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Brillouin scattering study of the fast dynamics of m-toluidine

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Abstract

Brillouin light and x-ray scattering have been used to investigate the dynamic structure factor of supercooled and glassy m-toluidine in the temperature range between 34 and 303 K. In addition to the ubiquitous α relaxation, evidence is given of a fast relaxation process active in the ns-ps time region. Information on the activation energy of the fast process is obtained from the attenuation of longitudinal acoustic modes.

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1. Introduction

The fast dynamics of liquids and glassy systems is dominated by different molecular motions. The most studied is the cooperative motion, commonly referred to as α -process, whose characteristic time progressively increases when decreasing the temperature, eventually diverging when approaching the liquid to glass transition. The mode coupling theory explains the nature of the α -relaxation process at the early stage of supercooling of a liquid as originating from nonlinear coupling between density correlators [1].

In addition to this relaxation process, one or more secondary relaxations are typically revealed in real liquids, which remain active also in the glassy state, whose nature is still not completely understood.

M-toluidine is a fragile glass former characterized by a spatial organization of the molecules induced by hydrogen bonds. A recent inelastic x-ray scattering (IXS) investigation of the dynamic structure factor of m-toluidine has given evidence for a cusp-like behaviour of the nonergodicity factor and of a critical nonergodicity parameter which oscillates in phase with the static structure factor, showing that local order at molecular level can coexist with the signatures of glass transition predicted by the idealized version of the mode-coupling theory [2].

M-toluidine has already been the subject of experimental investigations concerning its acoustic properties and dynamical processes by means of ultrasonic measurements [3-5] and Brillouin light scattering (BLS) experiments [6]. In this paper we contribute to this topic reporting new BLS measurements taken on m-toluidine, which extend the study of the dynamics of density fluctuations to the glassy phase ($T_g=187$ K). From the frequency position and linewidth of Brillouin lines, related to the velocity and the attenuation of longitudinal acoustic modes propagating in the system, and from a comparison with previous IXS data, we give evidence of a fast relaxation process active also below the glass transition temperature, we estimate its activation energy and discuss its nature.

2. Experimental details

M-toluidine ($\text{CH}_3\text{-C}_6\text{H}_4\text{-NH}_2$), purchased at 99 % from Merck, has been distilled in order to obtain a high-purity sample and prevent crystallization. The sample was transferred into a cylindrical pyrex cell, 1 mm inner diameter, which was sealed in dry nitrogen environment. A Cryomech ST405 cryostat was used to regulate temperature. A Coherent-Innova 300 model Ar⁺

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3 laser was operated with a typical power of 300 mW on a single mode of the 514.5 nm line. The light
4 scattered from the sample in the backscattering geometry was analysed by means of a Sandercock-
5 type (3+3)-pass tandem Fabry-Perot interferometer characterized by a finesse of about 100 and a
6 contrast ratio higher than 10^9 . Spectra were collected in the temperature range between 34 and 303
7 K. IXS measurements were performed at the very high energy resolution IXS beamline ID16 [7] at
8 the European Synchrotron Radiation Facility from 54 to 293 K. At each temperature, five different
9 Q-values are typically detected, namely $Q=1, 2, 4, 7,$ and 10 nm^{-1} , as described in Ref. [2]. Both
10 experiments have been performed on cooling.
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21 3. Results and discussion

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23 Figure 1 shows typical BLS and IXS spectra of m-toluidine taken at values of the exchanged
24 wavevector $Q = 0.038$ and 2 nm^{-1} , respectively, at ambient temperature. Both spectra show inelastic
25 features, the so called Brillouin peaks, at about 10 and 600 GHz, respectively. The presence of
26 relaxation processes coupled with density fluctuations can be revealed by the temperature and Q
27 behaviours of velocity and attenuation of acoustic modes, proportional to the frequency position Ω
28 and linewidth Γ of Brillouin lines. In all measured BLS spectra the linewidth of Brillouin peaks is
29 larger than the instrumental function and a non-negligible quasielastic (Mountain) contribution is
30 observed in the central part of the spectra, indicating the presence of relaxation processes. Among
31 these, the structural relaxation is the most important for temperatures higher than T_g . For
32 temperatures close and below the glass transition, however, the characteristic time of the structural
33 relaxation becomes so long that it cannot be responsible for the hypersonic absorption. This result
34 gives a direct evidence of the presence, in the ten GHz frequency region, of some secondary
35 relaxation process which remains activated even in the glassy phase. This seems to be a peculiarity
36 of fragile systems, as recently reported in Ref. [8].
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51 [Insert Fig. 1 about here]
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54 To be more quantitative, the values of Ω and Γ have been obtained by fitting the BLS spectra
55 in a narrow frequency region around the Brillouin peak by means of the damped harmonic oscillator
56 (DHO) model function
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$$I(q, \omega) = \frac{I_0}{\pi} \frac{\Gamma \Omega^2}{(\omega^2 - \Omega^2)^2 + (\Gamma \omega)^2} \quad [1]$$

