Frequency and time resolved light scattering on longitudinal phonons in molecular supercooled liquids

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Abstract
The coupling of the rotational dynamics of anisotropic molecules to longitudinal phonons gives rise to different effects in the interaction of light with supercooled liquids formed of such molecules. One is the opening of new light scattering channels in Brillouin scattering; this can alter the corresponding phonon lineshape. Another one is the possible appearance of a depolarized signal in transient grating experiments (TG), also called impulsive stimulated scattering. We give a brief theoretical description of these two effects for supercooled liquids formed of linear rigid molecules. We also present preliminary results on the analysis of such a TG experiment performed on *m*-toluidine.

1. Introduction

In a molecular liquid formed of anisotropic molecules, both the molecular dielectric anisotropy and the density fluctuations can contribute to the scattering of light. Moreover, the mean local orientation of the molecules is coupled to the local shear of the liquid and this shear is an inherent part of both the longitudinal and the (diffusive or propagative) transverse phonons. The interpretation of the light scattering experiments involving these phonons either in the frequency, or in the time domain, requires an expression for the equations of motion of the density and of this mean molecular orientation, as well as an appropriate model for the local dielectric fluctuations. In the case of a supercooled liquid formed of rigid linear molecules, some of us have proposed, Dreyfus *et al* (1998, 1999), that the two conservation laws,

$$\dot{\rho}(\vec{r}, t) + \operatorname{div} \vec{J}(\vec{r}, t) = 0, \tag{1}$$

$$\dot{\vec{J}}(\vec{r}, t) = \operatorname{div} \overline{\overline{\sigma}}(\vec{r}, t), \tag{2}$$

where ρ is the mass density, $\vec{J}$ is the mass current density and $\overline{\overline{\sigma}}$ is the stress tensor, should be complemented by the two constitutive equations

$$\overline{\overline{\sigma}} = (-\delta P + \eta_b \otimes \operatorname{div} \vec{v})\overline{\overline{I}} + \eta_s \otimes \overline{\overline{\tau}} - \mu \otimes \dot{\overline{\overline{Q}}}, \tag{3}$$

$$\ddot{\overline{\overline{Q}}} = -\omega_R^2 \overline{\overline{Q}} - \Gamma' \otimes \dot{\overline{\overline{Q}}} + \Lambda'\mu \otimes \overline{\overline{\tau}}. \tag{4}$$

Here $\overline{\overline{Q}}$ is a symmetrical traceless tensor representing the local orientational probability of the molecules, $\overline{\overline{I}}$ is the unit tensor, $\vec{J}$ is related to the mean molecular velocity, $\vec{v}$, through

$$\vec{J} = \rho_m \vec{v}, \tag{5}$$

where ρ_m is the mean mass density, $\overline{\overline{\tau}}$ is the strain rate, traceless, second rank tensor,

$$\tau_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\operatorname{div} \vec{v}\delta_{ij}, \tag{6}$$

and $\delta P(\vec{r}, t)$ is a pressure change related to the instantaneous mass density change $\delta\rho(\vec{r}, t)$ by

$$\delta P(\vec{r}, t) = c_a^2 \delta\rho(\vec{r}, t) \tag{7}$$

where c_a is the adiabatic sound velocity, $\eta_b(t)$, $\eta_s(t)$, $\mu(\tau)$ and $\Gamma'(t)$ are, respectively, the bulk and shear viscosities, the rotation–translation coupling and the orientational relaxation functions, the symbol $\otimes$ representing a convolution product with respect to time, ω_R is the libration frequency of the axial molecules and Λ' is the rotation–translation coupling constant, a quantity that takes into account, *inter alia*, that ρ and $\overline{\overline{Q}}$ have different dimensions.

It was finally proposed in Dreyfus *et al* (1998, 1999) that the local dielectric fluctuations should be related to $\delta\rho(\vec{r}, t)$ and $\overline{\overline{Q}}(\vec{r}, t)$ through

$$\delta\varepsilon(\vec{r}, t) = a\delta\rho(\vec{r}, t)\overline{\overline{I}} + b\overline{\overline{Q}}(\vec{r}, t). \tag{8}$$

