Analysis of a heterodyne-detected transient-grating experiment on a molecular supercooled liquid. I. Basic formulation of the problem

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We present the basic equations necessary to interpret heterodyne-detected transient-grating experiments performed on a supercooled liquid composed of anisotropic molecules. The final expressions are given under a form suitable for their direct application to a test case.

I. INTRODUCTION

During the last decade, time resolved light-scattering spectroscopy has been recognized as a very important tool for the study of the dynamics of supercooled molecular liquids. One such technique is the optical Kerr effect (OKE), in which a very intense laser beam with short duration ($\sim 10^{-4}$ ns) (the pump), whose frequency is not absorbed, travels through the liquid. Its electric field slightly orients the molecules, creating an optical anisotropy. The anisotropy is probed at a sequence of later times by the change it produces on the polarization of a second beam (the probe), which propagates in the previously illuminated region along the same direction as the pump. This technique gives very precise information on the pure rotational relaxation dynamics of molecules with an anisotropic polarizability tensor, over a time scale extending typically from 10^{-4} ns up to 10 ns. OKE has been used to study, *inter alia*, salol [1], orthoterphenyl (*o*-TP) [2], *m*-toluidine [3], benzophenone and biphenyl methanol [4], and, more recently, supercooled water [5]. The OKE time window is well-suited to compare the recorded relaxation dynamics with the predictions of mode coupling theory (MCT) above its critical temperature, T_c, because T_c typically corresponds, in real supercooled liquids, to relaxation times of the order of 10–10^2 ns. This comparison has been quite fruitful and has demonstrated the existence, in the relaxation dynamics, not only of the primary α relaxation process, but also of its precursors, the von-Schweidler and the so-called β-fast processes [6] and, more recently [7], at yet shorter times, of pseudologarithmic dynamics evidenced in [4] in the 10^{-3}–10^{-2} ns regime, that had escaped previous theoretical analyses.

The other important time-resolved optical spectroscopy method for the study of supercooled liquids is the transient-grating (TG) technique, which explores a much longer time interval and is better adapted to the lower temperature domain. In this method, two pulses originating from a single laser propagate in nearly parallel directions, crossing at a small angle and interfering in the liquid. The duration of the pulses is typically 10^3 longer than in an OKE experiment. The technique turns out to be most powerful when the pump frequency is such that the liquid slightly absorbs the pump

beams. In the classical description of this experiment [8], the interference between the electric field of the two pump beams creates a density grating, both directly, through an electrostrictive effect, and indirectly, through a temperature grating created by the energy absorption. The time evolution of the amplitude of a continuous probe beam diffracted by the grating monitors its decay. The duration of the recorded signal corresponds either to the lifetime, τ_B, (typically 10 to 10^3 ns), of the longitudinal phonons with wave vector $\vec{q}$ launched by the pumps or, when energy absorption takes place, to the lifetime, τ'_h, (10^4–10^5 ns) of the thermal grating, which is limited by the heat diffusion process. One thus records signals in a time domain quite different from the OKE domain and very different information can be deduced from such experiments. This was recognized as early as 1995 by Nelson *et al.* [8] who proposed, on the basis of an elementary analysis of the origin of the signal, that an α relaxation time, τ'_L, could be directly accessed when the condition $\tau_B < \tau'_L < \tau'_h$ is fulfilled. The other pieces of information to be deduced would be the apparent phonon frequency, ω_B, and its lifetime, $\tau_B = 1/\Gamma_B$, as well as the value of τ'_h. The latter turned out to exhibit an apparent strong increase for $\tau'_L \approx \tau'_h$, followed by a more important decrease below its high temperature value when $\tau'_L > \tau'_h$; this last effect had, in fact, been already noticed, more than 20 years before, by Allain *et al.* [9], through an early version of a TG experiment. Salol [10], CKN [11], glycerol [12], and *o*-TP [13] have been analyzed within the Nelson *et al.* framework, all revealing similar features. The theory had to be revisited [14] when the accuracy introduced by the use of the heterodyne-detection method (HD-TG) allowed one to show that, in some supercooled liquids composed of sufficiently anisotropic molecules, the transient grating was also optically anisotropic; different polarizations of the probe beam led to signals with different shapes [14,15]. An elementary theory of the signals recorded in *m*-toluidine, at different temperatures and with different polarizations of the probe, was presented in [14].

