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## Light scattering by transverse waves in supercooled metatoluidine

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**Abstract.** We establish hydrodynamic equations which describe the shear dynamics of a supercooled liquid composed of anisotropic molecules. We use these equations to analyse 90° depolarized light scattering experiments performed in supercooled metatoluidine, and show that the shear viscosity values extracted from the analysis are consistent with independent static measurements performed in the same temperature range.

### 1. Introduction

In molecular liquids formed of rigid anisotropic molecules, the depolarized light scattering spectra measured in backscattering geometry exhibit a more or less broad central line, with typical linewidths of the order of 10–100 GHz, which is due to the reorientational motion of the molecules. The rotation of the molecules has two different effects: it represents the probed dynamics; it provides also the detection mechanism, the rotation of a molecule producing a rotation of the rigid anisotropic polarizability tensor attached to it.

The situation is different in other scattering geometries. Experiments performed by ultrasonic techniques in the early 1960s [1] had shown that, for glass forming liquids with viscosities larger than  $\sim 100$  poise, transverse waves could propagate. It was natural to think that they should also appear in Brillouin scattering experiments when they were symmetry allowed. The first experiments [2, 3], performed on liquids with typical shear viscosities of the order of 1 cP in scattering geometries different from the backscattering one, revealed indeed a depolarized spectrum with a minimum at  $\omega = 0$ , the so-called Rytov dip [4], with two symmetric maxima in the vicinity of 1–2 GHz. Writing equations which coupled molecular reorientations with the strain rate existing in a fluid, Keyes and Kivelson [5] and Anderson and Pecora [6] showed that at such low viscosities, the minimum at  $\omega = 0$  was the result of an interference between the orientational dynamics and the diffusive shear modes originating from a finite shear viscosity of the liquid. They also predicted that, at much higher viscosities and under specific circumstances, transverse modes could propagate and could be detected as normal transverse Brillouin lines. Indeed such a phenomenon was reported by Bezot *et al* [7] then by Enright and Stoicheff [8] for viscosities around or above 100 cP but the shape of the spectra could not be properly fitted with the help of the original formula [5, 6]. Convincing fits required the introduction of additional dynamical variables [9], the dynamics of which was not detected by other techniques. This made all the information deduced from the fitting

of the spectra rather questionable. The development of new approaches to the liquid-glass transition, which involves the systematic introduction of memory functions in the description of all the friction forces appearing in the viscous fluid, made it attractive to revisit this old problem. Moreover, progress [10] in light scattering methods make possible precise recording and analysis of low frequency spectra with broad line shapes. This theoretical and experimental progress led us to reformulate the original equations, following a route already partly explored by Quentrec [11] and Wang [12], and to determine if those spectra could be interpreted in terms of physically pertinent parameters. We briefly present here these equations and show that their use in the case of the fragile molecular glass forming liquid metatoluidine brings indeed new insight into the viscoelastic properties of this supercooled liquid.

## 2. The basic equations and their consequences

The equations of motion which are pertinent for our problem may be constructed as follows. The typical relaxation time of the heat diffusion in dielectric liquids is of the order of 100 ns, which means that this effect falls below the resolving power of the instrumental technique used here. One can then consider an adiabatic scheme where one is left with two hydrodynamic equations which describe the mass conservation and the momentum conservation:

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

$$\dot{J}_i(\mathbf{r}, t) - \text{div}_j \sigma_{ij}(\mathbf{r}, t) = 0 \quad (2.2)$$

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

The expression of  $\sigma$ , and of an additional equation to be discussed below, may be constructed in two steps. For not too viscous fluids, as proposed more than 30 years ago [11], one writes

$$\boldsymbol{\sigma} = (-\delta P + \eta_b \text{div } \mathbf{v})\mathbf{l} + \eta_s \boldsymbol{\tau} - \mu \dot{\mathbf{Q}} \quad (2.3)$$

where  $\delta P$  is the fluctuation of the hydrostatic pressure,  $\mathbf{l}$  is the unit tensor while  $\eta_b$  and  $\eta_s$  are respectively the bulk and shear viscosities,  $\tau_{ij}$  being the traceless part of the strain rate tensor:

$$\tau_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \text{div } \mathbf{v} \delta_{ij}. \quad (2.4)$$