Equations (1)–(4) can, in fact, be derived, Franosch *et al* (2002) from a microscopic theory of such a liquid through a Mori–Zwanzig technique that considers $\rho(\vec{r}, t)$, $\vec{J}(\vec{r}, t)$, $\overline{\overline{Q}}(\vec{r}, t)$ and $\dot{\overline{\overline{Q}}}(\vec{r}, t)$ as the only relevant variables of the problem. With the help of this technique, the four memory functions can be shown to have reasonable time and temperature variations, i.e. have long time behaviours that can be characterized by relaxation times increasing with decreasing temperature[7]. Furthermore, defining the Laplace transform through the convention $f(\omega) = i\int_0^\infty f(t)\exp(-i\omega t)\,dt$, it has been shown in Franosch *et al* (2002) that the imaginary parts of $\Gamma'(\omega)$, $\eta_b(\omega)$ and $\eta_s(\omega)$ are positive whatever the frequency (relations A), and that the following inequality holds: $\operatorname{Im}(\Gamma'(\omega))\operatorname{Im}(\eta_s(\omega)) - \Lambda'(\operatorname{Im}(\mu(\omega))^2 \geqslant 0$ (relation B).

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[7] Note that the same technique can be applied to the case where only $\rho(\vec{r}, t)$, $\vec{J}(\vec{r}, t)$ and $\overline{\overline{Q}}(\vec{r}, t)$ are the relevant variables. In that case, equations (3) and (4) are replaced by

$$\overline{\overline{\sigma}} = (-\delta P + \hat{\eta}_b \otimes \operatorname{div} \vec{v})\overline{\overline{I}} + \hat{\eta}_s \otimes \overline{\overline{\tau}} - \lambda \otimes \overline{\overline{Q}}, \tag{3b}$$

$$\dot{\overline{\overline{Q}}} = -M \otimes \overline{\overline{Q}} + \frac{\Lambda'}{\omega_R^2}\lambda \otimes \overline{\overline{\tau}}. \tag{4b}$$

Yet (cf Franosch *et al* 2002), one can show that the Laplace transforms of the three memory functions $\hat{\eta}_s(t)$, $\lambda(t)$ and $M(t)$ do not have, at low temperature, the physically meaningful time and temperature dependence of their counterparts in the four-variable theory. The two preceding equations are thus inappropriate for the study of supercooled molecular liquids because the corresponding memory functions cannot be *a priori* modelled in a reasonable way.

2. Light scattering by longitudinal phonons

It has been shown in Dreyfus *et al* (1998, 1999) that the set of equations (1)–(4) complemented by equation (8) allows us to describe the intensity detected in a Brillouin depolarized scattering experiment. The same technique can be used to derive the intensity obtained in a VV Brillouin scattering experiment, Pick *et al* (2002). One obtains

$$I_{VV}(\vec{q}, \omega) = I_1(\omega) + I_2(\vec{q}, \omega), \tag{9}$$

with

$$I_1(\omega) = \frac{I_0}{\omega} \operatorname{Im} \frac{4b^2}{3} \left(1 - \frac{\omega_R^2}{D(\omega)} \right) \langle |Q_{V\perp'}^0|^2 \rangle, \tag{10}$$

$$I_2(\vec{q}, \omega) = \frac{I_0}{\omega} \operatorname{Im} \left(\frac{\rho_m}{\Lambda'} (\omega_R q)^2 P_L(q, \omega) \left[a + \frac{2\Lambda'}{3\rho_m} br(\omega) \right]^2 \right) \langle |Q_{V\perp'}^0|^2 \rangle, \tag{11}$$

where $\langle |Q_{V\perp'}^0|^2 \rangle$ is the thermal average of $|Q_{V\perp'}^0|^2$, $Q_{V\perp'}^0$ being the $V\perp'$ component of Q_{ij} and $\perp'$ being the direction of the scattering plane perpendicular to $\vec{q}$. Equation (11) takes into account that the thermal averages of the orientational fluctuations, $\langle |Q_{VV}^0|^2 \rangle$, and of the density fluctuations, $\langle |\delta\rho^0|^2 \rangle$, are related by

$$\frac{3\omega_R^2}{4\Lambda'} \langle |Q_{VV}^0|^2 \rangle = \frac{c_a^2}{\rho_m} \langle |\delta\rho^0|^2 \rangle \propto k_B T. \tag{12}$$