The complete expression of the HD-TG signals recorded when studying a supercooled molecular liquid formed of axially symmetric molecules was given in [16]. The theory made use of a set of equations, deduced from phenomeno-

logical considerations. Its major improvement over the previous formulation [8] was the introduction, following a method already used by some of us in [17],

(1) on the one hand, of a coupling between the longitudinal phonons and the mean local orientation of the molecules and

(2) on the other hand, of the influence of these two quantities on the modulation of the local dielectric tensor.

Relaxation mechanisms were also introduced in all the couplings, and the whole set of equations was later derived [18] with the help of a Zwanzig Mori technique. The theoretical expressions showed that different relaxation mechanisms, related, in particular, to the propagation of the longitudinal phonons and to their coupling with the mean orientation could, in principle, be deduced from the signals measured with different polarizations.

In the current paper, we present the results of the first analysis of a HD-TG experiment, performed at LENS on *m*-toluidine and conducted along the lines proposed in [16] in two successive papers. This first paper, Paper I, describes the way the theory has to be approximated and adapted to the experimental situation in order to extract some specific information. Section II recalls the basic ingredients of the theory and the physical meaning of the results obtained in [16]. Section III gives the formulas which will be compared with the experimental signals and the principal approximations necessary for fitting the data in a meaningful way. In the second paper, paper II [19], the results of paper I are tested on *m*-toluidine, and are found to provide many different results.

II. THE THEORETICAL FORMULATION

A. The HD-TG response function

In this section, we briefly present the theoretical formulation leading to the expressions needed to interpret HD-TG data. The details of the method have been previously presented in [16] and we mostly emphasize here the physical aspects necessary for the understanding of the fitting procedure. References [16,17] assumed that the local fluctuations of the dielectric tensor, $\delta\bar{\bar{\varepsilon}}(\vec{r},t)$, are linearly related to both the local mass density fluctuations, $\delta\rho(\vec{r},t)$, and to the local orientational fluctuations, $\bar{\bar{Q}}(\vec{r},t)$, of the liquid where $\bar{\bar{Q}}(\vec{r},t)$ is a traceless, symmetrical, tensor which characterizes the mean orientation of molecules with axial symmetry at point $\vec{r}$ and time t

$$\delta\bar{\bar{\varepsilon}}(\vec{r},t) = a\,\delta\rho(\vec{r},t)\bar{\bar{I}} + b\bar{\bar{Q}}(\vec{r},t). \qquad (2.1)$$

In a HD-TG experiment, one directly monitors the time evolution of $\delta\bar{\bar{\varepsilon}}(\vec{r},t)$ after an initial perturbation at time $t=0$, so that a and b characterize the two detection channels of the signal. Let $\vec{E}_1$ and $\vec{E}_2$ be the electric fields associated with the two coherent pump beams with wave vectors, respectively, $\vec{k}_1=\vec{q}_0+\frac{\vec{q}}{2}$ and $\vec{k}_2=\vec{q}_0-\frac{\vec{q}}{2}$, with $\vec{q}_0=q_0\hat{z}$, $\vec{q}=q\hat{x}$, and $q\ll q_0$. The two vectors $\vec{k}_1$ and $\vec{k}_2$ define the scattering plane. In the TG experiment we discuss here, $\vec{E}_1$ and $\vec{E}_2$ are both either per-

pendicular to that plane (VV polarization), or in that plane (HH polarization) thus always (nearly) parallel to each other. Interference between the two coherent electric fields of the pumps creates in the liquid a spatially modulated electric field, $\vec{E}_{\text{int}}(\vec{r},t)$, which is the origin of a spatially modulated energy density, $U(\vec{r},t)$. This density reads, in the impulsive limit we consider in this section,

$$U(\vec{r},t) = \varepsilon_m \vec{E}_1 \cdot \vec{E}_2 \cos(qx)\delta(t), \qquad (2.2)$$

where $\delta(t)$ is a Dirac function and ε_m the mean dielectric constant of the liquid. A small fraction, H, of $U(\vec{r},t)$ is absorbed by the liquid and produces a thermal grating which instantaneously (on the time scale of the experiment) generates a density grating.

