

Fast Relaxational Dynamics in the *o*-Terphenyl Glass

G. Monaco,¹ D. Fioretto,² C. Masciovecchio,³ G. Ruocco,¹ and F. Sette³

¹*Dipartimento di Fisica and INFM, Università di L'Aquila, I-67100, L'Aquila, Italy*

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

³*European Synchrotron Radiation Facility, B.P. 220 F-38043 Grenoble, Cedex France*

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The dynamic structure factor $S(q, \omega)$ of *o*-terphenyl, obtained by Brillouin light scattering ($q \approx 0.04 \text{ nm}^{-1}$) in the 1 to 30 GHz range, shows signatures of relaxation phenomena at temperatures well within the glassy phase. Using a phenomenological ansatz for the density fluctuations memory function and $S(q, \omega)$ data obtained by inelastic x-ray scattering at high momentum transfer ($q = 1\text{--}6 \text{ nm}^{-1}$), we describe this relaxational dynamics in terms of two distinct processes: (i) one in the 10^{-11} s range and slightly temperature dependent, and (ii) an “instantaneous” one, representing the microscopic transient and giving rise to a T -independent contribution to the Brillouin linewidth. [S0031-9007(99)08497-5]

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The nature of the microscopic mechanisms which are at the basis of the glass transition is an intriguing open question in condensed matter physics. One of the main obstacles to a thorough comprehension of this problem lies in the difficulties to unify the descriptions used above and below the glass transition temperature, T_g .

In liquids, one of the key concepts appearing in the description of the dynamics of the density fluctuations is that of *relaxation*. Considering a density fluctuation $\delta\rho_q$ with wave vector q , a relaxation process usually refers to a mechanism responsible for the dissipation of the energy initially associated to $\delta\rho_q$ towards other degrees of freedom. Since a truly microscopic interpretation of the relaxation processes is still lacking, their description is often kept at a phenomenological level introducing some specific model for the time and wave vector dependent memory function for $\delta\rho_q$ [1]. On general grounds, the correlation function of the density fluctuations, $F(q, t) = \langle \delta\rho_q(t) \delta\rho_q^*(0) \rangle$, shows a decay with at least two characteristic time regions. These are, respectively, the short time “microscopic” region, where $\delta\rho_q$ loses correlation in atomic vibrations around quasiequilibrium positions, and the structural (α) relaxation region, which mirrors the rearrangement of the intermolecular environment. The α relaxation is known to be strongly temperature dependent, and its characteristic time τ_α becomes as long as 10^2 s around T_g , corresponding to the “freezing” of the molecular structure in the glass. On the contrary, the microscopic region is expected to stay almost unchanged going from the liquid to the glassy phase. Besides these very general features, *fast* (i.e., in the 10^{-12} s range) relaxations in several glasses have been observed with different experimental techniques, e.g.,—in the case of the *o*-terphenyl (OTP) glass—incoherent neutron scattering [2], ^2H NMR [3], and depolarized light scattering [4,5]. Such features have been often interpreted [2,3,5] in terms of the mode coupling theory (MCT) [6], which has been proven to describe many details of the dynamics in the strongly supercooled region. However, in the glassy phase MCT gives

less general predictions, due to the complex interplay between a system-independent dynamics (the so-called β region) and a system-dependent one (hopping processes); although some experimental data have been shown to be compatible with the extended MCT predictions [5], different models have also been proposed [4,7]. In fact, there is still no general consensus on the description of the fast relaxational dynamics in glasses.

We have recently presented measurements of the dynamic structure factor, $S(q, \omega)$, of different glasses in the $\text{nm}^{-1} q$ range using inelastic x-ray scattering (IXS) [8,9]. In these studies, it has been shown that the main spectral features are reasonably well represented in terms of a Markovian approximation (representing the microscopic transient) for the memory function. With this simple model, which describes a completely unrelaxed dynamics, one finds (i) quantitative agreement with the sound velocity measured with lower frequency techniques and (ii) a q^2 hydrodynamiclike behavior of the Brillouin linewidth [8–10]. On this background, we have performed a Brillouin light scattering (BLS) experiment in order to look for possible signatures of the fast relaxational dynamics on the $S(q, \omega)$ of the OTP glass at frequencies lower than those probed by IXS. In fact, incoherent techniques such as depolarized light scattering suggest that the density fluctuations at the q values probed by BLS should be affected by such fast processes [11].

