Intramolecular origin of the fast relaxations observed in the Brillouin light scattering spectra of molecular glass formers

G. Monaco,[1] S. Caponi,[2] R. Di Leonardo,[3] D. Fioretto,[2] and G. Ruocco[3]

[1]*European Synchrotron Radiation Facility, Boîte Postale 220, F-38043 Grenoble Cedex, France*

[2]*INFM and Dipartimento di Fisica, Università di Perugia, I-06100, Perugia, Italy*

[3]*INFM and Dipartimento di Fisica, Universitá di L'Aquila, I-67100, L'Aquila, Italy*

The Brillouin light scattering spectra of the *o*-terphenyl single crystal are compared with those of the liquid and the glass phases. This shows (i) the direct evidence of a fast relaxation at frequencies $\nu \approx 5$ GHz in both the single crystal and the glass; (ii) a similar temperature dependence for the attenuation of the longitudinal sound waves in the single crystal and the glass; and (iii) the absence of coupling between the fast relaxation and the transverse acoustic waves. These results allow us to assign such a relaxation to the coupling between the longitudinal acoustic waves and intramolecular vibrations, and therefore to exclude any relationship between it and the glass transition.

The study of the atomic dynamics of systems undergoing the structural liquid to glass transition is nowadays a very fertile topic in the condensed matter physics, and is stimulating many relevant developments on both the experimental and the theoretical side [1]. This study is historically characterized by the attempt to extend our knowledge of the dynamics to larger and larger time ranges. Traditionally, this attempt has been focused on the time range of the structural relaxation, which shows prominent spectral changes in the glass transition region. In more recent years, conversely, much of the attention has shifted towards shorter times, i.e., towards the so-called fast processes range.

The interest in extending as much as possible the probed time window has been much stimulated by the development of the mode coupling theory (MCT) [2], which describes the time evolution of the *q*-component of the density-density correlation function, $F(q,t)$, of a *simple* liquid when its temperature is changed across the metastable undercooled region. In fact, the MCT makes, among the others, specific predictions on the time range comprising the earliest part of the structural relaxation and the latest part of the fast processes, the β-region [2].

The MCT predictions have been the subject of extensive experimental studies [3]. Among them, the ones which really probe $F(q,t)$ [or its time Fourier transform, the dynamic structure factor, $S(q,\omega)$] are based on inelastic neutron scattering (INS) in the 10 nm^{-1} *q* range [4], and on Brillouin light scattering (BLS) in the 10^{-2} nm^{-1} *q* range [5]. In these studies, the relevance of the short-times region for a proper spectral description has been underlined; this region has been associated to the MCT β-region, and several MCT predictions have been tested, e.g., the cusplike discontinuity in the Debye-Waller factor at the dynamical transition temperature, T_c [4,5]. Unfortunately, while the MCT predictions are developed for ideal systems (hard spheres or monoatomic systems), the glass formers which are the object of experimental studies are mostly molecular compounds. These latter ones are obviously characterized by an intramolecular dynamics which, in principle, could just be effective in the β-region [6].

Some of us have recently reported on a fast relaxational dynamics in the 10^{-11} s time range which appears in the $S(q,\omega)$ spectra obtained by BLS in glassy OTP [7]. This fast dynamics has also been analyzed using a phenomenological ansatz for the memory function and has been found to be active in both the glass and the liquid, and to be essentially temperature independent [8]. Relaxation processes in a similar time window had been observed in previous studies on similar glass formers [5], and had been described in terms of the MCT β-region.

In order to clarify the nature of this relaxation, we have performed on an OTP single crystal a further BLS experiment, on the results of which we report in this paper. As a matter of fact, we observe in the spectra of the single crystal the same fast relaxation which was observed in both the liquid and the glass [8,7]. As a consequence, we conclude that this fast relaxation is *not* related to the glass transition and should not be associated with the MCT β-region. Moreover, by comparing the longitudinal (*L*) and transverse (*T*) sound attenuation in the liquid and the glass with the *L* sound attenuation in the single crystal, we also conclude that the fast relaxation arises from the coupling of density fluctuations to intramolecular degrees of freedom.