The dielectric grating has two other origins, both linked to Eq. (2.1). Because the dielectric tensor changes with the density [the first term of the right-hand side (rhs) of this equation], the liquid tends to further minimize its modulated energy density by creating a mass density modulation with the same wave vector $\vec{q}$. The amplitude of this modulation is proportional to $a=\partial\varepsilon_m/\partial\rho$. Similarly, another minimization of the energy density can be obtained by orienting the molecules with respect to $\vec{E}_{\text{int}}(\vec{r},t)$. The latter creates a torque on the molecules that eventually generates a nonzero, modulated, $\bar{\bar{Q}}(\vec{r},t)$ with the same wave vector as above[1] and with an amplitude proportional to b. This spatially modulated molecular orientation is the third source of the dielectric grating, the corresponding contribution to the dielectric tensor being locally anisotropic, see Eq. (2.1) This anisotropy depends on the common direction of $\vec{E}_1$ and $\vec{E}_2$: an index $\varepsilon_{\text{ex}}=1$ ($\varepsilon_{\text{ex}}=-1$) indicates a VV (HH) polarization of the pumps, thus the two possible independent torques. Similarly, the continuous, polarized, probe beam diffracted by this transient dielectric grating has amplitude and a change in polarization that decay as these density and orientational gratings decay. When $\vec{E}_1$ and $\vec{E}_2$ are parallel, with H or V polarization, there are [16], for each polarization, two, and only two, independent signals that can be obtained by varying the polarization of the probe and of the diffracted beams: the first corresponds to the two beams having the same V polarization, the second to their having H polarization; the index ε_d takes the value 1 for VV polarization, and -1 for HH polarization.

Let us now turn to the expression of the equations of motion of all the variables of the problem. Reference [16] showed that, in the absence of sources, the Navier-Stokes equations which govern the dynamics of a molecular supercooled liquid formed of axially symmetric molecules should be written as:[2]

$$\bar{\bar{\sigma}} = (-c_i^2\delta\rho + \eta_b \otimes \text{div}\,\vec{v} - \rho_m\beta \otimes \delta T)\bar{\bar{I}} + \eta_s \otimes \bar{\bar{\tau}} - \mu \otimes \dot{\bar{\bar{Q}}},$$
$$(2.3a)$$

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[1]This can be described as a spatially modulated OKE.

[2]A somewhat more complex expression of Eq. (2.3c) was derived in [18] but that paper also showed that the extra term does not play any role in a TG experiment.

$$\ddot{\bar{\bar{Q}}} = -\omega_R^2 \bar{\bar{Q}} - \Gamma \otimes \dot{\bar{\bar{Q}}} + \Lambda' \mu \otimes \bar{\bar{\tau}}, \qquad (2.3b)$$

$$C_V \otimes \dot{T} - T_m \beta \otimes \dot{\rho} - \lambda \nabla^2 T = 0, \qquad (2.3c)$$

where $\bar{\bar{\sigma}}(\vec{r}, t)$ is the stress tensor, related to the mass density current, or momentum density, $\vec{J}(\vec{r}, t)$, by the momentum conservation equation:

$$\dot{\vec{J}} = \operatorname{div} \bar{\bar{\sigma}}, \qquad (2.4)$$

while $\vec{J}(\vec{r}, t)$ is related to the mass density by the mass conservation equation

$$\dot{\rho} + \operatorname{div} \vec{J} = 0. \qquad (2.5)$$

Here, $\delta T(\vec{r}, t)$ is a local temperature fluctuation, $\bar{\bar{\tau}}(\vec{r}, t)$ is the strain rate tensor, defined through the mean velocity field $\vec{v}(\vec{r}, t)$, and $\otimes$ indicates a time convolution product while $\eta_b(t)$, $\eta_s(t)$, $\mu(t)$, and $\Gamma(t)$ are, respectively, the bulk viscosity, the shear viscosity, the rotation-translation coupling, and the pure orientational relaxation functions. c_i is the isothermal sound velocity, ω_R a (very high) libration frequency, λ is the heat diffusion coefficient, Λ' a rotation-translation coupling constant, ρ_m the mean mass density, and T_m the mean temperature of the liquid. Finally, $C_V(t)$ and $\beta(t)$ are the time-dependent specific heat at constant volume and tension (or thermal pressure) functions. References [16,18] showed that those two functions contain not only a time dependent part but also an instantaneous part and should be written as

$$C_v(t) = C_V^\infty \delta(t) - \delta \dot{C}_V(t), \qquad (2.6a)$$

$$\beta(t) = \beta^\infty \delta(t) - \delta \dot{\beta}(t), \qquad (2.6b)$$

where C_V^∞ and β^∞ are these instantaneous parts, while $\delta C_V(t)$, and $\delta \beta(t)$ are normal relaxation functions. Consequently, the specific heat at constant volume, C_V^{th}, and the pressure coefficient, β^{th}, which are measured in a usual thermodynamic measurement, are given by

$$C_V^{\text{th}} = \int_0^\infty C_V(t) dt = C_V^\infty + \delta C_V(t=0) \equiv C_V^\infty + \delta C_v^0, \qquad (2.7a)$$

$$\beta^{\text{th}} = \int_0^\infty \beta(t) dt = \beta^\infty + \delta \beta(t=0) \equiv \beta^\infty + \delta \beta^0. \qquad (2.7b)$$

