E.1a) reduces to g_0, a quantity that has the dimension of the square of a velocity. g_0 relates c_a, the adiabatic sound velocity c_i, the isothermal sound velocity, through

$$c_i^2 = c_a^2 - g_0 = c_a^2 - \rho_m T_m \frac{\left(\beta^{th}\right)^2}{C_V^{th}}. \tag{E.2}$$

This equation describes the coupling of a wave, normally propagating in an adiabatic regime, with the heat flow. This coupling decreases the velocity of the wave, the coupling coefficient, β^{th}, appearing twice, as expected. A classical thermodynamic treatment of the factors entering g_0 shows that

$$g_0 = c_i^2(\gamma - 1), \tag{E.3a}$$

with

$$\gamma = \frac{C_P^{th}}{C_V^{th}}, \tag{E.3b}$$

where C_P^{th} is the specific heat at constant pressure. The structure of the second term of the r.h.s. of equation (E.1a) shows that the preceding coupling takes place only when $\omega\tau_h(q) \approx 1$, in which case

$$\bar{g}(q,\omega) = i\omega g_0 \tau_h(q), \tag{E.4}$$

and the coupling of the isothermal sound wave with heat results in a very low frequency damping.

The inclusion of the frequency dependence in $C_V(\omega)$ and $\beta(\omega)$ simply adds a third term in the decomposition of $g(q,\omega)$

$$\begin{aligned}g(q,\omega) = &-i\rho_m T_m \frac{\beta^2(0)}{C_V(0)} - i\rho_m T_m\left(\frac{\beta^2(\omega)}{C_V(\omega)} - \frac{\beta^2(0)}{C_V(0)}\right)\\ &+ i\rho_m T_m \frac{\beta^2(\omega)}{C_V(\omega)}\frac{1}{1+i\omega\tau_h(q,\omega)},\end{aligned} \tag{E.5}$$

where we have replaced β^{th} (respectively C_V^{th}) by $-i\beta(\omega = 0)$ (respectively $-iC_V(\omega = 0)$), see equations (D.3). Equation (E.5) differs from equation (E.1a) in only two respects:

- the second term of its r.h.s. represents an additional contribution to the bulk viscosity, as it has the same analytical structure as $\rho_m^{-1}\omega\eta_b(\omega)$. Indeed, this term is equal to zero for zero-frequency and the results of Appendix D show that its real part has a finite value for $\omega\tau \gg 1$. Also, its imaginary part is proportional to ω at low frequency and tends to zero when $\omega\tau \gg 1$;
- the last terms of equations (E.1, E.5) are identical, except for a frequency dependence of $\beta(\omega)$, $C_V(\omega)$ and $\tau_h(q,\omega)$. This simply adds an additional damping channel and a renormalisation of the heat diffusion time (see Sect. 6.3).