Finally, in equation (2.3),  $Q_{ij}$  is the local fluctuation of the traceless part of the density of tensor of inertia and its introduction under the form  $-\mu \dot{Q}_{ij}$  deserves some comment. It originates from a perturbation of the isotropy of the molecular orientations in the liquid. The appearance of a time derivative in equation (2.3) stresses the fact that it is the relaxation of this fluctuation which generates an additional contribution to the shear tensor of the liquid, while  $\mu$  is a constant. Also, for an elongated molecule, an elementary discussion of the shear created by its relaxation to an equilibrium orientation shows that  $\mu$  is positive. Equation (2.4) must be complemented by an equation of motion for the molecular orientation:

$$\ddot{\mathbf{Q}} = -\omega_0^2 \mathbf{Q} - \Gamma \dot{\mathbf{Q}} + \Lambda' \mu \boldsymbol{\tau}. \quad (2.5)$$

This equation results from the fact that three forces act on  $Q$ . The first one is an ordinary restoring force and should lead to undamped librations of the molecules, should the two last terms in equation (2.5) be neglected. The damping is described as follows: the  $\dot{Q}$  term is the ordinary damping of the librations while the last one results from the rotation–translation coupling. This effect is evidenced by the usual flow birefringence existing in a molecular liquid made of anisotropic molecules. For elongated molecules, this leads to a positive factor in front

of it, whence its writing in equation (2.5), the coefficient  $\Lambda$  being some positive number taking into account the different units appearing in equations (2.3) and (2.5). The second step consists in generalizing equations (2.3) and (2.5) in order to take into account retardation effects. The theoretical development on the physics of the liquid-glass transition has taught us that all the friction forces which appear in the problem may be subjected to retardation effects. It is thus consistent with such considerations to generalize equations (2.3) and (2.5) to

$$\boldsymbol{\sigma} = (\delta P - \eta_b \otimes \text{div } \mathbf{v})\mathbf{1} - \eta_s \otimes \boldsymbol{\tau} + \mu \otimes \dot{\mathbf{Q}} \quad (2.6)$$

$$\ddot{\mathbf{Q}} = -\omega_0^2 \mathbf{Q} - \hat{\Gamma} \otimes \dot{\mathbf{Q}} + \Lambda' \mu \otimes \boldsymbol{\tau} \quad (2.7)$$

where  $\otimes$  means a convolution product, and where we have written that the same  $\mu(t)$  acts in equations (2.6) and (2.7). In fact,  $\omega_0$  is a libration frequency which is in the THz region, while the spectra we are interested in are in the 1–10 GHz domain. It is thus tempting to neglect the l.h.s. of equation (2.7) with respect to the first term of its r.h.s.; though this is mathematically incorrect, the result obtained by taking without care the Laplace transforms of equation (2.6) and truncated equation (2.7) turns out to be the correct one, provided that one takes into account a remark which we shall make above equation (2.13).

We perform here depolarized light scattering experiments in which the scattering angle is  $\theta$ . In molecular liquids, at low frequencies, the main source of depolarized light is the traceless part,  $\beta$  of the molecular polarizability tensor. It is consistent with the hydrodynamics approach used above to write

$$\beta = b\mathbf{Q}. \quad (2.8)$$

A lengthy calculation [13b] of the orientational correlation functions related to this VH geometry shows that the scattered intensity at frequency  $\omega$  is proportional to

$$I(\omega) \approx I^0 \frac{b^2}{\omega} \text{Im} \left( R(\omega) + \cos^2 \frac{\theta}{2} R_1(\omega) \right) \quad (2.9)$$