A long calculation [16,18] based on the Navier-Stokes equations and involving the three sources described above gives the Laplace transform[3] (LT) of the response of the liquid to the pumps. In the impulsive limit of Eq. (2.2), and for the detection mechanism described by Eq. (2.1), this LT reads,

up to a factor proportional to $E_1 E_2$, as the sum of three terms.[4]

$$R_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega) = R^1_{\varepsilon_d \varepsilon_{\text{ex}}}(\omega) + R^2_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega) + R^3_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega), \qquad (2.8)$$

where

$$R^1_{\varepsilon_d \varepsilon_{\text{ex}}}(\omega) = i \frac{1 + 3\varepsilon_d \varepsilon_{\text{ex}}}{3} [b] D^{-1}(\omega) \left[\frac{\Lambda'}{\rho_m} b \right], \qquad (2.9a)$$

$$R^2_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega) = \left[a + \frac{\Lambda'}{\rho_m} b \frac{3\varepsilon_d - 1}{3} r(\omega) \right] P_L(\vec{q}, \omega)$$
$$\times \left[\frac{\rho_m \beta(\omega)}{\lambda} \frac{H}{1 + i\omega \tau_h(\vec{q}, \omega)} \right], \qquad (2.9b)$$

$$R^3_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega) = -iq^2 \left[a + \frac{\Lambda'}{\rho_m} b \frac{3\varepsilon_d - 1}{3} r(\omega) \right] P_L(\vec{q}, \omega)$$
$$\times \left[a + \frac{\Lambda'}{\rho_m} b \frac{3\varepsilon_{\text{ex}} - 1}{3} r(\omega) \right], \qquad (2.9c)$$

where $\tau_h(\vec{q}, \omega)$ is the heat diffusion time for wave vector q and frequency ω

$$\tau_h(\vec{q}, \omega) \equiv \tau_h^0(q) \frac{C_V(\omega)}{C_V(\omega = 0)} = -i \frac{C_V(\omega)}{\lambda q^2}, \qquad (2.10)$$

this equation defining the heat diffusion time $\tau_h^0(q)$.

Equations (2.9) are written in such a way that, in each of them, the rhs is the product of a detection channel(s) (first square bracket), the source(s) (second square bracket), and, between the two brackets, a dynamical response function. The first term of Eq. (2.8), $R^1_{\varepsilon_d \varepsilon_{\text{ex}}}(\omega)$, is the LT of an OKE signal; it describes the pure relaxation dynamics of the molecular orientation after their initial orientation by $\vec{E}_{\text{int}}(\vec{r}, t)$. This dynamics is fast enough not to be studied in the HD-TG experiments, so that $D(\omega)$ may be approximated by

$$D(\omega) = \omega_R^2. \qquad (2.11)$$

The second term, $R^2_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$, and the third term, $R^3_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$, of Eq. (2.8), have been called, respectively, in [16] the generalized ISTS (impulsive stimulated thermal scattering) signal[5] and the generalized ISBS (impulsive stimulated brillouin scattering) signal. Both contain three frequency-dependent factors. As the left-hand side factor

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[3] We define the Laplace transform of a response function $f(t)$ [$f(t)$ real, equal to zero for $t < 0$ and tending to zero for $t \to \infty$ by $[f(\omega)] \equiv \text{LT}[f(t)]_{(\omega)} = i \int_0^\infty f(t) \exp(-i\omega t) dt$, which implies that its inverse can be written as $f(t) = \frac{2}{\pi} \int_0^\infty \text{Im}[f(\omega)] \cos(\omega t) dt$.

[4] Equations (2.8) and (2.9) formally differ from those appearing in [16], Eqs. (3.16) and (3.17), because, on the one hand, we have already separated here, under the form of $R^2_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$ and $R^3_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$, the two signals that will be called below the generalized ISTS and ISBS signals, and, on the other hand, we have made use of the proportionality of the electrostrictive source with a, and of the orientational source with b.

