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Transient grating study of *m*-toluidine from 330 to 190 K

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Abstract

We present the first detailed analysis of a transient grating (TG) experiment on a supercooled molecular liquid, *m*-toluidine, from 330 K (1.75 T_g) to 190 K (1.01 T_g) based on the theoretical model proposed in Pick *et al* (2004 *Eur. Phys. J. B* **39** 169). This hydrodynamic model of the TG response function yields a complete description of the experimental data and a characterization, over a wide dynamical range, of the different physical phenomena giving rise to the signals, including the rotation–translation coupling process. Using a disentanglement procedure of the isotropic from the anisotropic part of the TG response and a careful fitting analysis, we obtain detailed information on the rotation–translation coupling function. We also extract the structural relaxation times related to the ‘longitudinal’ viscosity over almost 10 decades in time. The value of some other parameters and information on their thermal behaviour is also reported.

1. Introduction

Transient grating (TG) experiments have a long history (see, for references, Pick *et al* (2004)) in the study of supercooled liquids. In such experiments, see e.g. Torre *et al* (2001), two coherent, intense and very short light pulses (the pumps), with 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 ($\sim 6^\circ$ for the $q = 0.63 \mu\text{m}^{-1}$ wavevector used in the present experiment). The interference between these two beams produces an electric field, $\vec{E}(\vec{r}, t)$, which is a standing wave with wavevector $\vec{q}/2$, with $\vec{q} = \vec{q}_2 - \vec{q}_1$. In a liquid formed from anisotropic molecules, this electric field generates 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;

(iii) it partly orients the molecules along the direction of the field through its coupling with the anisotropic part of the molecular polarizability tensor (the optical Kerr effect, OKE).

The local pressure induced by (i) and (ii) generates a modulated density perturbation that propagates through the liquid in the form of two longitudinal phonons with opposite wavevectors \vec{q} and $-\vec{q}$, while the molecular orientation produced by the OKE is the third origin for those phonons. Also, the coupling between the mean local orientation of the molecules and the anisotropic deformation created by the phonons generates an optical anisotropy in the grating.

At a later time, this transient grating diffracts a polarized probe beam and, in the heterodyne detection (HD) technique used here, the amplitude of the beam diffracted with the same polarization is recorded as a function of time. The pioneer work of Yang and Nelson (1995) ignored the molecular (or iono-molecular) aspect of the liquids being studied and thus did not take into account the OKE aspect of the experiment (point (iii)) or the optical anisotropy of the grating. The theory had to be revisited when it was noticed (Taschin *et al* 2001) that, in some molecular liquids, different polarizations of the probe and diffracted beams led to different signals. A complete theory of the effect was given in Pick *et al* (2004). This theory will be briefly summarized in section 2; we shall then report its first application, performed on HD–TG signals recorded in *m*-toluidine (section 3) and discuss in section 4 the main new results that have been obtained.

2. Summary of the theory

In a HD–TG experiment, one tests as a function of time the local change of the dielectric tensor, $\delta\bar{\bar{\epsilon}}(\vec{r}, t)$, induced by the action of the pumps at time $t = 0$. In a liquid formed of anisotropic molecules, this change has to be written as

$$\delta\bar{\bar{\epsilon}}(\vec{r}, t) = a\delta\rho(\vec{r}, t)\bar{\bar{I}} + b\bar{\bar{Q}}(\vec{r}, t) \quad (1)$$

where $\delta\rho(\vec{r}, t)$ is the local change in mass density and $\bar{\bar{Q}}(\vec{r}, t)$ is a second order symmetric traceless tensor characterizing the mean local orientation of the molecules (all the components of $\bar{\bar{Q}}(\vec{r}, t)$ are equal to zero at thermal equilibrium). b/a thus characterizes the relative efficiency of the local orientation and of the mass density modulation in the detection of the signal. As shown by Pick *et al* (2004), the a and b terms of equation (1) are also the origins of, respectively, the effects (ii) and (iii) listed above. The same paper showed that the relative efficiency of these two sources is identical to their relative efficiency in the detection mechanism.