where  $I^0$  is the incoming light beam intensity. In equation (2.9),  $R(\omega)$  is the spectrum detected in the backscattering geometry. It describes the orientational fluctuation dynamics of the molecules. The second term,  $R_1(\omega)$ , is the result of the coupling of the strain rate tensor with the time derivative of the orientational fluctuations and depends specifically on the scattering vector  $q$ . It may be written as

$$R_1(\omega) = \frac{q^2 \rho_m^{-1} G(\omega)}{\omega^2 - q^2 \rho_m^{-1} [\omega \eta_s(\omega) - G(\omega)(1 - R(\omega))^{-1}]} \quad (2.10)$$

with:

$$G(\omega) = \Lambda' \omega_0^2 \left( \frac{\mu(\omega)}{\hat{\Gamma}(\omega)} \right)^2 R^2(\omega) \quad (2.11)$$

where  $\rho_m$  is the mass density, while  $R(\omega)$  is related to  $\Gamma(\omega)$  by

$$R(\omega) = \frac{\omega \hat{\Gamma}(\omega)}{[\omega_0^2 + \omega \hat{\Gamma}(\omega)]}. \quad (2.12)$$

The form of  $R(\omega)$  that we are going to use deserves some comments. From a formal point of view,  $R(\omega)$  is the Laplace transform, as defined in [13b], of the correlation function of the component  $Q_{\perp\perp'}$  of  $\mathbf{Q}$  where  $\mathbf{u}_{\perp}$  and  $\mathbf{u}'_{\perp}$  are two mutually orthogonal directions, both perpendicular to  $\mathbf{q}$ . For such a component, the last term of equation (2.7) drops out which explains why  $R(\omega)$  is a pure orientational function involving only  $\hat{\Gamma}(\omega)/\omega_0^2$ .

Furthermore, it is now well documented that in supercooled liquids above  $T_g$ , any normalized correlation function first decreases from the value 1 to a value called here  $R^0$ ,

also defined as the nonergodicity parameter related to this function; this decrease takes place in a time of the order of  $\omega_0^{-1}$ . At much longer times, the orientational correlation function enters into the  $\alpha$  relaxation regime, which is usually well described by a stretched exponential with a  $t = 0$  value equal to  $R^0$  (we neglect in this section, for the sake of simplicity, an intermediate  $\beta$  fast regime which takes place between the microscopic motion and the  $\alpha$  relaxation regime). The regime that we may probe in our Brillouin scattering experiments corresponds only to the long time dynamics of this correlation function, i.e. only to the  $\alpha$ -relaxation regime. This implies that the integral of equation (2.12) will not be  $\pi$  but  $\pi R^0$  with  $0 < R^0 < 1$ . The existence of this coefficient is then a natural consequence of the theory, and previous studies of this dynamics have shown that  $R(\omega)$  can be properly represented in the frequency range of interest by

$$R(\omega) = R^0 \left[ 1 - \left( \frac{1}{1 + i\omega\tau_R} \right)^\beta \right]. \quad (2.13)$$

where  $\tau_R$  and  $\beta$  can be measured in a backscattering depolarized experiment.

The very idea of introducing retardation effects in the equations of motion leads us to assume for  $\omega\eta_s(\omega)$  an expression similar to equation (2.13)

$$\omega\eta_s(\omega) = \eta_s^0 \left[ 1 - \left( \frac{1}{1 + i\omega\tau_s} \right)^\beta \right] \quad (2.14)$$

and also to propose that  $\mu$  and  $\Gamma$  have similar dynamics. This has two consequences: the term in the bracket appearing in the denominator of equation (2.10) can be viewed either as  $i\omega$  times a viscosity term or as the square of a frequency dependent sound velocity. By taking the  $\omega > 0$  limit of this bracket, the first interpretation allows to deduce the value of the static shear viscosity:

$$\eta_s = \beta\eta_s^0\tau_s \quad (2.15)$$

which shows that this static viscosity is only due to the motion of the centres of mass.