[5] In the language of [16], this is rather the phonon part of the ISBS signal, the other part being the OKE signal, but, as the two signals do not appear in the same time domain, we shall here stick to this more physically meaningful denomination.

(first square bracket) involves a, b, and ε_d, the shape of those two signals depends on the polarization of the probe and of the detection beams, and the two channels contribute to the detection mechanism. The second factor, $P_L(\vec{q}, \omega)$, is the propagator of a longitudinal phonon with wave vector $\vec{q}$ and the right-hand side factor (second square bracket) depends on the sources. $R^2_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$ is generated by the heat absorption and thus does not depend on ε_{ex}. Conversely, $R^3_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$ originates, as $R^1_{\varepsilon_d \varepsilon_{\text{ex}}}(\omega)$, from the coupling of the pumps to $\delta \bar{\bar{\varepsilon}}(\vec{r}, t)$ and depends on ε_{ex} because the pumps tend to orient the molecules. This orientational aspect appears through the quantity $br(\omega)$, present in Eqs. (2.9b) and (2.9c), where

$$r(\omega) = \frac{\omega \mu(\omega)}{\omega_R^2} \tag{2.12}$$

and thus involves the rotation-translation coupling function, $\mu(\omega)$. This coupling generates, in Eq. (2.9c), a modulated stress that launches longitudinal phonons; vice versa, the latter orient the molecules and induce a contribution to $R^2_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$ and $R^3_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$ that depends on the polarization of the probe and diffracted beams. In fact, as shown in [16], the function $br(\omega)$ mostly influences the shape of the $R^2_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$. While its a contribution is always negative and does not change much with temperature, its b contribution exhibits a strong thermal variation, both in amplitude and in shape: in amplitude because $br(\omega)$ has a negligible value as long as the rotation-translation lifetime, τ_μ, of $\mu(\omega)$, is such that $\omega_B \tau_\mu \ll 1$ while it cannot be neglected at lower temperatures where $\omega_B \tau_\mu \gg 1$; in shape because the duration of $r(\omega)$ is limited by the relaxation time τ_μ. Conversely, as also shown in [16], the $br(\omega)$ term affects much less the shape of $R^3_{\varepsilon_d \varepsilon_{\text{ex}}}(\vec{q}, \omega)$: all its components oscillate at the phonon frequency around a zero mean value and decay as the phonon lifetime, τ_B.

Finally, $P_L(\vec{q}, \omega)$, the second factor of Eqs. (2.9b) and (2.9c), is the longitudinal phonon propagator, the inverse of which can be expressed [16] as

$$P_L^{-1}(\vec{q}, \omega) = \omega^2 - q^2 \left(c_a^2 + \rho_m^{-1} \omega \tilde{\eta}_L(\omega) \right.$$
$$\left. + i \rho_m T_m \frac{\beta^2(\omega)}{C_V(\omega)} \frac{1}{1 + i \omega \tau_h(\vec{q}, \omega)} \right). \tag{2.13}$$

Here, c_a is the adiabatic sound velocity while $\tilde{\eta}_L(\omega)$ is called the "longitudinal" viscosity and contains contributions from all the relaxation functions entering Eqs. (2.3). The last term of Eq. (2.13), called (see below) the isothermal contribution to $P_L(\vec{q}, \omega)$, is the counterpart of the change from the isothermal velocity, c_i, to the adiabatic velocity in the propagator; this aspect is recalled, as well as the exact form of $\tilde{\eta}_L(\omega)$, in the Appendix. At high temperatures, this isothermal contribution can be neglected and the corresponding $P_L(\vec{q}, \omega)$ is called the adiabatic phonon propagator [16,18]. Conversely, this contribution will be necessary to explain the final part of the ISTS signal at low temperatures, i.e., when the relaxation times involved in $\tilde{\eta}_L(\omega)$ are of the same order of magnitude as $\tau_h(\vec{q}, \omega)$. This more complete phonon propagator takes

into account the heat diffusion process that accompanies a quasistatic isothermal strain, and is thus called the isothermal phonon propagator, which explains the name given to the last term of Eq. (2.13).

III. THE EXPERIMENTAL SIGNALS AND THEIR ANALYTICAL EXPRESSION

Equations (2.9b), (2.9c), and (2.13) represent exact expressions for the different signals, in the ideal case of perfect instrumentation and when the three sources contribute to the formation of the grating. They need, on the one hand, to be adapted to a realistic experimental situation and, on the other hand, to be transformed into expressions that will allow one to extract numerical information from the experimental signals.