Equation (10) has been written in such a way that $I_1(\omega)$ is exactly 4/3 of $I_{VHb}(\omega)$, where $I_{VHb}(\omega)$ is the intensity that would be obtained in a back-scattering depolarized experiment performed with the same incident intensity, while $D(\omega)$ is given by

$$D(\omega) = \omega_R^2 + \omega\Gamma'(\omega) - \omega^2. \tag{13}$$

Equation (10) represents a pure rotational dynamics independent of the value of the scattering vector, $\vec{q}$. Conversely, equation (11) represents what is usually called the 'phonon part' of the Brillouin spectrum. This term is, apart from an unimportant factor, the product of a longitudinal phonon propagator, $P_L(q, \omega)$, by the square of a bracketed term. Here,

$$P_L^{-1}(q, \omega) = [\omega^2 - q^2 \rho_m^{-1} (c_a^2 \rho_m + \omega\eta_L(\omega))] \tag{14}$$

with

$$\eta_L(\omega) = \eta_b(\omega) + \frac{4}{3} \left(\eta_s(\omega) - \frac{\Lambda'}{\omega} D(\omega) r^2(\omega) \right), \tag{15}$$

$$r(\omega) = \omega\mu(\omega)[D(\omega)]^{-1}, \tag{16}$$

$r(\omega)$ being the signature of the rotation–translation coupling.

The bracket $a + \frac{2\Lambda'}{3\rho_m} br(\omega)$ that appears in equation (11) is linear in a and b, the term in b being proportional to $\Lambda' r(\omega)$. Its form makes it clear that both the density and the orientation fluctuations associated with the longitudinal phonons play a role in their detection; the bracket appears as a square because these fluctuations are not only the detection mechanism of these phonons but also their source.

The line shape of the 'phonon' spectrum is usually considered to be simply given by $1/\omega \operatorname{Im}(P_L(q, \omega))$, the term proportional to a^2 in equation (11), which can be called the density-only channel. The existence of terms involving $br(\omega)$ at different powers in equation (11) alters the shape of the phonon spectrum. This effect is mostly visible in the temperature range where the relaxation times related to the four memory functions are of the same order of magnitude as the longitudinal phonon period. This is exemplified in figure 1 where we have fitted the full
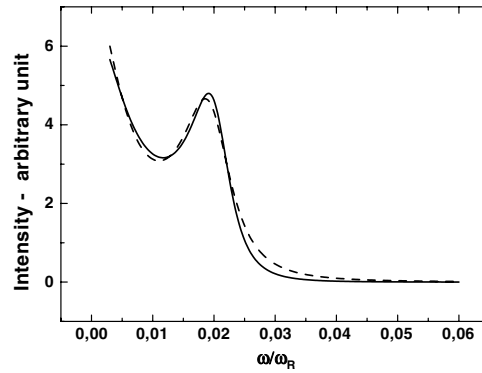
Figure 1. Full phonon contribution—equation (11) (dashed curve)—of a numerical spectrum (see the text) and its best fit with a 'density-only' model (full curve). The full phonon spectrum has been computed with a Debye relaxation time, τ_L, such that the corresponding $\omega_B \tau_L$ is equal to 0.93, with $\omega_B = c_a q$.

spectrum given by equation (11) (obtained by choosing for these memory functions Debye expressions with identical relaxation times and reasonable amplitudes, Pick *et al* (2002)) by a density-only model, $\eta_L(\omega)$ also being characterized by a single Debye process. Not only does the fitted relaxation time differ from the original one (the fitted time equals 67.7 ns for an original one of 50 ns) but the phonon peak becomes asymmetric, with more intensity on the high frequency side and less on the low frequency one than can be predicted by a density-only channel model. This effect is such that, at low temperature, the intensity related to equation (11) may become negative at very low frequency. Nevertheless, one can show that, whatever the values of a and b, relations A and B ensure that independently, $3/4 I_1(\omega) = I_{VHb}(\omega)$ and $I_2(\vec{q}, \omega) + 1/4 I_1(\omega)$ are positive whatever the frequency, so that $I_{VV}(\vec{q}, \omega)$ is always positive; this is not a trivial result since the first term of $I_2(\vec{q}, \omega) + 1/4 I_1(\omega)$ depends on $\vec{q}$ while the second does not. Equation (9), supplemented by the relations A and B, thus contains all the necessary information to take into account the coupling of translation and rotation motions in a supercooled molecular liquid, and this coupling presumably plays a role in the phonon line shape of a supercooled liquid such as *m*-toluidine (see section 4).