The second interpretation of this bracket shows that, at low temperatures, when the transverse modes are well characterized, the transverse sound velocity is not only determined by the infinite frequency shear modulus corresponding to the centres of mass motion,  $\eta_s^0$ , but is renormalized by the translation rotation coupling:

$$v_T = \left( \frac{\eta_s^0}{\rho_m} \left( 1 - \frac{G^\infty}{\eta_s^0} (1 - R^0)^{-1} \right) \right)^{1/2} = \left[ \frac{\eta_s^0}{\rho_m} \right]^{1/2} r \quad (2.16)$$

where  $G^\infty$  is the  $\omega \rightarrow \infty$  limit of  $G(\omega)$ ;  $r$  can then be called the renormalization factor.

### 3. Experiment and data analysis

#### 3.1. Experiment

A first test [13] of our description of the transverse hydrodynamics of supercooled glass forming liquids, of our ability to determine the most relevant coefficients related to this theory and of the consistency of the results with other independent measurements has been performed on metatoluidine,  $\text{CH}_3\text{-C}_6\text{H}_6\text{-NH}_2$  (melting temperature  $T_m = 243$  K; thermodynamic glass transition temperature  $T_g = 178$  K).

The thermal variations of the refraction index and of the density are given by [14]:

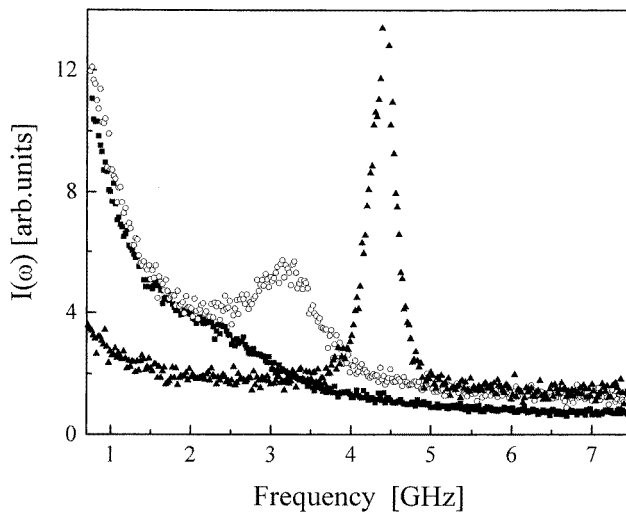
$$n(T) = -4.5 \times 10^{-4} T \text{ (K)} + 1.692(5) \quad (3.1)$$

$$\rho(T) = -8.1 \times 10^{-4} T \text{ (K)} + 1.225(0). \quad (3.2)$$

Low temperature, low frequency depolarized light scattering spectra have been measured in two different geometries for various temperatures. A first series of experiments was performed with different instruments in order to measure and analyse the pure rotational  $\alpha$  relaxation spectrum over a large temperature range (178 K–300 K) [15, 16]. The whole series of corresponding orientational relaxation times thus obtained could be fitted by a Vogel–Fulcher law, from where values of  $\tau_R$  were obtained for all the intermediate temperature values used here, as well as the values of the stretching coefficient  $\beta$  of equation (2.13).

The second series of experiments consisted of  $90^\circ$  VH light scattering experiments. They were performed on a eight-pass tandem Fabry–Pérot instrument, the source being a Coherent Innova 90 monomode  $\text{Ar}^+$  laser ( $\lambda = 514.5$  nm). The spectra were recorded between 0.75 GHz and 8 GHz.