A. Theoretical expressions for the experimental signals

1. Experimental aspects

The experimental signals that are represented in, e.g., [13], or in Paper II where we will present an analysis of m-toluidine [19], are not the inverse Laplace transforms of Eqs. (2.9b) and (2.9c) for three different reasons.

First, there is an experimental uncertainty on the time the pumps start to act. In [19], this time will be negative and we thus write it as $-t_0$.

Second, the response function of the experimental setup, including the duration of the pulses of the pumps, is not a $\delta(t)$ function, but a function $F(t)$, which extends over a time long enough not to be neglected.

Finally, the long-time part of the experimental signals is dominated by the aH (thermal grating detected by the density modulation) term of $R^2_{\varepsilon_d, \varepsilon_{\text{ex}}}(\vec{q}, \omega)$ which, as shown in [16], is negative. Conversely the experimental signals, see, e.g., [13], are always represented with a positive long time part. A factor (-1) has to be added to the preceding formulas before comparing them to the experimental signals.

2. The isotropic and anisotropic signals

Equations (2.9b) and (2.9c) are too general because, as already indicated in [14], when one limits the study of the HD-TG signals of supercooled liquids to times longer than, say 5 ns for $q=0.63 \ \mu\text{m}^{-1}$, either the signals exhibit no polarization effects (e.g., for glycerol, or o-TP), or these effects are limited to the role of the probe and detection beams (e.g., for salol, or m-toluidine). No case is known where ε_{ex} plays a role in this time regime, which implies that the molecular orientation source [the $b \frac{3 \varepsilon_{\text{ex}} - 1}{3} r(\omega)$ term of Eq. (2.9c)] may be neglected and the index ε_{ex} dropped from any formula. The roles of $\delta \rho(\vec{r}, t)$ and $\bar{\bar{Q}}(\vec{r}, t)$ can then be disentangled if one defines the two following linear combinations of the experimental signals $S^{\text{expt}}_{\text{VV}}(\vec{q}, \omega)$ ($\varepsilon_d = 1$) and $S^{\text{expt}}_{\text{HH}}(\vec{q}, \omega)$ ($\varepsilon_d = -1$):

$$S^{\text{expt}}_{\text{iso}}(\vec{q}, t) = \left[\frac{2 S^{\text{expt}}_{\text{VV}}(\vec{q}, t) + S^{\text{expt}}_{\text{HH}}(\vec{q}, t)}{3} \right], \tag{3.1a}$$

$$S_{\text{aniso}}^{\text{expt}}(\vec{q},t) = \frac{S_{\text{VV}}^{\text{expt}}(\vec{q},t) - S_{\text{HH}}^{\text{expt}}(\vec{q},t)}{2}. \qquad (3.1b)$$

In view of the three points made in Sec. III A 1 and Footnote 3, those two signals have to be compared with

$$S_\alpha(\vec{q},t) = \frac{2}{\pi} \int_0^\infty \text{Im}[S_\alpha(\vec{q},\omega)] \cos \omega(t + t_0) d\omega, \quad (3.2)$$

where α stands either for "iso" or for "aniso" with

$$S_{\text{iso}}(\vec{q},\omega) = iaI^0 P_L(\vec{q},\omega) \left[\frac{\rho_m \beta(\omega)}{\lambda} \frac{H}{1 + i\omega\tau_h(\vec{q},\omega)} \right.$$
$$\left. - iaq^2 \right] F(\omega), \qquad (3.3a)$$

$$S_{\text{aniso}}(\vec{q},\omega) = \frac{\Lambda' b}{\rho_m a} r(\omega) S_{\text{iso}}(\vec{q},\omega), \qquad (3.3b)$$

I^0 representing the intensity on the detector.