The OTP single crystal has been prepared from 99% purity powder (Aldrich Chemicals) by ricrystallization in a methanol solution. The typical dimensions of the obtained needle-shaped crystals are $2 \times 2 \times 10$ mm^3. The crystals have been characterized by x-ray diffractometry, and the measured lattice parameters of the orthorhombic unit cell ($P2_12_12_1$ symmetry) are in agreement with previous determinations ($a = 6.024$, $b = 11.729$, and $c = 18.582$ Å) [9]. The main axis of the needles is along the *a* axis, and the lateral faces are found to be parallel to the 011 and the 023 lattice planes.

The BLS spectra of the single crystal have been collected in backscattering geometry, with the exchanged wave vector *q* along the (001) direction. In the chosen configuration, only the *L* Brillouin peaks are allowed. As the exciting line, we have used the single mode from a Coherent compass 532/400 laser operating at $\lambda_o = 532$ nm with a typical power of
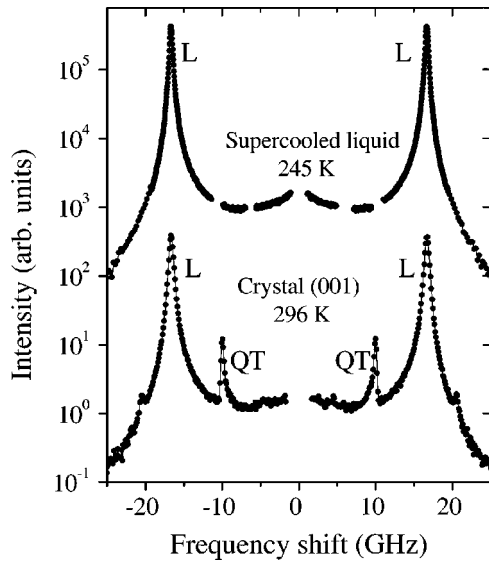
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FIG. 1. BLS spectra in backscattering geometry of the single crystal [q along the (001) direction] and of the strongly supercooled OTP at the indicated temperatures.

≈ 300 mW. The scattered light has been analyzed by a Sandercock-type $(3+3)$-pass tandem Fabry-Perot frequency analyzer, with a finesse of ≈ 100 and a contrast $> 5 \times 10^{10}$ [10], set to a free spectral range of ≈ 10 GHz. No analysis in polarization has been done, and the measurements have been performed in the 37/303 K temperature range (the melting temperature is $T_m = 329$ K). The same experimental setup has been used to measure the Brillouin peaks in the OTP glass in the temperature range 27/150 K (the glass transition temperature is $T_g = 244$ K). Moreover, further measurements in the 90° scattering geometry and with a VH polarization configuration have been collected in the 250/310 K temperature range in order to reveal the T Brillouin peaks. A dilute aqueous suspension of Latex particles (120 nm in diameter) has been used to determine the instrumental resolution function. In the 90° geometry measurements, the linewidths of the T Brillouin peaks are affected not only by the resolution function of the spectrometer, but also by the finite solid angle, which is defined by the collection optics. This effect, negligible for scattering angles close to 180°, gives a non vanishing contribution at 90°, and must be carefully taken into account in order to extract the true linewidth. The deconvolution procedure used for this purpose is described elsewhere [11].