3. Transient grating experiments—theoretical aspects

In a transient grating (TG) experiment, see Torre *et al* (2001), two coherent light pulses (the pumps), with wavelength λ and wavevectors $\vec{q}_1$ and $\vec{q}_2$, are sent, at time $t = 0$, into the liquid, $\vec{q}_2$ forming with $\vec{q}_1$ a small angle, θ ($\sim 6°$ for $q = 0.63\ \mu m^{-1}$). These two beams interfere to produce an electric field, $\vec{E}(\vec{r}, t)$, which is a standing wave with wavevector $\vec{q}/2$, where $\vec{q} = \vec{q}_2 - \vec{q}_1$. This electric field generates in the liquid a grating of wavevector $\vec{q}$ through three distinct mechanisms:

(i) it is partly absorbed, generating a local heating,
(ii) it creates an instantaneous electrostrictive pressure and
(iii) it partly orients the molecules along its electric field through its coupling with the anisotropic part of the molecular polarizability tensor (optical Kerr effect—OKE).

The local pressure induced by the two first effects generates a density perturbation that propagates through the liquid under the form of two longitudinal phonons with opposite wavevectors $\vec{q}$ and $-\vec{q}$, while the molecular orientation produced by the OKE is a third origin of those phonons.

The TG diffracts, at a later time, a polarized probe beam and the diffracted beam with the same polarization is recorded as a function of time through a heterodyne detection technique (HD). If $\delta\varepsilon_{ij}(q, t)$ is the polarizability change of the liquid due to the grating at time t, the HD signal, $S^{HD}(t)$, obtained in the impulsive limit of the pumps, can be written as

$$S^{HD}(t) \propto \delta\varepsilon_{ij}(q, t) \propto R^{\varepsilon}_{ijkl}(q, t)F^{ex}_{kl} \qquad (17)$$

where F^{ex}_{kl} represents the instantaneous exciting force(s) produced by these pumps, and is a linear combination of products of two Cartesian components of $\vec{E}(\vec{r}, t)$. Defining the scattering plane by $\vec{q}_1$ and $\vec{q}_2$, in the present experiment, both the probe and the diffracted beams are in this scattering plane, and their polarization, as well as those of the two pump beams, are either V (perpendicular to the scattering plane) or H (in that plane). Furthermore, due to the very small scattering angle, all the H polarizations can be considered to be parallel to $\vec{q}$. We shall be interested here only in the $R^{\varepsilon}_{\alpha\alpha\beta\beta}(q, t)$ components of $R^{\varepsilon}_{ijkl}(q, t)$ where α (respectively β) is either V or H.

The interpretation of such experiments requires two extensions of equations (3) and (4). Firstly, the timescale of the response function is such that thermal diffusion can no longer be ignored. This requires

 (i) writing down a fifth equation for the conservation of energy which explicitly introduces the notion of temperature,
 (ii) adding a new term in the rhs of equation (3), because the pressure fluctuations depend now both on the density and the temperature fluctuations.

Secondly, no source term appeared in equations (3) and (4); they have to be added in order to describe stimulated experiments, each mechanism representing a distinct source. Introducing those sources in a phenomenological way, and taking into account memory effects as suggested by considerations of generalized hydrodynamics (Götze and Latz 1989), see also Franosch *et al* (2001), some of us (Pick *et al* 2003), extending a previous description of the problem by Yang and Nelson (1995a), have recently proposed to write those equations as

$$\overline{\overline{\sigma}} = (-c_i^2\delta\rho + \eta_b \otimes \text{div } \vec{v} - \rho_m\beta \otimes \delta T)\overline{\overline{I}} + \eta_s \otimes \overline{\overline{\tau}} - \mu \otimes \dot{\overline{\overline{Q}}} + KU\overline{\overline{I}}, \qquad (18)$$

$$\ddot{\overline{\overline{Q}}} = -\omega_R^2\overline{\overline{Q}} - \Gamma' \otimes \dot{\overline{\overline{Q}}} + \Lambda'\mu \otimes \overline{\overline{\tau}} + FU\overline{\overline{C}}, \qquad (19)$$

$$C_v \otimes \dot{T} - T\beta \otimes \dot{\rho} - \lambda\Delta T = HU, \qquad (20)$$

$KU\overline{\overline{I}}$, $FU\overline{\overline{C}}$ and HU being, respectively, the precise expressions of the sources, $\overline{\overline{F}}^{es}$, $\overline{\overline{F}}^{et}$ and F^{hd}, introduced in Di Leonardo *et al* (2003).