In this Letter we report on the shape of the $S(q, \omega)$ of the OTP glass in the 1–30 GHz frequency range, as determined from a BLS experiment. From a general point of view, the obtained spectra demonstrate the presence of a secondary relaxation process in the GHz range as evidenced by both a Mountain-like central band and a T -dependent width for the Brillouin peaks. A quantitative analysis of the $S(q, \omega)$ spectra is also presented, based on a two relaxation, phenomenological model for the memory function, chosen as the simplest one able to satisfactorily describe our data. The first relaxation process, described here by a simple Debye ansatz, is found to be

only slightly temperature dependent and to have a characteristic time τ in the 10^{-11} s range: it likely corresponds to the fast dynamics also observed with *incoherent* techniques [2–5]. The second one gives a T -independent contribution to the Brillouin linewidth, and is described here by an “instantaneous” process which represents the microscopic transient. This simple model also consistently describes the $S(q, \omega)$ spectra recently measured by IXS in the high q range ($q \approx 1\text{--}6 \text{ nm}^{-1}$) [9].

In the BLS q range, the $S(q, \omega)$ spectrum is proportional to the isotropic spectrum, $I_{\text{ISO}}(\omega)$, which can be derived from the polarized [$I_{\parallel}(\omega)$] and depolarized [$I_{\perp}(\omega)$] spectra measured in backscattering geometry according to the relation [12] $I_{\parallel}(\omega) = I_{\text{ISO}}(\omega) + rI_{\perp}(\omega)$. Here r^{-1} is the depolarization ratio, which gets the value 0.75 in the hypothesis that isotropic induced effects are negligible [13]. Starting from the measured spectra, and exploiting the fact that the $I_{\text{ISO}}(\omega)$ contribution to $I_{\parallel}(\omega)$ rapidly goes to zero at frequencies higher than the Brillouin peak position, it is then possible to obtain $I_{\text{ISO}}(\omega)$ by overlapping the tails of $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ using an adjustable factor and then subtracting the latter from the former. Finally, the dynamic structure factor can be obtained on an absolute scale exploiting the $S(q, \omega)$ second sum rule [1].

In our experiment, we used 99% purity OTP (Aldrich Chemicals; $T_g = 244$ K, $T_m = 329$ K), and details on the sample purification are reported in Ref. [14]. The light scattering measurements were performed using a single mode at $\lambda_o = 514.5$ nm from a Coherent Innova 300 Ar⁺ laser, with a typical power of ≈ 300 mW. We have measured the depolarization ratio, r^{-1} , in the 30–300 GHz range and at room temperature (297 K), in the deeply undercooled phase, using a SOPRA double monochromator [15]. We got the result $r^{-1} = 0.73 \pm 0.03$, constant in the whole probed frequency range, consistent with the fully depolarized expected value. We are then confident that isotropic induced effects are negligible, and that the previously discussed subtraction procedure correctly gives the dynamic structure factor. In the BLS experiment, the scattered light was analyzed by a Sandercock-type (3 + 3)-pass tandem Fabry-Pérot interferometer, with a finesse of ≈ 100 and a contrast $> 5 \times 10^{10}$ [16]. Both $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ spectra were collected in standard backscattering geometry. The integration time was of ≈ 10 s/channel and the effect of the dark counts (< 1 counts/s) on the data analysis was checked to be negligible. In order to obtain high resolution spectra sufficiently extended in frequency for the discussed subtraction procedure to be safe, at each temperature and polarization we collected and then joined two spectra with different free spectral ranges (FSR) (≈ 10 and 30 GHz, corresponding to an effective FSR for the tandem configuration of ≈ 200 and 600 GHz, respectively). A 0.5 nm bandwidth (HWHM) filter was used to suppress the signal from high interference orders transmitted by the frequency analyzer. Such a choice guarantees that the 30 GHz FSR spectra are unaffected by spurious contributions. For what

concerns the 10 GHz FSR spectra, a slight background, arising from the two adjacent orders transmitted by the filter + interferometer system, has been observed. This background is fully depolarized, as the isotropic signal goes to zero above ≈ 30 GHz, and while it can seriously affect the shape of the depolarized spectra [17], it has only minor effects on the polarized ones. In fact, this effect induces a systematic error at 2 GHz of $\approx 10\%$ on our depolarized measurements and of only $\approx 2\%$, a value comparable to the statistical error, on the much more intense polarized ones (see inset of Fig. 1a, where $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ spectra in the $[-60, 60]$ GHz frequency range are presented for a typical case). Moreover, the effect of this spurious contribution is canceled out in the isotropic, difference spectra. Finally, by using different FSRs and pinhole sizes, we have checked that our spectra are unaffected, at frequencies higher than ≈ 1 GHz, by the strong elastic stray light coming from spurious reflections. The elastic scattering from a dilute aqueous suspension of latex particles (120 nm diameter) was used to determine the instrumental resolution function.