The room temperature ($T = 296$ K) spectrum of the OTP single crystal with q along the (001) direction is presented on a log-linear scale in the lower part of Fig. 1. Apart from the small leakage of the quasitransverse modes, observed at ≈ 10 GHz and due to the residual misalignment from the (001) direction, this spectrum shows clear signatures of anharmonic effects: broad Brillouin peaks and a broad central band. In the upper part of the same figure, the spectrum of the supercooled liquid at $T = 245$ K is also reported, for comparison. The two spectra have been collected under identical experimental conditions and, at the chosen temperatures, show comparable linewidths for the Brillouin peaks. The similarity between the two spectra is remarkable, in particular for what concerns the central region which, in the super-
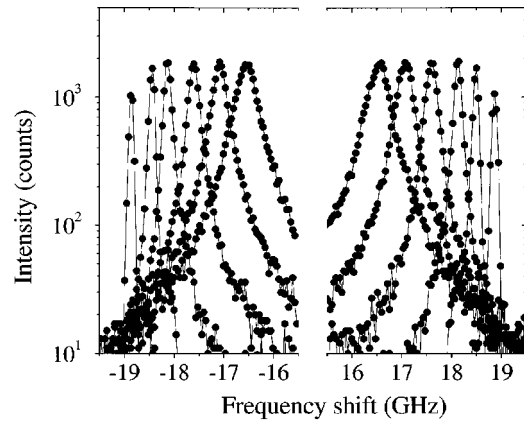

FIG. 2. BLS spectra of the OTP single crystal at the following temperatures (from high to low peak position): 37, 96, 138, 194, 251, and 303 K. The spectra have been collected in the backscattering geometry with the exchanged q-vector along the (001) direction. The overall instrumental resolution was 100 MHz FWHM.

cooled liquid and in the glass, has been described in terms of a secondary relaxation [8,7]. This figure by itself already suggests that this relaxation arises from the anharmonic coupling between the acoustic waves and other degrees of freedom.

In order to have a deeper insight into this anharmonic process, we have measured the temperature dependence of the single crystal BLS spectra. In Fig. 2 we present a few spectra at selected temperatures. Here, in order to emphasize the temperature dependence of the linewidth, only the Brillouin peaks are reported. On cooling, a strong reduction of the linewidth can directly be observed.

A quantitative description of the reduction of the Brillouin linewidth with temperature has been obtained by fitting the peaks region of the current spectra (i.e., of the measured spectra multiplied by the frequency squared) with a Lorentzian lineshape convoluted to the experimental resolution function. The values of $2\Gamma_c$ [full width at half maximum (FWHM)] resulting from the fits are reported in Fig. 3 ($\diamond$) in the 55–303 K temperature range. At temperatures lower than 55 K the Brillouin linewidth is almost indistinguishible
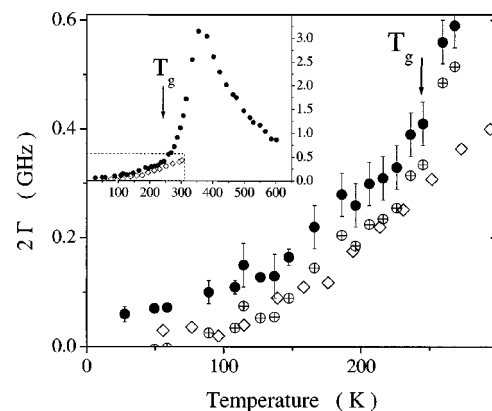

FIG. 3. Temperature dependence of the measured linewidths in the OTP single crystal ($\diamond$) and glass-liquid ($\bullet$). The inset shows the same data on a larger temperature range [8]. The symbol $\oplus$ represents the only contribution of the secondary, fast relaxation to the linewidth in the glass.

from that of the instrumental resolution function, and thus Γ_c could not be reliably obtained. In the same figure the similar quantities, $2\Gamma_d$, measured in the liquid and glassy OTP are also reported (●): the data above 114 K are taken from Ref. [8], and we have here extended in temperature those measurements down to 27 K. The inset reports the same data on a larger T range. We want to underline that this kind of comparison neglects the difference between $2\Gamma_c$ and $2\Gamma_d$, which arises from the difference in the refractive index between the crystal and the liquid-glass. We measured the refractive index of the OTP polycrystal at room temperature and we got the value $n_c = 1.72$, which is $\approx 4\%$ larger than that of the supercooled liquid at the same temperature ($n_d = 1.65$, [12]). This accounts for $\approx 8\%$ of the difference between $2\Gamma_c$ and $2\Gamma_d$; a value which is, however, comparable with the standard deviation of the FWHM data. Thus, given the lack of measurements of the refraction index of the OTP single crystal and given statistical accuracy of the present data, the direct comparison between $2\Gamma_c$ and $2\Gamma_d$ can be considered to be appropriate.