Here, c_i is the isothermal velocity, $C_v(t)$ and $\beta(t)$ are, respectively, the memory functions associated with the specific heat at constant volume per unit volume, and with the tension coefficient defined as $\frac{1}{\rho_m}\left(\frac{\partial P}{\partial T}\right)_\rho$; λ is the thermal conductivity, the frequency dependence of which can be neglected since the structural relaxation does not slow down the exchange of energy.

Furthermore:

$$U \equiv U(\vec{r}, t) = \frac{E^2}{2}[1 + \cos(\vec{q} \cdot \vec{r})]\delta(t) \qquad (21)$$

where E is the amplitude of $\vec{E}(\vec{r}, t)$, $\hat{e}$ being the direction of its polarization and where $\delta(t)$ is the Dirac delta function.

In equation (18), KU represents the additional energy per unit volume introduced by the interaction of $\vec{E}(\vec{r}, t)$ with the mean polarizability of the liquid (electrostrictive effect).

Similarly, the term in FU in equation (19) is the torque exerted on the molecules by the electric field due to their polarizability anisotropy with

$$C_{ij} = \hat{e}_i \hat{e}_j - \tfrac{1}{3}\delta_{ij}. \tag{22}$$

Finally, HU represents the heat absorbed by the liquid from the pump. Using techniques similar to those used in Pick *et al* (2002), one can derive from equations (18)–(20), supplemented by equations (1), (2) and (8), the expression of $R^{\varepsilon}_{\alpha\alpha\beta\beta}(q, t)$, which reads

$$R^{\varepsilon}_{\alpha\alpha\beta\beta}(q, t) = \frac{1}{2\pi} \int_0^{\infty} \cos \omega t \, \mathrm{Re}(R^{\varepsilon}_{\alpha\alpha\beta\beta}(q, \omega)) \, \mathrm{d}\omega \tag{23}$$

with

$$R^{\varepsilon}_{\alpha\alpha\beta\beta}(q, \omega) = FE^2 D(\omega)^{-1} \frac{b(1 + 3\varepsilon_{ex}\varepsilon_p)}{6} + A(q, \omega) P'_L(q, \omega)\left[a + \frac{(3\varepsilon_p - 1)}{3}\frac{\Lambda'}{\rho_m}br(\omega)\right], \tag{24}$$

$$A(q, \omega) = \left\{-\mathrm{i}\frac{\rho_m}{\lambda}\frac{\beta(\omega)}{1 + \mathrm{i}\omega\tau_h(\omega)}H - q^2\left[K + \frac{(3\varepsilon_{ex} - 1)}{6}r(\omega)F\right]\right\}E^2 \tag{25}$$

where the index α (respectively β) is defined by the value of ε_p (respectively ε_{ex}), the polarization V (respectively H) corresponding to $\varepsilon = 1$ (respectively $\varepsilon = -1$).

Here, $\tau_h(\omega)$ is the heat diffusion time for wavevector q and frequency ω, $\tau_h(\omega) = -\mathrm{i}\frac{C_v(\omega)}{\lambda q^2}$, $P'^{-1}_L(q, \omega)$ is the inverse of the longitudinal phonon propagator, renormalized by the change from adiabatic propagation at usual frequencies to isothermal propagation at very low frequencies, $P'^{-1}_L(q, \omega) = P^{-1}_L(q, \omega) + q^2 g(\omega)$, where c_a (cf equation (7)) is related to c_i (cf equation (18)) by

$$c_a^2 = c_i^2 - \mathrm{i}\frac{\rho_m T\beta(0)^2}{C_v(0)}, \tag{26}$$

while

$$g(\omega) = -\mathrm{i}\rho_m T\left[\frac{\beta(0)^2}{C_v(0)} - \frac{\beta(\omega)^2}{C_v(\omega)}\frac{\mathrm{i}\omega\tau_h(\omega)}{1 + \mathrm{i}\omega\tau_h(\omega)}\right] \tag{27}$$

(note that, in the analysis we shall perform in section 4, the role of $g(\omega)$ has been ignored).