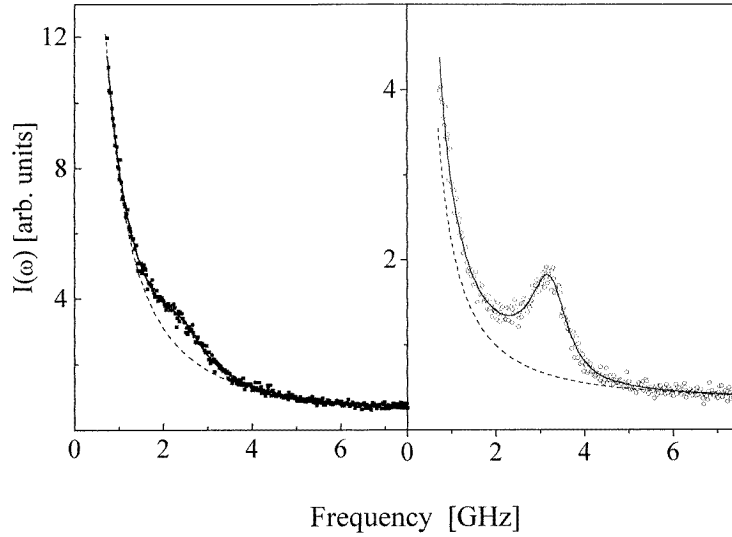
The check of the consistency of our hydrodynamic equations implied the direct verification of equation (2.15), and thus the knowledge of the static viscosity on a large temperature range. Previous measurements of this viscosity coefficient made above 254 K were used. Lower temperature values were obtained though the use of Rheometrics RHS-800 viscometer down to 191 K.



**Figure 1.** 90 degrees depolarized spectra of supercooled metatoluidine at 248 K (●), 228 K (○) and 218 K (Δ).

### 3.2. Data analysis

A selected set of the  $90^\circ$  VH spectra is shown in figure 1. At the highest temperature (248 K), a weak bump (see also figure 2) emerges around 2.5 GHz from a broad central peak while, at 208 K, the transverse phonon appears as a quite narrow peak located at 4.5 GHz. We fitted the spectra with equations (2.9)–(2.11) where  $R(\omega)$  and  $\omega\eta(\omega)$  are given by equations (2.13) and (2.16) respectively,  $R^0$  being the only parameter of equation (2.13) not fixed by the backscattering experiments. In order to reduce the number of fit parameters we made the further approximation that  $\mu(\omega)/\hat{\Gamma}(\omega)$  is constant. Finally, we had to take into account to some extent the up-to-now neglected higher frequency relaxation processes which should in principle be introduced both in the viscosity function,  $\omega\eta_s(\omega)$ , and in the orientational function),  $R(\omega)$ . In the data analysis we present here, we have used a very crude approximation in introducing



**Figure 2.** Fits to the data at—left 248 K—right 233 K.

only an extra damping term  $-i\omega\gamma_0$  in the denominator of equation (2.10). Furthermore,  $\gamma_0$  was assumed to be temperature independent and determined from the remaining linewidth of the transverse modes in the glass phase (178 K), where the relaxation processes appearing in the term in bracket of the denominator of equation (2.10) are all frozen out.

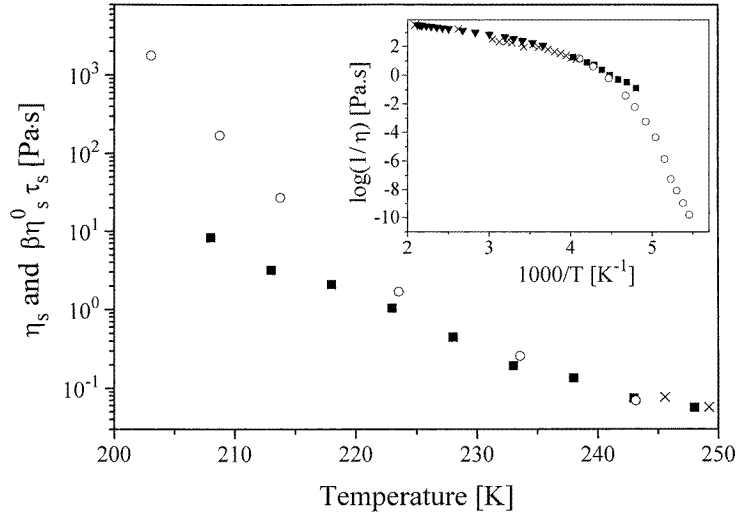
#### 4. Results and discussion

The parameters obtained with such a simplifying hypothesis are reported in table 1 while the quality of the fits is exemplified in figure 2 for the two temperatures  $T = 248$  K and  $T = 233$  K. The value and the temperature variations of the quantities reported in table 1 deserve a certain number of comments which originate also from other fits made with a more realistic representation of the  $\beta$  relaxation process and which will be presented elsewhere [17].