In the usual HD–TG set-up, the probe and diffracted beams propagate in the scattering plane defined by the two pump beams. Let us define \hat{V} to be a unit vector perpendicular to that plane and \hat{H} to be the unit vector parallel to \vec{q} . In practice, \hat{H} is perpendicular to \vec{q}_1 and \vec{q}_2 and also to the direction of the probe and diffracted beams. It was shown in Pick *et al* (2004) that, when the polarizability anisotropy of the molecules is weak (but non-negligible), for times longer than the OKE signal and for parallel polarization of the pump beams, only two independent signals can be measured: they correspond either to a common V polarization of the probe and diffracted beams, $S_{VV}(\vec{q}, t)$, or to their common H polarization, $S_{HH}(\vec{q}, t)$, their shape being independent of the common polarization of the pumps. It was then shown that

$$S_{\text{iso}}(\vec{q}, t) = \left[\frac{2S_{VV}(\vec{q}, t) + S_{HH}(\vec{q}, t)}{3} \right] \quad (2)$$

and

$$S_{\text{aniso}}(\vec{q}, t) = \frac{S_{VV}(\vec{q}, t) - S_{HH}(\vec{q}, t)}{2} \quad (3)$$

were respectively proportional to $\delta\rho(\vec{q}, t)$ and to the VV component, $Q_{VV}(\vec{q}, t)$, of $\bar{Q}(\vec{q}, t)$ created by the action of the pumps at $t = 0$.

Both signals are the inverse Laplace transforms of, respectively, $S_{\text{iso}}(\vec{q}, \omega)$ and $S_{\text{aniso}}(\vec{q}, \omega)$, and, under assumptions reasonable for the analysis of the present experiment, one deduces from Pick *et al* (2004) that

$$S_{\text{aniso}}(\vec{q}, \omega) = A \frac{a}{b} \omega g_{\mu}(\omega\tau_{\mu}) S_{\text{iso}}(\vec{q}, \omega), \quad (4)$$

where A is a material dependent coefficient and $g_{\mu}(\omega\tau_{\mu})$ represents the dynamics of the orientation–anisotropic deformation (also called translation–rotation) coupling, i.e. it describes how the molecular orientation follows a local anisotropic deformation. For the present analysis, $\omega g_{\mu}(\omega\tau_{\mu})$ and, more generally, any function written as $\omega g_i(\omega\tau_i)$ will be represented by a Cole–Davidson function with a relaxation time τ_i and a stretching coefficient β_i :

$$\omega g_i(\omega\tau_i) = 1 - \left(\frac{1}{1 + i\omega\tau_i} \right)^{\beta_i}. \quad (5)$$

Also,

$$S_{\text{iso}}(\vec{q}, \omega) \propto i P_L(\vec{q}, \omega) \left(B \frac{\beta(\omega)}{\beta(\omega = 0)} \frac{H}{1 + i\omega\tau_h(\vec{q}, \omega)} - a q^2 \right), \quad (6)$$

where $P_L(\vec{q}, \omega)$ is the longitudinal phonon propagator while the second factor of equation (6) represents the action of sources (i) and (ii). Both factors need to be discussed in order to understand the pieces of information that can be obtained from the analysis of $S_{\text{iso}}(\vec{q}, t)$.

In the second factor, B is a material dependent factor, $\beta(\omega)$ is the Laplace transform of the thermal pressure (or tension) relaxation function, i.e. the pressure response of the liquid to a temperature change $\delta T(\omega)$, H describes the part of the energy absorbed by mechanism (i) while $\tau_h(\vec{q}, \omega)$ is the heat diffusion time at constant volume when an inhomogeneous temperature change with wavevector \vec{q} is forced on the liquid at the frequency $\omega/2\pi$. As it is the specific heat at constant volume which is frequency dependent, it is convenient to express $\tau_h(\vec{q}, \omega)$ as

$$\tau_h(\vec{q}, \omega) = \tau_h(\vec{q}, \omega = 0) \frac{C_V(\omega)}{C_V(\omega = 0)} \equiv \tau_h^0 \frac{C_V(\omega)}{C_V(\omega = 0)}, \quad (7)$$

where τ_h^0 is proportional to q^{-2} . Note that the heat diffusion time appears in the sources because, as long as the thermal grating due to the heat absorption has not disappeared through the heat diffusion process, the liquid is thermally anisotropic, with a corresponding mass density modulation.