In equation (24), the first term of the rhs represents the q-independent orientational contribution (OKE term) and is the TG counterpart of equation (10): this term is proportional to $FE^2 b$ (instead of b^2 in equation (10)), making clear that, if the detection mechanism is the same and proportional to b in both experiments, the source is the torque, proportional to FE^2, and not the orientational fluctuations, proportional to b. A similar analysis can be done for the second term of the rhs of equation (24). It is, as for equation (11), the product of three factors, the last one being the detection mechanism, which, as in that equation, is equal to $a + \frac{2\Lambda'}{3\rho_m}br(\omega)$ for a V polarization of the detection mechanism. The second factor is the longitudinal phonon propagator in which the change from the adiabatic regime to the isothermal one at very low frequency has been taken into account. Finally, $A(\vec{q}, \omega)$ is a sum of three terms, each one being one of the sources of the grating; the existence of a term in $\tau_h(\omega)$ associated with HE^2 makes it clear that the thermal grating disappears because of the heat diffusion process while the term in F underlines that the OKE is, at least in principle, one of the origins of the longitudinal phonons through the rotation–translation coupling memory function, $r(\omega)$.

A priori, the shape of $S^{HD}(t)$ depends on the polarization of both the pump and the probe beams. In practice (Taschin *et al* 2001), for the different supercooled liquids that have been studied so far at LENS, the pump polarization does not affect this shape. This implies that the FE^2 term always has a negligible effect with respect to the other two sources, so that F can

be safely put equal to zero in equation (24). The role of the two detection mechanisms can then be disentangled by playing with the probe polarization and one obtains

$$R_{iso}(\omega) = \frac{1}{3}(2R_{vvvv}^{\varepsilon} + R_{hhvv}^{\varepsilon}) = a\,P_L'(q,\omega)\left(-\mathrm{i}\frac{\rho_m}{\lambda}\frac{\beta(\omega)}{1+\mathrm{i}\omega\tau_h(\omega)}H - q^2K\right)E^2, \tag{28}$$

$$R_{aniso}(\omega) = \frac{1}{2}(R_{vvvv}^{\varepsilon} - R_{hhvv}^{\varepsilon}) = \frac{\Lambda'}{\rho_m}br(\omega)P_L'(q,\omega)\left(-\mathrm{i}\frac{\rho_m}{\lambda}\frac{\beta(\omega)}{1+\mathrm{i}\omega\tau_h(\omega)}H - q^2K\right)E^2. \tag{29}$$

The two preceding expressions differ only by a factor $r(\omega)$; this means that, if $R_{aniso}(t)$ is detectable and $R_{iso}(t)$ can be properly analysed, a further analysis of $R_{aniso}(t)$ will yield precise information[8] on $\mu(\omega)$ at temperatures at which $\eta_L(\omega)$ has been already determined.

4. Impulsive stimulated thermal scattering—application to *m*-toluidine

Taschin *et al* (2001) performed an optical heterodyne TG experiment with selective polarization configurations on *m*-toluidine, a molecular glass-former. They showed that, in this material, sending onto the liquid near-infrared pulses, the induced grating is mainly due to the heating effect. In this case, the TG experiment is also called impulsive stimulated thermal scattering (TG-ISTS), see Yang and Nelson (1995a, 1995b).

m-toluidine has an MCT critical temperature $T_c = 220 \pm 5$ K, Torre *et al* (2000), with $T_g = 187$ K. The experiments were performed at 11 temperatures between 225 and 195 K with three different wavevectors, $q = 1, 0.63$ and $0.338\ \mu\mathrm{m}^{-1}$. The isotropic TG-ISTS signal exhibits the typical evolution already found, e.g., in Yang and Nelson (1995b). As for the anisotropic signal, in agreement with a numerical analysis of equations (28) and (29), it starts to have a detectable amplitude, with a shape different from the isotropic one, in the vicinity of T_c, where the relaxation time τ_L associated with $\eta_L(t)$ is of the order of 10 ns, while the order of magnitude of $\tau_h(0)$ is 10^4 ns. This anisotropic intensity increases with decreasing temperature and, when $\tau_L \gg \tau_h(0)$, the two signals end up having the same shape, the liquid behaving as an isotropic solid in this limit. This is exemplified in figure 2 where both signals are shown for three different temperatures, ascertaining, for this liquid, the existence of a sizeable b-detection mechanism in this temperature range.