References

1. H. Eichler, G. Salje, H. Stahl, J. Appl. Phys. **44**, 5383 (1973); D.W. Pohl, S.E. Schwarz, V. Irniger, Phys. Rev. Lett. **31**, 32 (1973)
2. C. Allain, P. Lallemand, J. Phys. France **40**, 679 (1976); C. Allain, P. Lallemand, J. Phys. France **40**, 693 (1976)
3. K.A. Nelson, R.J. Dwayne Miller, D.R. Lutz, M.D. Fayer, J. Appl. Phys. **53**, 1144 (1982)
4. H.J. Eichler, P. Günter, D.W. Pohl, *Laser-Induced Dynamics Gratings* (Springer Berlin, 1986)
5. Y.X. Yan, L.T. Cheng, K.A. Nelson, J. Chem. Phys. **88**, 6477 (1988)
6. Y. Yang, K.A. Nelson, J. Chem. Phys. **103**, 7722 (1995)
7. A.R. Duggal, K.A. Nelson, J. Chem. Phys. **94**, 7677 (1991)
8. Y. Yang, K.A. Nelson, J. Chem. Phys. **103**, 7732 (1995)
9. Y. Yang, K.A. Nelson, J. Chem. Phys. **104**, 5429 (1996)
10. D.M. Paolucci, K.A. Nelson, J. Chem. Phys. **112**, 6725 (2000)
11. R. Torre, A. Taschin, M. Sampoli, Phys. Rev. E **64**, 061504 (2001)
12. A. Taschin, R. Torre, M. Ricci, M. Sampoli, C. Dreyfus, R.M. Pick, Europhys. Lett. **56**, 407 (2001)
13. R.M. Pick, C. Dreyfus, A. Azzimani, A. Taschin, M. Ricci, R. Torre, T. Franosch, J. Phys.: Condens. Matter **15**, S825 (2003)
14. C. Glorieux, K.A. Nelson, G. Hinze, M.D. Fayer, J. Chem. Phys. **116**, 3384 (2002)
15. G. Hinze, R.S. Francis, M.D. Fayer, J. Chem. Phys. **111**, 2710 (1999)
16. S.M. Rytov, Soviet Physics JETP **6**, 401 (1958)
17. V.S. Starunov, E.V. Tiganov, I.V. Fabelinski, JETP Lett. **5**, 260 (1967)
18. G.I.A. Stegeman, B.P. Stoicheff, Phys. Rev. Lett. **21**, 202 (1968)
19. T. Keyes, D. Kivelson, J. Chem. Phys. **54**, 1786 (1971)
20. H.C. Andersen, R. Pecora, J. Chem. Phys. **54**, 2584 (1971); H.C. Andersen, R. Pecora, J. Chem. Phys. **55**, 1496 (1972)
21. G.D. Enright, B.P. Stoicheff, J. Chem. Phys. **64**, 3658 (1976)
22. C. Dreyfus, A. Aouadi, R.M. Pick, T. Berger, A. Patkowski, W. Steffen, Europhys. Lett. **42**, 55 (1998); C. Dreyfus, A. Aouadi, R.M. Pick, T. Berger, A. Patkowski, W. Steffen, Eur. Phys. J. B **9**, 401 (1999)
23. A. Latz, M. Letz. Eur. Phys. J. B **19**, 323 (2001)
24. T. Franosch, A. Latz, R.M. Pick, Eur. Phys. J. B **31**, 229 (2003)
25. R.M. Pick, T. Franosch, A. Latz, C. Dreyfus, Eur. Phys. J. B **31**, 217 (2003)
26. H.P. Zhang, A. Brodin, H.C. Barshilia, G.Q. Shen, H.Z. Cummins, H.P. Zhang, A. Brodin, H.C. Barshilia, G.Q. Shen, H.Z. Cummins, R.M. Pick, Phys. Rev. E **69**, June Issue (2004); R.M. Pick, Phys. Rev. Lett. (submitted); H.P. Zhang, A. Brodin, H.C. Barshilia, G.Q. Shen, H.Z. Cummins, R.M. Pick, `cond-mat/0405202`
27. T. Franosch, R.M. Pick, in preparation
28. C. Dreyfus, A. Azzimani, R.M. Pick, A. Taschin, M. Ricci, R. Torre, in preparation
29. R. Di Leonardo, A. Taschin, R. Torre, M. Sampoli, G. Ruocco, J. Phys.: Condens. Matter **15**, S1181 (2003); R. Di Leonardo, A. Taschin, M. Sampoli, R. Torre, G. Ruocco, Phys. Rev. E **67**, 015102 (R) (2003)
30. J.P. Boon, S. Yip, *Molecular Hydrodynamics* McGraw-Hill (NewYork, 1980), Chap. 5-2
31. R. Torre, P. Bartolini, M. Ricci, R.M. Pick, Europhys. Lett. **52**, 324 (2000)
32. T. Franosch, M. Fuchs, A. Latz, Phys. Rev. E **63**, 061209 (2001)
33. T. Franosch, H.Z. Cummins, R.M. Pick, in preparation
34. A. Taschin, P. Bartolini, M. Ricci, R. Torre, Philos. Mag. B (in press)
35. R. Torre, M. Ricci, P. Bartolini, C. Dreyfus, R.M. Pick, Philos. Mag. B **79**, 1897 (1999)
36. I.C. Halalay, K.A. Nelson, J. Chem. Phys. **97**, 3557 (1992)
37. N.O. Birge, S.R. Nagel, Phys. Rev. Lett. **54**, 2674 (1985); N.O. Birge, Phys. Rev. B **34**, 1631 (1986)
38. P.K. Nixon, Phys. Rev. B **42**, 8179 (1990); O. Bustin, M. Descamps, J. Chem. Phys. **110**, 10982 (1999); L. Carpentier, M. Descamps, J. Phys. Chem. B **107**, 271 (2003)
39. W. Götze, A. Latz, J. Phys.: Condens. Matter **1**, 4169 (1989)
40. F. Sciortino, private communication