B. Fit formula for $S_{\text{iso}}(\vec{q},\omega)$ and $S_{\text{aniso}}(\vec{q},\omega)$

In order to express $S_{\text{iso}}(\vec{q},\omega)$ and $S_{\text{aniso}}(\vec{q},\omega)$ under forms adapted to a fit of the experimental signals, it is convenient to write, e.g., $\beta(\omega)$ in the form, see Eqs. (2.6b) and (2.7b),

$$\beta(\omega) = i\beta^{\text{th}}[1 - \nu_\beta \omega g_\beta(\omega\tau_\beta)], \qquad (3.4)$$

with

$$\nu_\beta \omega g_\beta(\omega\tau_\beta) \equiv \frac{\omega\delta\beta(\omega)}{\beta^{\text{th}}}, \qquad (3.5)$$

where, by definition, whatever the index i, a function $g_i(\omega\tau_i)$ is the LT of a relaxation function $g_i(t)$ which has a value equal to 1 for $t=0$ and whose final relaxation dynamics is governed by a relaxation time τ_i. Following Eq. (3.5), ν_i is then the $\omega \to \infty$ limit of the corresponding rhs. In practical applications, $g_i(t)$ will be, for instance, a Kohlrausch function, or $\omega g_i(\omega\tau_i)$ will be a Cole-Davidson function.

Using similar notations for $C_V(\omega)$ and $\omega\mu(\omega)$, Eqs. (3.3a) and (3.3b) may then be expressed as

$$S_{\text{iso}}(\vec{q},\omega) = -I_{\text{iso}} P_L(\vec{q},\omega) \left[\frac{1 - \nu_\beta \omega g_\beta(\omega\tau_\beta)}{1 + i\omega\tau_h(\vec{q},\omega)} - ia_0 \right] F(\omega),$$
$$(3.6)$$

$$S_{\text{aniso}}(\vec{q},\omega) = K_{\text{aniso}} \omega g_\mu(\omega\tau_\mu) S_{\text{iso}}(\vec{q},\omega) \qquad (3.7)$$

with

$$\omega\tau_h(\vec{q},\omega) = \omega\tau_h^0(q)[1 - \nu_{C_V} \omega g_{C_V}(\omega\tau_{C_V})], \qquad (3.8)$$

$$a_0 = \frac{\lambda q^2}{\rho_m \beta^{\text{th}}} \frac{a}{H}, \qquad (3.9a)$$

$$K_{\text{aniso}} = \frac{\Lambda'}{\rho_m} \frac{\nu_\mu}{\omega_R^2} \frac{b}{a} \qquad (3.9b)$$

and

$$I_{\text{iso}} = \frac{I^0 \rho_m \beta^{\text{th}}}{\lambda} Ha; \qquad (3.10)$$

for a given wave vector $\vec{q}$, a_0 thus characterizes the relative efficiencies of a and H as sources of the signal while K_{aniso} characterizes the relative efficiencies of the molecular orientation and mass density channels in the detection mechanism.

$P_L^{-1}(\vec{q},\omega)$, Eq. (2.13), also needs to be parametrized. We shall write its $\omega\tilde{\eta}_L(\omega)$ term under the approximate form

$$\omega\tilde{\eta}_L(\omega) = \Delta_L^2 \omega g_L(\omega\tau_L) + i\omega\bar{\gamma}, \qquad (3.11)$$

where $g_L(\omega\tau_L)$ is the LT of a "longitudinal" relaxation function, governed at long times by a unique relaxation time, τ_L, while $\bar{\gamma}$ represents a weakly temperature dependent instantaneous normal damping process. Also, as the isothermal contribution to $P_L(\vec{q},\omega)$ represents a correction to the adiabatic phonon propagator, we neglect the frequency dependence of $C_V(\omega)$ and of $\beta(\omega)$ in the first factor of this correction. One thus obtains for this isothermal contribution

$$i\rho_m T_m \frac{\beta^2(\omega)}{C_V(\omega)} \frac{1}{1 + i\omega\tau_h(\vec{q},\omega)} \cong -\rho_m T_m \frac{(\beta^{\text{th}})^2}{C_V^{\text{th}}} \frac{1}{1 + i\omega\tau_h(\vec{q},\omega)}$$
$$= c_a^2 \left(\frac{1}{\gamma} - 1 \right) \frac{1}{1 + i\omega\tau_h(\vec{q},\omega)}. \qquad (3.12)$$

Here, γ is the usual ratio between the specific heat at constant pressure and at constant volume, in their thermodynamic limit, and the relation between the two last terms of Eq. (3.12) is discussed in the Appendix. $P_L^{-1}(\vec{q},\omega)$ is thus approximated by

$$P_L^{-1}(\vec{q},\omega) = \omega^2 - q^2 \left[c_a^2 + \Delta_L^2 \omega g_L(\omega\tau_L) + i\omega\bar{\gamma} + c_a^2 \left(\frac{1}{\gamma} - 1 \right) \right.$$
$$\left. \times \frac{1}{1 + i\omega\tau_h(\vec{q},\omega)} \right], \qquad (3.13)$$