These spectra have been analysed with a least squares fitting procedure making use of equations (28) and (29) in which the longitudinal viscosity and the rotation–translation memory function have been approximated by

$$\omega\eta_L(\omega)\rho_m^{-1} = \Delta_L^2\left[1 - \left(\frac{1}{1+\mathrm{i}\omega\tau_L}\right)^{\beta_L}\right] + \mathrm{i}\omega\gamma_L, \tag{30}$$

$$\omega\mu(\omega) = \Delta_\mu^2\left[1 - \left(\frac{1}{1+\mathrm{i}\omega\tau_\mu}\right)^{\beta_L}\right], \tag{31}$$

the frequency dependence of both $\beta(\omega)$ and $C_v(\omega)$ being ignored. The fit parameters are thus $c_a, \Delta_L, \tau_L, \beta_L, \gamma_L, \tau_\mu$ and $-\mathrm{i}C_v(0)/\lambda$. These different parameters mostly influence the signal in different time regions (c_a and Δ_L for times shorter than 10^2 ns, β_L and τ_L for times between 10^2 and 10^4 ns and $C_v(0)/\lambda$ for longer times) in the isotropic case, τ_μ being specific to the anisotropic signals; consequently, the correlation between the different fit parameters is not too large, in spite of their large number. The analysis of the recorded spectra is far from complete and we present here only tentative conclusions.

[8] In a TG-ISTS experiment, $c_a q$ is of the order of $10^{-3}\omega_R$, so that $D(\omega)$ can be safely approximated by ω_R^2 in equation (13).
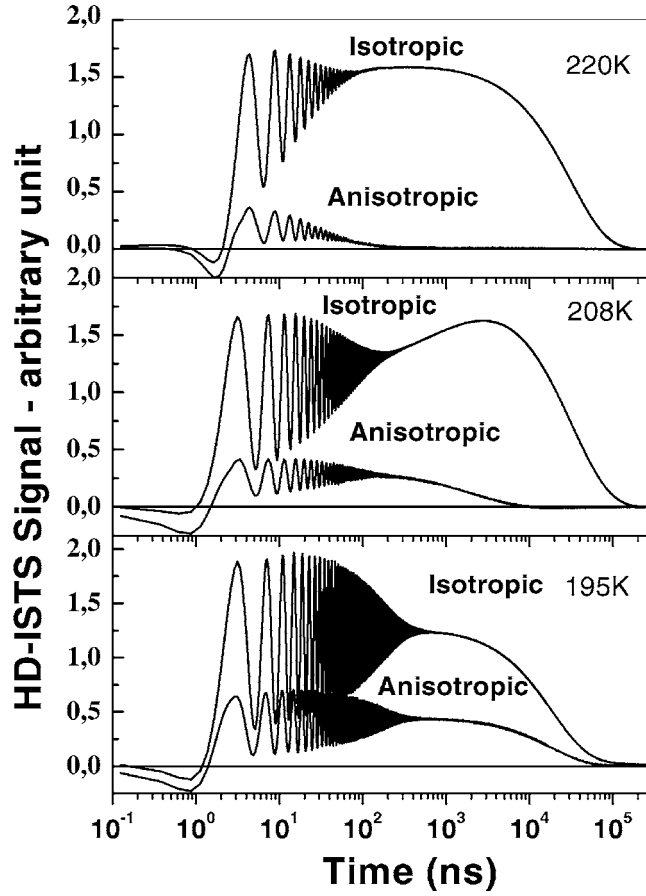
Figure 2. The isotropic and anisotropic signals (cf equations (28) and (29)) of *m*-toluidine for $q = 0.63 \ \mu \text{m}^{-1}$, at three different temperatures.

(a) The values of $c_a(T)$ and $\Delta_L(T)$ are consistent with those deduced from a previous Brillouin scattering experiment (Aouadi *et al* 2000). The accident on $\Delta_L(T)$ visible in figure 3 in the vicinity of 205 K, and which does not show up on $c_\infty = \sqrt{c_a^2 + \Delta_L^2}$ is strongly correlated with the incorrect values of $\tau_L(T)$ in the same temperature region (see (d)).

(b) γ_L is always negligibly small.

(c) The low frequency part of the rotational dynamics (see equation (10)) was analysed at high temperature in Aouadi *et al* (2000), assuming that it could be represented by

$$I_1(\omega) = \frac{I_0'}{\omega} \text{Im} \left[1 - \left(\frac{1}{1 + i\omega\tau_R} \right)^{\beta_R} \right]. \tag{32}$$

