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 intra-molecular vibrations, and therefore to exclude any relationship between it and the glass transition.

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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 $\beta$-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 $\beta$-region, and several MCT predictions have been tested, e.g. the cusp-like discontinuity in the Debye-Waller factor at the dynamical transition temperature, $T_c$ [6]. 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 intra-molecular dynamics which, in principle, could just be effective in the $\beta$-region [2].

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 [5]. Relaxation processes in a similar time window had been observed in previous studies on similar glass-formers [7], and had been described in terms of the MCT $\beta$-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 [5]. As a consequence, we conclude that this fast relaxation is not related to the glass transition and should not be associated with the MCT $\beta$-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 intra-molecular degrees of freedom.

The OTP single crystal has been prepared from 99% purity powder (Aldrich Chemicals) by recrystallization in a methanol solution. The typical dimensions of the obtained needles-shaped crystals are 2x2x10 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 ($a = 6.024$ Å, $b = 11.729$ Å, and
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 wavevector \( q \) 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 \( \lambda_0 = 532 \) nm with a typical power of \( \approx 300 \) mW. The scattered light has been analyzed by a Sandercock-type (3+3)-pass tandem Fabry-Perot frequency analyzer, with a finesse of \( \approx 100 \) and a contrast \( >5 \times 10^{10} \) \( [11]\), set to a free spectral range of \( \approx 10 \) GHz. No analysis in polarization has been done, and the measurements have been performed in the 37-\( \pm \)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-\( \pm \)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-\( \pm \)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 de-convolution 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 quasi-transverse modes, observed at \( \approx 10 \) 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 supercooled liquid and in the glass, has been described in terms of a secondary relaxation \( [37]\). 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 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\( \Gamma_c \) (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 indistinguishable from that of the instrumental resolution function, and thus \( \Gamma_c \) 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 (\( \bigcirc \)). The data above 114 K are taken from Ref. \( [8,7]\), and we have here extended in temperature those measurements down to 27 K. The inset reports the same data on a larger \( T \)-range.

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 \( \Gamma_d \) below \( T_g \). Here, however, \( \Gamma_d \) is still temperature dependent, and this has been attributed to the presence of a secondary, fast relaxation \( [36,37]\). On cooling, eventually, \( \Gamma_d \) seems to approach a limiting value, \( \Gamma_o \). 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. \( [8] \) (120\( \pm \)20 MHz), where it was inferred by using the \( \Gamma_d \) values for \( T > 114 \) K and by scaling high frequency Inelastic X-ray Scattering (IXS) data \( [31]\). From the comparative analysis of the IXS and the BLS data, \( \Gamma_o \) 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: \( \Gamma_d(T) = \Gamma_o + \Gamma_f(T) + \Gamma_a(T) \), where \( \Gamma_a(T) \) 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 \( \Gamma_o \) 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 \( \Gamma_o \) from the total linewidth \( \Gamma_d \). The difference data are also reported in Fig. 3 (\( \pm \)), 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, $\Gamma_c$, shows a $T$-dependence which, below $T_g$, closely follows that of $\Gamma_d$ and, furthermore, nicely agrees with that of $\Gamma_f$. 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] do share a common origin. As a consequence, we rule out the possibility that the secondary process observed in OTP, both in the glass and in the liquid, is related to the $\beta$-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) intra-molecular degrees of freedom (vibrational relaxation) or with ii) other inter-molecular 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 [13], and the coupling with the shear waves can take place only through the much less efficient mechanism of the translation-rotation coupling [4].

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, $D_L$ and $D_T$ 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 (\(•\)) and the T (\(△\)) Brillouin peaks. We also report the results of previous literature measurements for the T linewidths (\(\ast\)) [15]; 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 $\alpha$ 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 emphasised that the presence of such a kind of secondary processes in a molecular system like OTP is not surprising. In fact, the class of the fragile glass-formers (as OTP [8] has a strong overlap [8] with the so-called Kneser liquids [8]). These systems have been widely studied by ultrasonics, and they are known to be characterized by the presence of secondary relaxations in the $10^{-9} \div 10^{-11}$ s time range. Moreover, 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 [8].

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] 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 transverse sound waves, and thus we attribute it to a vibrational relaxation of intra-molecular 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. Actually, the large ultrasonic literature on related systems [4] would suggest that this kind of 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 hinder features intrinsic to the glass transition as, for example, the MCT $\beta$-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, as it has often been done [3]. This would certainly be the case for OTP.

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[1] For a recent review, see: M. C. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. 100, 13200 (1996).
[2] W. Götze, in Liquids, Freezing and the Glass Transition, Eds. J.P. Hansen, D. Levesque, and J. Zinn-Justin, North-Holland, Amsterdam (1991), pag. 287.
[3] For a recent review, see: W. Goetze, J. Phys.: Condens. Matter 11, A1 (1999).
[4] A. Tölle, H. Schober, J. Wuttke, and F. Fujara, Phys. Rev. E 56, 809 (1997), and references therein.
[5] As an example, see G. Li, W.M. Du, J. Hernandez, and H.Z. Cummins, Phys. Rev. E 48, 1192 (1993).
[6] K. F. Herzfeld, and T. A. Litovitz, in Absorption and Dispersion of Ultrasonic Waves, Academic Press, New-York (1959).
[7] G. Monaco et al., Phys. Rev. Lett. 82, 1776 (1999).
[8] G. Monaco, Thesis, University of L’Aquila, Italy (1997).
[9] S. Aikawa, Y. Maruyama, Y. Ohashi, and Y. Sasada, Phys. Rev. E 56, 809 (1997), and references therein.
[10] F. Nizzoli, and J. R. Sandercock, in Dynamical Properties of Solids, Eds. G. Horton, and A. A. Maradudin, North-Holland, Amsterdam (1990).
[11] S. Caponi, Thesis, University of Perugia, Italy (1999).
FIGURE CAPTIONS

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.

FIG. 2 - BLS spectra of the OTP single crystal at the following temperatures (from high to low peak position): 37, 96, 138, 194, 251, 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.

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

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. [15] (⋆). The dashed line indicates the low temperature limiting value of the longitudinal apparent kinematic viscosity, $D_0 = 4\pi\Gamma_0/q^2$. 
Figure 1

Supercooled liquid
245 K

Crystal (001)
296 K

Intensity (a.u.)

Frequency shift (GHz)
Figure 2
Figure 3
Figure 4