where the expression of $\omega\tau_h(\vec{q},\omega)$ is given by Eq. (3.8): the adiabatic approximation of $P_L(\vec{q},\omega)$ then consists simply in making $\gamma=1$ in Eq. (3.13) while γ takes a larger value in the isothermal case. This remark is of practical importance because, as shown in [16], the long time part of the IST signal, thus of $S_{\text{iso}}(\vec{q},t)$, relaxes on the time scale

$$\bar{\tau}_h^0(q) = \gamma\tau_h^0(q). \qquad (3.14)$$

Equations (3.2), (3.6)–(3.8), and (3.13) represent the formulas that have to be used to interpret a HD-TG series of experiments performed on a supercooled liquid formed of anisotropic molecules. However, those expressions still contain too many temperature dependent parameters to allow for their reliable determination; some of them have to be determined from independent experiments. We shall illustrate this point in Paper II [19] where we shall make use of these equations to interpret m-toluidine data recorded between 330 and 190 K at LENS.

APPENDIX

It was shown in [16] that the inverse of the phonon propagator, $P_L^{-1}(\vec{q}, \omega)$, was given by

$$P_L^{-1}(\vec{q}, \omega) = [\omega^2 - q^2(c_i^2 + \rho_m^{-1}\omega\eta_L(\omega) + g(q, \omega))], \quad \text{(A1)}$$

where

$$\eta_L(\omega) = \eta_b(\omega) + \frac{4}{3}\eta_T(\omega) \quad \text{(A2)}$$

and

$$g(q, \omega) = -i\rho_m T_m \frac{\beta^2(\omega)}{C_V(\omega)} \frac{i\omega\tau_h(\vec{q}, \omega)}{1 + i\omega\tau_h(\vec{q}, \omega)}. \quad \text{(A3)}$$

In Eq. (A2), $\eta_b(\omega)$ is the LT of the bulk viscosity relaxation function while $\eta_T(\omega)$, called the "transverse" viscosity, see [20], is given by

$$\eta_T(\omega) = \eta_s(\omega) - \frac{\Lambda'}{\omega}D(\omega)r^2(\omega). \quad \text{(A4)}$$

The second term of the rhs of Eq. (A4) shows that this transverse viscosity results from the renormalization of $\eta_s(\omega)$, the LT of the shear viscosity, by the coupling of the transverse phonon to the orientational density. Furthermore, $g(q, \omega)$ can be expressed as

$$g(q, \omega) = -i\rho_m T_m \frac{\beta^2(\omega = 0)}{C_V(\omega = 0)} - i\rho_m T_m\left(\frac{\beta^2(\omega)}{C_V(\omega)} - \frac{\beta^2(\omega = 0)}{C_V(\omega = 0)}\right)$$

$$+ i\rho_m T_m \frac{\beta^2(\omega)}{C_V(\omega)} \frac{1}{1 + i\omega\tau_h(\vec{q}, \omega)}. \quad \text{(A5)}$$

The first term of the rhs of Eq. (A5) can be added to c_i^2 to give

$$c_i^2 - i\rho_m T_m \frac{\beta^2(\omega = 0)}{C_V(\omega = 0)} = c_i^2 + \rho_m T_m \frac{(\beta^{\text{th}})^2}{C_V^{\text{th}}} = c_i^2 + c_i^2(\gamma - 1)$$

$$\equiv c_a^2, \quad \text{(A6)}$$

where we have made used of the classical thermodynamic relation

$$\rho_m T_m \frac{(\beta^{\text{th}})^2}{C_V^{\text{th}}} = c_i^2(\gamma - 1) \quad \text{(A7)}$$

with

$$\gamma = \frac{C_P^{\text{th}}}{C_V^{\text{th}}}. \quad \text{(A8)}$$

This introduces the adiabatic phonon velocity. Furthermore, adding the second term of the same rhs to $\rho_m^{-1}\omega\eta_L(\omega)$ in Eq. (A1) yields

$$\tilde{\eta}_L(\omega) = \eta_b(\omega) + \frac{4}{3}\eta_T(\omega) - \frac{i\rho_m^2 T_m}{\omega}\left(\frac{\beta^2(\omega)}{C_V(\omega)} - \frac{\beta^2(\omega = 0)}{C_V(\omega = 0)}\right), \quad \text{(A9)}$$

which is the "longitudinal" viscosity appearing in Eq. (2.13), the third term of the same rhs being the isothermal contribution.

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