Values of $\tau_R(T)$ and $\beta_R(T)$ were deduced, in the same paper, in the 225–195 K domain, from a similar analysis performed on PCS data. We obtain here $\beta_L(T)$ values much lower than the corresponding $\beta_R(T)$ of Aouadi *et al* (2000). This appears to be in line with the fact that, if one writes

$$\omega\Gamma'(\omega) = \Delta_{\Gamma'}^2 \left[1 - \left(\frac{1}{1 + i\omega\tau_{R'}} \right)^{\beta_{R'}} \right] \tag{33}$$
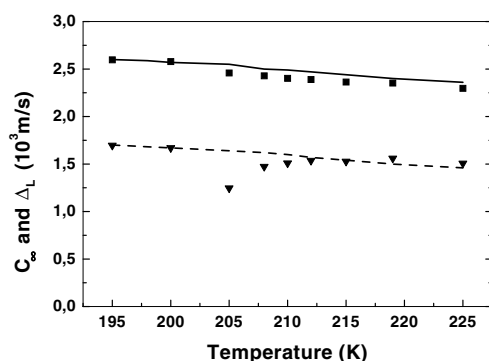
Figure 3. m-toluidine: $c_\infty = \sqrt{c_a^2 + \Delta_L^2}$ (■) and Δ_L (▼) versus temperature deduced from the isotropic spectra and their comparison with the Brillouin scattering values (respectively full and dashed lines) obtained in Aouadi *et al* (2000).
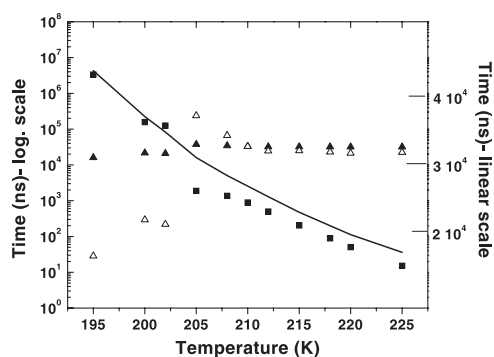

Figure 4. m-toluidine: τ_R (full curve) deduced from Aouadi *et al* (2000), τ_L (■) and τ_h (▲ and △) deduced from the isotropic spectra for $q = 0.63$ μm^{-1}, neglecting $g(\omega)$ and the frequency dependence of $C_V(\omega)$ and $\beta(\omega)$. The full triangles (▲) correspond to the logarithmic scale (left) and the empty triangles (△) to the linear scale (right) to emphasize the 'anti-crossing' behaviour of τ_L and τ_h around $T = 205$ K where $\tau_L \approx \tau_h$.

with $\Delta_{\Gamma'} \approx \omega_R$, as suggested by the direct study of $I_1(\omega)$, the values of $\beta_{R'}(T)$ deduced from $\beta_R(T)$ with the use of equations (10) and (13) are close to those of $\beta_L(T)$.

(d) $\tau_h = \mathrm{i}C_v(0)/\lambda q^2$ is temperature independent as long as $\tau_L < \tau_h$, while τ_L strongly increases with decreasing temperature. Yet, in this temperature domain, τ_L/τ_R is smaller than unity, the ratio increasing when $\tau_R \approx \tau_h$. At lower temperatures, our fits yield values of $\tau_h(T)$ that are definitely shorter, while the analysis suggests that $\tau_L/\tau_R \approx 1$. This 'anti-crossing' behaviour of τ_L and τ_h, shown in figure 4, indicates that the role of the frequency dependence of $C_v(\omega)$ and $\beta(\omega)$ and that of $g(\omega)$ have to be explored in detail before a definite conclusion can be drawn on the origin(s) of the effect.

(e) Finally, as already suggested in Taschin *et al* (2001), we find that τ_μ is larger than τ_L. A constant ratio of τ_μ/τ_L close to 2.5 seems to describe properly the anisotropic signal in the region 225–208 K in which τ_L increases by a factor larger than 10^2.

5. Conclusion

In molecular supercooled liquids formed of anisotropic molecules, the coupling between the orientation and the centre of mass motions of the molecules is characterized by a memory function $\mu(t)$ and an amplitude Λ', while light may be scattered by both the density and the molecular orientation fluctuations. When Λ' is large enough, the line shape of the Brillouin spectrum is notably different from what it would be with $\Lambda' = 0$ when the longitudinal phonon relaxation time, τ_L, and the phonon frequency, ω_B, are such that $\omega_B \tau_L \approx 1$. In the case of TG experiments, the rotation–translation coupling leads to the existence, on top of the already known isotropic signal, of an anisotropic signal. Their successive analysis allows us to determine all the parameters which determine the shape of the isotropic signal, to compare directly τ_L with the translation–rotation relaxation time, τ_μ, and to compare both of them with the independently measured rotational relaxation time, τ_R, in the 10–10^6 ns time window.

Acknowledgments

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