Selected $S(q, \omega)$ spectra obtained with the described procedure are presented in Fig. 1 at the indicated temperatures. They are clearly characterized by the typical signatures of a relaxation process active in the GHz range. Such a relaxation is obviously different from the α one. In fact, at the probed temperatures, the latter is completely buried in the instrumental resolution function since its characteristic time, τ_{α} , is larger than $\approx 10^2$ s. In particular, the spectra in Fig. 1a, reported in log-log scale, show, beside the Brillouin line, a Mountain-like tail extending to the lowest investigated frequencies. This tail is the direct spectral manifestation of such a secondary relaxation, whose presence also appears as a T dependence of the Brillouin peak widths. This effect is shown in Fig. 1b, where we report on an enlarged frequency scale the details of the Brillouin peaks: the Brillouin linewidth is always larger than the resolution function and shows a marked temperature dependence.

Once we assessed the presence of this relaxational dynamics, we performed a quantitative analysis of the spectra in terms of the generalized Langevin equation for the density autocorrelation function, whose second memory function can be written as q^2 times the kinematic longitudinal viscosity $\nu_L(\omega)$ [1]. Within this framework, and neglecting the constant-pressure entropy fluctuations contribution, the $S(q, \omega)$ can be expressed as [1]

$$S(q, \omega) = \frac{2v_o^2 q^2}{\omega} \text{Im}\{\omega^2 - c_o^2 q^2 - i\omega q^2 \nu_L(\omega)\}^{-1}, \quad (1)$$

where c_o is the adiabatic sound velocity and v_o is the thermal velocity. Different choices are, at this stage, possible for $\nu_L(\omega)$. In what follows, we will rely on a simple, phenomenological model. We will show that this model is able, with a minimal number of free parameters, to consistently describe both the $S(q, \omega)$