The comparison between the Brillouin linewidth of the single crystal and the liquid-glass comes out to be very instructive. At temperatures above T_g, in the undercooled and normal liquid phase, the linewidth is dominated by the structural relaxation which, however, is expected to be of no influence on Γ_d below T_g. Here, however, Γ_d is still temperature dependent, and this has been attributed to the presence of a secondary, fast relaxation [8,7]. On cooling, eventually, Γ_d seems to approach a limiting value, Γ_o. This latter value is here estimated to be $2\Gamma_o = 70 \pm 10$ MHz by a quadratic fit on the data below 150 K. The present value is slightly smaller than that reported in Ref. [8,7] (120 ± 20 MHz), where it was inferred by using the Γ_d values for $T > 114$ K and by scaling high frequency inelastic x-ray scattering (IXS) data [13]. From the comparative analysis of the IXS and the BLS data, Γ_o has been attributed to the presence of topological disorder in the glass [8,7]. To sum up, the linewidth of the liquid and glassy OTP has been described as the sum of three different contributions: $\Gamma_d(T) = \Gamma_o + \Gamma_f(T) + \Gamma_\alpha(T)$, where $\Gamma_\alpha(T)$ is the contribution of the structural relaxation and becomes negligible below T_g, $\Gamma_f(T)$ is the contribution of the secondary, fast relaxation, and Γ_o is the contribution of the topological disorder. Within this picture, we can get a direct estimate of $\Gamma_f(T)$ below T_g by simply subtracting Γ_o from the total linewidth Γ_d. The difference data are also reported in Fig. 3 (⊕), and they represent the only contribution of the secondary relaxation to the total linewidth.

The present measurements on the OTP single crystal not only strongly support the previous picture, but furthermore give us a fundamental hint to understand the nature of the secondary relaxation. In fact, as reported in Fig. 3, the linewidth of the single crystal, Γ_c, shows a T dependence which, below T_g, closely follows that of Γ_d and, furthermore, nicely agrees with that of Γ_f. Thus, we can conclude that (i) the description of the linewidth as the sum of the previously discussed contributions is a reasonable and physical ansatz, and (ii) the anharmonic process observed in the single crystal and the fast process observed in the liquid and glass [8,7] do share a common origin. As a consequence, we rule out the possibility that the secondary process observed in OTP, both
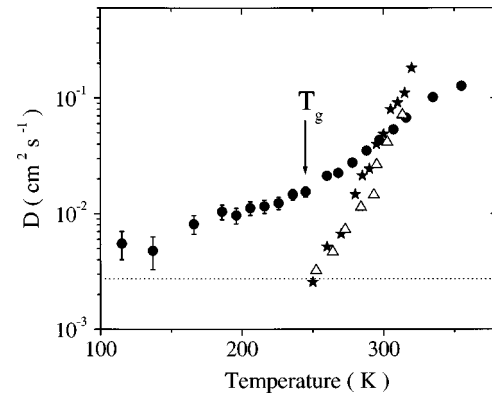

FIG. 4. Temperature dependence of Brillouin linewidths normalized by q^2: longitudinal data from Ref. [8] (●); T data from this work (△), and literature data from Ref. [16] (★). The dashed line indicates the low temperature limiting value of the longitudinal apparent kinematic viscosity, $D_o = 4\pi\Gamma_o/q^2$.

in the glass and in the liquid, is related to the β-region discussed by the MCT, and, more generally, that this process is related to the glass transition itself.