**Table 1.** Fitting parameters for metatoluidine VH spectra.  $\tau_s$ ,  $\eta_s^0$ ,  $\Lambda(\mu/\Gamma)^2$  and  $R^0$ , as described in the text.  $\tau_R$  is taken from [15] (the time reported by Dreyfus *et al* (1998) is erroneous);  $r$ ,  $v_T$  and  $\beta\eta_s^0\tau_s$  are deduced from the fitting parameters (see text) and  $\eta_s$  is the static shear viscosity value interpolated from the mechanical spectroscopy measurements.

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

The viscosity relaxation times  $\tau_s$  are definitely shorter than the rotational relaxation  $\tau_R$ , whatever the temperature considered. The infinite frequency shear modulus  $\eta_s^0(T)$ , related solely to the motion of the centres of mass, has a definite important decrease with temperature. Conversely, the rotation–translation coupling,  $r(T)$ , has a small effect ( $\sim 10\%$ ) on the effective velocity of transverse sound waves and the importance of this effect does almost not vary with temperature. We must point out that, since pioneering work [1] in the 1960s, effective velocity of the transverse sound has been known to strongly decrease with increasing temperature. The present results show that, at least in metatoluidine, this variation is a centre of mass effect and does not originate from an increase of the translation–rotation coupling efficiency.



**Figure 3.** Comparison between  $\beta\eta_s^0\tau_s$  (■) as obtained from table 1—present paper, fit parameters, and the Couette viscosity measurements (○), as a function of temperature. The inset presents static viscosity data over a larger range of temperature: × [22] and ▼ [23].

The consistency of our hydrodynamic equations and of our analysis is checked in figure 3, where direct measurements of the static shear viscosity are compared to the values obtained through equation (2.15). Both sets of values agree well, within the possible accuracy of the measurements, between 248 K (i.e. just above the melting temperature) and 223 K, i.e. from 0.06 Pa s (0.6 P) to 2 Pa s (20 P). The divergence which takes place at lower temperatures is probably related to our very poor description of the fast  $\beta$  process: it gives rise to a very strong correlation between its actual description and the value of  $\tau_s$  at low temperature, making impossible an estimate of the latter in this last case. We have recently verified [17] that assuming  $\tau_R$  and  $\tau_s$  to be proportional is enough to fulfil equation (2.15) for a variation of the viscosity of five orders of magnitude with a good accuracy without altering any of the previous conclusions, and with reasonable shapes for the  $\beta$  relaxation processes.

In conclusion, we have measured the shear relaxation time,  $\tau_s$ , and found it to be always shorter than the reorientation relaxation time,  $\tau_R$ , the increase of the ratio  $\tau_R/\tau_s$  with decreasing temperature, being possibly the result of the neglect of fast relaxation processes. We have found that it is possible to obtain, from data measured in the supercooled phase by light scattering experiments, values of the static shear viscosity which compare well with direct measurements. Another question is related to the temperature variation of the coefficient  $\eta_s^0$ , the infinite frequency limit of  $\omega\eta_s(\omega)$  (see equation (2.16)). We found that in



metatoluidine,  $\eta_s^0$  decreases strongly with increasing temperature while  $r$ , which expresses the rotation–translation coupling, is almost constant. We may point out that this result is the opposite of previous findings, in particular by Wang and his collaborators, who proposed in other molecular glass forming liquids [18, 19] that the rotational–translational coupling plays an important role in the decrease of the shear velocity of the corresponding liquid but they could not base this statement on a quantitative analysis of the corresponding spectra. As metatoluidine appears to be similar in many respects to those other molecular glass formers [20, 21], a complete analysis of those transverse spectra needs to be performed with the experimental accuracy presently available before a firm conclusion on the thermal evolution of their  $\eta_s^0$  and  $r$  factor can be made.

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