For analysing $S_{\text{iso}}(\vec{q}, t)$, we wrote the inverse of the longitudinal phonon propagator as

$$P_L^{-1}(\vec{q}, \omega) = \omega^2 - q^2 (c_a^2 + \Delta_L^2 \omega g_L(\omega\tau_L) + i\omega\bar{\gamma} - K(\omega\tau_h(\vec{q}, \omega))) \quad (8)$$

where c_a is the adiabatic sound velocity, Δ_L the strength of the structural part of the relaxation process that couples to the longitudinal phonon, $\omega g_L(\omega\tau_L)$ represents the dynamics of this process while $\bar{\gamma}$ corresponds to the anharmonic damping of the phonon. The term $K(\omega\tau_h(\vec{q}, \omega))$ has to be taken into account when the relaxation time τ_L becomes of the same order of magnitude as, or larger than, τ_h^0 and is negligible otherwise (see Azzimani *et al* (2007)); its role will not be discussed here.

3. The experiments and their analysis

$S_{VV}(\vec{q}, t)$ and $S_{HH}(\vec{q}, t)$ have been recorded in *m*-toluidine, a liquid for which $T_g = 187$ K, on the new HD–TG set-up of LENS, recently reviewed in Taschin *et al* (2006), from 330 K

($1.75 T_g$) to 190 K ($1.01 T_g$). The shape and thermal variations of the corresponding $S_{\text{iso}}(\vec{q}, t)$ and $S_{\text{aniso}}(\vec{q}, t)$ are similar to those already measured in an earlier experiment on the same liquid by Taschin *et al* (2001). Analysis of the complete set of data (26 different temperatures) was performed by looking, at each temperature, for the parameters entering into $S_{\text{iso}}(\vec{q}, \omega)$ and $S_{\text{aniso}}(\vec{q}, \omega)$ which, once inverse Laplace transformed, minimize the mean square difference between those inverse Laplace transforms and the experimental signals.

In order to analyse $S_{\text{iso}}(\vec{q}, t)$, c_a and Δ_L were extracted, at each temperature, from an earlier Brillouin scattering experiment of Aouadi *et al* (2000), while $\bar{\gamma}$ was taken to be proportional to T , using for $T = 175$ K the value obtained in that paper. Furthermore, for all the temperatures above 250 K, β_L was taken to be equal to the stretching coefficient obtained in Aouadi *et al* (2000), $S_{\text{iso}}(\vec{q}, t)$ not containing enough information for a reliable estimate of this coefficient; on the contrary, this coefficient was determined from $S_{\text{iso}}(\vec{q}, t)$ at all the temperatures below 250 K. Finally $\beta(\omega)$ was expressed as

$$\beta(\omega) = \beta(\omega = 0) [1 - \nu_\beta \omega g_\beta(\omega \tau_\beta)] \quad (9)$$

with a similar form for $C_V(\omega)$. τ_β and τ_{C_V} were assumed to have the same value as τ_L at each temperature while the latter was one of our fit parameters. Furthermore, ν_β and ν_{C_V} were taken to be equal to zero above 250 K, because, once more, of the small amount of information contained in $S_{\text{iso}}(\vec{q}, t)$ at those temperatures, while they were given a non-zero value below that temperature: ν_β was one of the fit parameters and $\nu_{C_V}(T)$ was derived from specific heat measurements performed close to T_g by Carpentier *et al* (2004), and from the assumption that ν_{C_V} linearly decreases to zero at $T = 2 T_g$. In short, τ_L and τ_h^0 were fit parameters of $S_{\text{iso}}(\vec{q}, t)$ at all temperatures, β_L and ν_β being additional fit parameters to be determined only below 250 K. Once $S_{\text{iso}}(\vec{q}, t)$ was parameterized, the fit of $S_{\text{aniso}}(\vec{q}, t)$ required only the determination of the two parameters τ_μ and β_μ , which could be precisely extracted only between 225 and 200 K.

4. Results and discussion

We describe here some of the results of our analysis, a more complete version of which will be presented in Azzimani *et al* (2007). The fitting technique used here has allowed us to determine τ_L which is reported in figure 1. The relative error is always smaller than a factor two above 205 K, and much less than an order of magnitude below. Figure 1 corresponds to a dynamical range close to 10^{10} and thus represents a very large improvement over the analytical technique proposed by Yang and Nelson (1995) to extract information from the TG experiments feasible at that time; it allowed (see e.g. Torre *et al* (2001)) only a 10^3 dynamical range, even with a HD-TG experiment.

The fit of $S_{\text{aniso}}(\vec{q}, t)$ yields the first measurement of τ_μ . This relaxation time could be determined only for a dynamical range of 10^4 . In this limited domain, τ_μ is equal to the pure orientational relaxation time, τ_R , measured in Aouadi *et al* (2000) (see figure 1), but the latter does not really scale with τ_L in the temperature range $1.20 T_g$ – $1.40 T_g$. Such a discrepancy is not anticipated in the mode coupling theory in that temperature range.