Left open is the question of the origin of the fast process. In particular one can associate this process to the coupling of the longitudinal acoustic waves either with (i) intramolecular degrees of freedom (vibrational relaxation) or with (ii) other intermolecular modes. A key experiment to solve this ambiguity is the determination of the absorption of the transverse sound waves. Indeed, in case (ii) one expects a transverse Brillouin linewidth comparable to the longitudinal one around T_g, and in any case with a similar T dependence. On the contrary, the anharmonicity of type (i) is expected to give a negligible contribution to the linewidth as the vibrational relaxations strongly couple only to the density fluctuations [14], and the coupling with the shear waves can take place only through the much less efficient mechanism of the translation-rotation coupling [15].

The comparison of the the L and T sound absorption is presented in Fig. 4, where we report the linewidths normalized by q^2, $D = 4\pi\Gamma/q^2$ [apparent kinematic viscosities, D_L (closed circles) and D_T (open triangles) for the L and T Brillouin peaks, respectively] in order to take into account the trivial contribution due to the different scattering geometries used to measure the L (closed circles) and the T (open triangles) Brillouin peaks. We also report the results of previous literature mesurements for the T linewidths (★) [16]; the agreement between the whole set of D_T data can be observed to be good. It is immediately seen from Fig. 4 that D_T, dominated by the contribution of the α process above T_g, does not follow D_L, and, in particular, that, on cooling, it drops to vanishingly small values at T_g. This is a clear indication that the transverse waves are not affected by the fast process and, therefore, that this process must be classified as vibrational in nature.

It has to be emphasized that the presence of such a kind of secondary processes in a molecular system such as OTP is not surprising. In fact, the class of the fragile glass formers (as OTP [17]) has a strong overlap [8] with the so-called Kneser liquids [6]. These systems have been widely studied by ultrasonics, and they are known to be characterized by the presence of secondary relaxations in the $10^{-9}/10^{-11}$ s time

range. The presence of similar relaxation processes has also been observed in BLS spectra of analogous systems, and in particular those characterized by the presence of phenyl rings [18]. Moreover, from the FWHM of the Brillouin peak $2\Gamma \approx 300$ MHz close to the glass transition, from the average relaxation time $\tau \approx 25$ ps of this process [7] and from the thermodynamic data collected in Ref. [8], the contribution to the specific heat of the vibrational motions responsible for the relaxation has been calculated by means of the procedure outlined in Ref. [19], giving as a result $C_{vib} = 65$ JK^{-1} mol^{-1}. This is a typical value for Kneser liquids [6], confirming the vibrational nature of the process here discussed.

In conclusion, by comparing the BLS spectra of the single crystal and the liquid-glass OTP, we have shown that the secondary, fast relaxation process previously observed in the OTP glass and liquid [8,7] is active also in the single crystal. This observation rules out the possibility that this process is related to the glass transition. Moreover, by comparing the longitudinal and transverse acoustic attenuation we have shown that the fast process does not couple to the tranverse sound waves, and thus we attribute it to a vibrational relaxation of intramolecular degrees of freedom.

Given this picture, it is natural to wonder whether the presence of a vibrational relaxation in the 10^{-11} s time range is a peculiarity of OTP. In fact, in strong glass formers secondary relaxations in a similar time scale are usually described invoking a different mechanism [20]. Actually, the ultrasonic literature [6] would suggest that vibrational relaxations couple to the density fluctuations in a wide class of molecular liquids, in particular the fragile glass formers. The presence of vibrational relaxations in real molecular systems could completely hide features intrinsic to the glass transition as, for example, the MCT β-region. Thus, it could come out to be dangerous, whether not incorrect, to describe the fast relaxation region of the memory function used to describe BLS spectra in terms of a simple MCT approach. This would certainly be the case for OTP.

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