convoluted to the instrumental function. In the case of IXS spectra, a Lorentzian function centred at zero frequency was added to account for the central line and the whole spectrum was convoluted by the instrumental function after correction for the detailed balance [2]. The results of the fit are reported in Fig. 2 in the form of longitudinal sound velocity (ω/Q) (see bottom panel of Fig. 2) and apparent kinematic viscosity (Γ/Q^2) (see top panel of Fig. 2). Here, the exchanged momentum Q has been determined through the relationship $Q=4\pi n/\lambda_i$, where n is the refractive index of the medium and λ_i is the incident wavelength of the laser source. For the determination of the refractive index as a function of temperature, we have proceeded as follows: for the liquid phase ($T>T_g$) the refractive index was taken from the literature [9]; for temperatures $T<T_g$, it has been estimated using the Clausius–Mossotti relation, where the thermal variation of the density has been deduced from the thermal expansion coefficient determined from $\alpha V= 5.3 \times 10^{-4} \text{ cm}^3 \text{ K}^{-1}$ - an expression valid in the crystal and in proximity of the glass transition [10] - and from the density value $\rho(T_g)= 1.0745 \text{ gr cm}^{-3}$.

In figure 2, together with our results we also report previous BLS data [6], obtained in a narrow temperature range, showing a satisfactory agreement between two series of data. The unrelaxed limit of Γ/Q^2 , providing the longitudinal kinematic viscosity η_∞/ρ , can be reached either for a given temperature at very high frequency or for a given frequency at very low temperature. This condition is met by IXS spectra in the whole reported T range and by BLS only in the low temperature limit, where the values of Γ/Q^2 obtained by the two techniques tend to coincide. When increasing the temperature, the BLS values of Γ/Q^2 increase and become a factor 3 higher than the unrelaxed limit even for $T<T_g$. This behaviour is common in other glass-formers, studied by some of us (see, for instance, Refs. [11-15]), where this excess of acoustic attenuation has been proved to be related to the interplay of acoustic modes with internal degrees of freedom. On these bases also in case of m-toluidine, we believe that the fast process that emerges from this analysis - a relaxation of density fluctuations with a characteristic relaxation time in the ns-ps timescale - could be associated to a coupling among the translational and one or more (still unidentified) intramolecular degrees of freedom, possibly associated to the presence of the NH_2 and CH_3 groups.

[Insert Fig. 2 about here]

In the hypothesis that this relaxation process is thermally activated, i.e. its characteristic time follows the Arrhenius law $\tau(T) = \tau_0 \exp(E_a/k_B T)$, the value of the activation energy E_a can be estimated from the temperature dependence of Γ . In fact it can be shown [13] that, if the strength of the fast relaxation process is negligibly temperature dependent, the major contribution to the width of Brillouin lines comes from the temperature dependence of the relaxation time through the relationship:

$$\lim_{\omega\tau \gg 1} \left(\frac{\Gamma}{Q^2} \right) = \frac{\eta_\infty}{\rho} + \frac{\Delta}{\rho} \sin\left(\frac{\beta\pi}{2}\right) \Omega^{-(\beta+1)} \tau_0^{-\beta} \exp\left(-\frac{\beta E_a}{k_B T}\right) \quad [2]$$

where β is the stretching parameter whose value is 1 for single exponential relaxation and $0 < \beta < 1$ for stretched functions, such as Cole-Davidson or Cole-Cole functions. By a fitting procedure of Eq. (2) to the data of Fig. 2, in the 34-134 K temperature range, the value $\beta E_a = (611 \pm 80)$ K is obtained, corresponding to the solid line in the figure.

As order of magnitude, the quantity βE_a , evaluated for m-toluidine, well compares with the values calculated in other fragile glass formers of different molecular weight: ortho-terphenyl [(140 ± 20) K], polybutadiene [(260 ± 20) K] and salol [(400 ± 40) K], where the existence of an intramolecular contribution in the spectrum of density fluctuations has been verified. [8,13,14,16]. Concerning this topic, a viscoelastic analysis of BLS spectra is currently in progress in order to gain further information on the temperature behaviour of the shape and of the characteristic time of this fast relaxation.

Finally, some additional comment would have to be reported with respect to the figure 2. Magnifying the image of the kinematic viscosity (Γ/Q^2) as a function of temperature, the appearance of two features can be identified, one at T_g where the slope drastically changes, and a second one at about 135 K. At the same time, observing the velocity (ω/Q) curves of fig. 2, this kink-like anomaly is present again in the BLS data. This feature in the acoustic properties at about 135 K could be related to an effect observed in the thermodynamic properties of m-toluidine. It is well known that the heat capacity undergoes a large drop in vicinity of the vitrification at the usual temperature of glass transition, T_g , named $T_{g\alpha}$. On further cooling, some systems exhibit another drop at a characteristic temperature, called $T_{g\beta}$. An exhausting explanation of this phenomenon still does not exist. A possible interpretation refers to fast local rearrangements that freeze out at a much lower temperature with respect to $T_{g\alpha}$ where long range diffusion ceases. First observed in