Information on several stretching coefficients has also been obtained. β_L decreases from 0.33 at 245 K down to 0.20 at 220 K and keeps that value at lower temperatures. Such low values seem to be specific to the longitudinal phonon relaxation processes, measured for example by Brillouin scattering by Comez *et al* (2003) or Zhang *et al* (2004). A specific heat stretching coefficient had been previously determined only in constant pressure measurements by Birge (1986) in glycerol and propylene carbonate, in the range T_g – $1.2 T_g$. In the same temperature range, our fits require values of β_{C_V} and β_β of the order of $1.5 \beta_L$, i.e. substantially

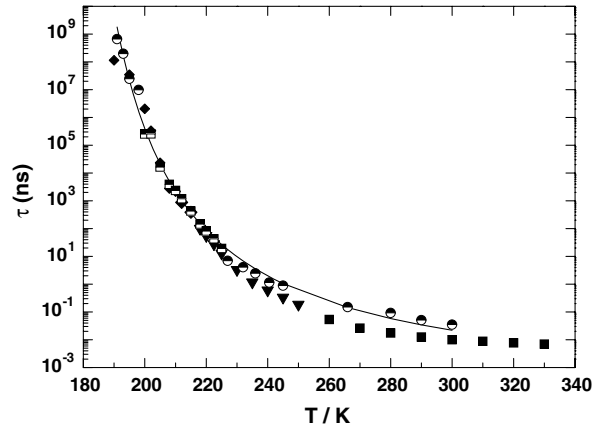


Figure 1. Comparison between the rotational relaxation time, τ_R , (3) and its Vogel–Fulcher interpolation, from Aouadi *et al* (2000), the translation–rotation relaxation time, τ_μ , (○), and the longitudinal relaxation time, τ_L , as obtained from the three temperature ranges (see text): 330–250 K (■), 245–215 K (▼) and 215–190 K (◆).

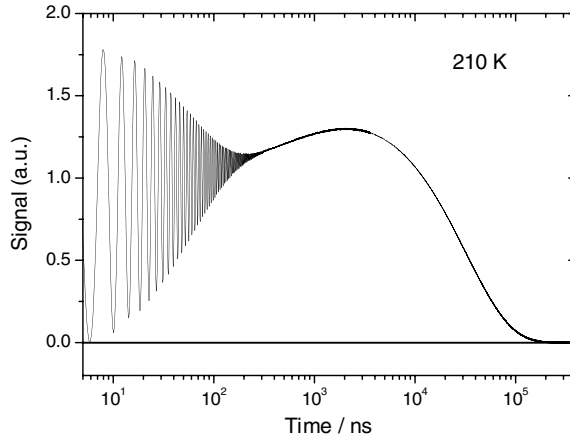


Figure 2. $S_{\text{iso}}(\vec{q}, t)$ for $T = 210$ K. Note the decay of the longitudinal phonon up to 500 ns and the increase of the signal after this time, stressing the increase of $\delta\rho(\vec{q}, t)$ towards the value imposed by the temperature modulation. The latter decreases on a much slower time scale imposed by τ_h^0 and the frequency dependence of $C_V(\omega)$.

lower than those of Birge, while, above 215 K ($1.2 T_g$), the fits are no longer sensitive to their value.

Our fitting technique also allows us to measure the relative weights of mechanisms (i), (ii) and (iii) in the formation of the signals. We have found that the relative efficiency of (iii) to (ii) is approximately 0.12 while the ratio between mechanisms (i) and (ii), which depends on the pump frequency, is equal to 5 with the Nd–YAG laser used here. This explains why (iii) can be neglected as a source but that $S_{\text{aniso}}(\vec{q}, t)$ can still be measured in our experiment.

Finally, below 215 K, $S_{\text{iso}}(\vec{q}, t)$ shown for $T = 210$ K in figure 2 has to be analysed with two different sets of τ_L , β_L values, one for $t < 500$ ns, 10^3 ns, the second for longer times: the relaxation of the phonon signal ($t < 500$ ns) takes place with a specific dynamics, some sort of ‘ β fast’ relaxation process, that differs from the usual α relaxation process governing the long

time decay. This represents the first light scattering evidence for such a process in a molecular liquid, in the vicinity of T_g .

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