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3 isopropylbenzene [17], this “secondary glass transition” has also been characterized for several
4 molecular liquids by Oguni and co-workers [18], and experimentally observed in m-toluidine by
5 Simionesco et al. [19]. In particular, $T_{g\beta}$ in m-toluidine turns out about to 130 K, a temperature
6 surprisingly similar to the one where the observed change can be recognised in our BLS data. This
7 evidence hints at a correspondence between dynamics and thermodynamics anomalies, which
8 deserves more efforts of understanding. Also, new data in systems which present similar features
9 would be precious.
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18 4. Conclusions

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21 In conclusion, a fast relaxation process has been reported to affect the dynamics of density
22 fluctuations of m-toluidine in the ns-ps range explored by Brillouin light scattering. The presence of
23 a secondary relaxation, beside the structural relaxation process, has been identified by examining
24 the temperature behaviour of longitudinal kinematic viscosity in proximity of the glass transition,
25 which shows an excess with respect to the unrelaxed value estimated through inelastic x-ray
26 scattering. This behaviour is strongly resembling to that of other fragile glass-formers where the
27 presence of an intramolecular contribution in the spectrum of density fluctuations has been
28 recognized. Further, the activation energy for the fast relaxation process evaluated here well
29 compares with those of the above mentioned glass-forming systems. This indication supports the
30 idea that the coupling with internal degrees of freedom as a reasonable origin for the fast relaxation
31 process revealed in m-toluidine in the BLS frequency region.
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Figure captions

Figure.1

BLS (top panel) and IXS (bottom panel) spectra of m-toluidine taken at ambient temperature and $Q=0.038 \text{ nm}^{-1}$ and $Q=2 \text{ nm}^{-1}$, respectively.

Figure.2

Apparent longitudinal kinematic viscosity (top panel) and longitudinal sound velocity of m-toluidine as obtained from X-ray scattering at $Q=2 \text{ nm}^{-1}$ (open squares) and from light scattering (full circles). The solid line in the top panel represents the result of the fitting procedure of Eq. (2)

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3 to the experimental data. Open circles are from Ref. [6]. Inset: Enlarged view of the region where
4 the fit has been performed to better visualize data and fitting curve.
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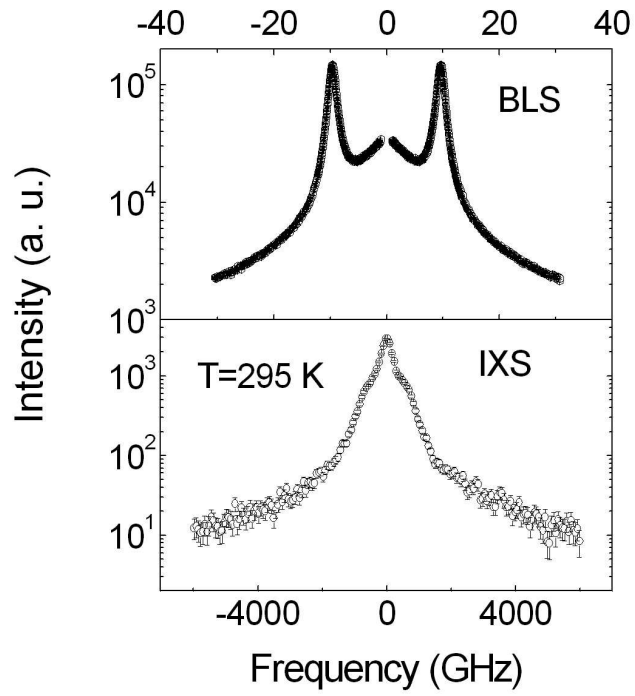


Figure 1
279x215mm (150 x 150 DPI)

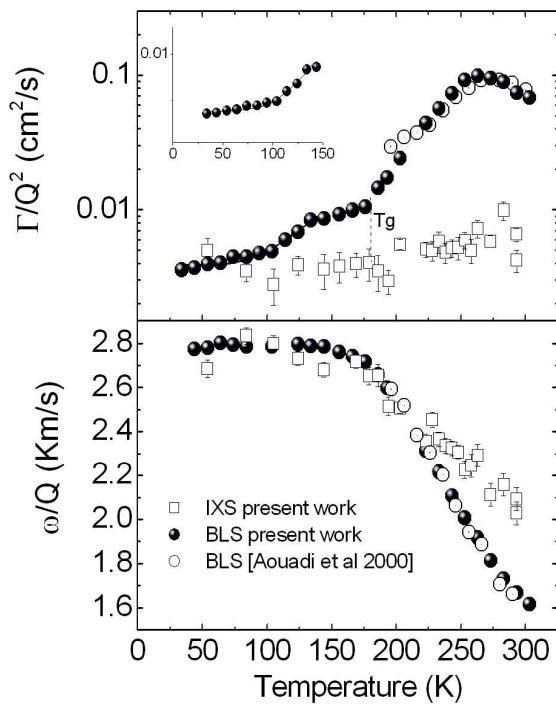


Figure 2
279x215mm (150 x 150 DPI)