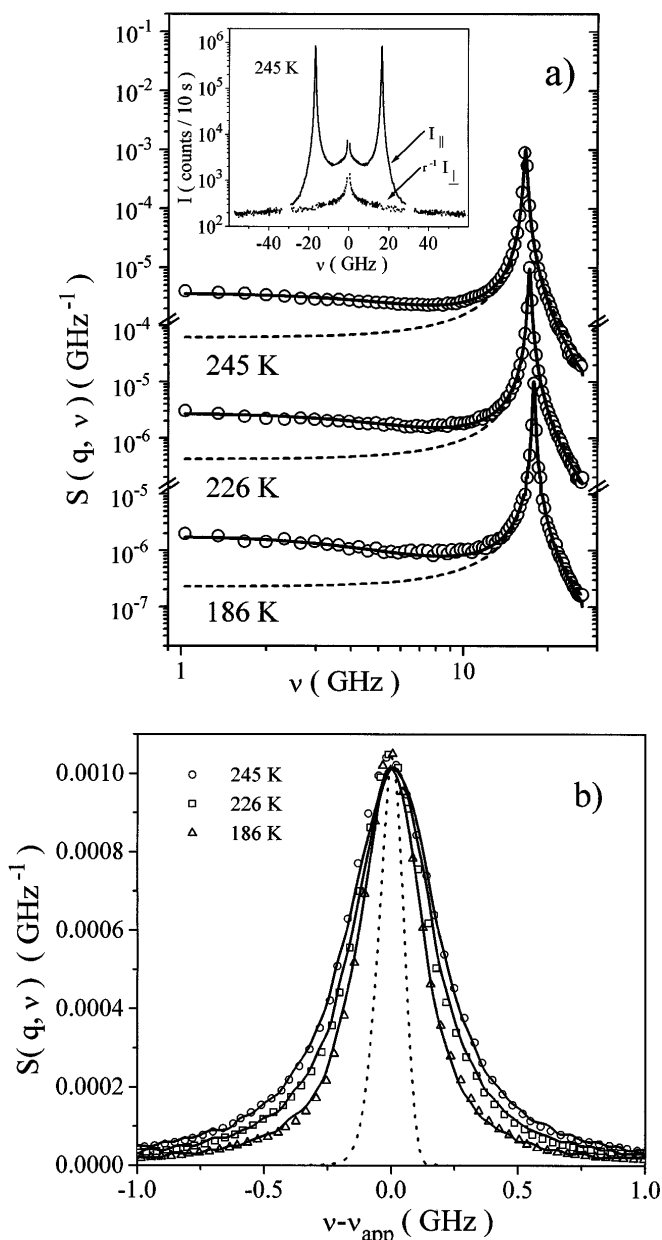


FIG. 1. (a) Examples of BLS $S(q, \nu)$ spectra in the *o*-terphenyl glass taken at the indicated temperatures. (Only $\approx 10\%$ of the data points are shown, for clarity). The solid and dashed lines are the fits obtained using either a two relaxations based memory function [Eq. (2)], or a simple unrelaxed ansatz [Eq. (2) with $c_\infty = c_{\alpha\infty}$], respectively. The inset reports the polarized and depolarized spectra measured at $T = 245$ K. The ghosts of the stray light, which appear at 30 GHz in the larger FSR spectra, have been removed, for clarity. (b) The same spectra and the corresponding fits as in (a) are reported on an enlarged frequency scale centered on the Brillouin peak, ν_{app} . The experimental resolution function is also shown (dotted line).

spectra presented here and those measured by inelastic x-ray scattering in the high q range ($q \approx 1\text{--}6 \text{ nm}^{-1}$) [9]. Specifically, we represent $\nu_L(\omega)$ as the sum of three different contributions. (i) The α process which, in the temperature and frequency range of interest, simply renormalizes the adiabatic sound speed and is described

by the term $\Delta_\alpha^2/i\rho\omega$, where ρ is the mass density and Δ_α^2 the α relaxation strength. (ii) A Markovian contribution D_o which accounts for the very fast, microscopic decay of the memory function. (iii) A further contribution, which takes into account the (secondary) relaxational effects appearing in the spectra and which we simply model in terms of a Debye ansatz (single exponential in time). The function $\nu_L(\omega)$ then reads

$$\nu_L(\omega) = \Delta_\alpha^2/i\rho\omega + D_o + \frac{(c_\infty^2 - c_{\alpha\infty}^2)\tau c_{\alpha\infty}^2}{(c_\infty^2 + i\omega\tau c_{\alpha\infty}^2)}. \quad (2)$$

Here $c_{\alpha\infty}$ (c_∞) represents the sound velocity at frequencies $\tau_\alpha^{-1} \leq \omega \leq \tau^{-1}$. In Eq. (2), τ is the characteristic time of the longitudinal compliance, rather than that of the modulus $\tau' = \tau(c_{\alpha\infty}/c_\infty)^2$. Within this model, and noting that $\Delta_\alpha^2 = \rho(c_{\alpha\infty}^2 - c_o^2)$, the fitting function to the dynamic structure factor spectra is found to be dependent on four free parameters, namely, τ , c_∞ , $c_{\alpha\infty}$, and D_o . The corresponding fits are reported as solid lines in Figs. 1a and 1b and show a reasonable agreement with the experimental data. We want to underline the fact that neglecting the secondary relaxation contribution in the memory function leads to a damped harmonic oscillator (DHO) line shape for the $S(q, \omega)$. This latter ansatz, which has been often used to describe the $S(q, \omega)$ spectra in the glassy phase, gives a poor fit to our experimental data (dashed lines in Fig. 1). The temperature dependence of the parameters obtained from the fits to the complete model, Eq. (2), are discussed in the following.

The parameter τ is found to be only slightly temperature dependent, decreasing from $\approx 30 \times 10^{-12}$ s at $T = 190$ K to $\approx 25 \times 10^{-12}$ s at T_g . This value corresponds to a characteristic frequency of $(2\pi\tau)^{-1} \approx 6$ GHz, which is in the middle of the frequency window accessible to Brillouin measurements, and compares qualitatively well with the ones obtained for the fast relaxation process observed in glassy OTP by *incoherent* experiments [2–5].

The c_∞ and $c_{\alpha\infty}$ parameters are reported in the inset of Fig. 2 together with their error bars. A sound velocity dispersion of about 2% is clearly visible outside the error bars. Being $\omega_{\text{app}}\tau \approx 1$, where ω_{app} is the Brillouin peak position, the apparent sound velocity, $c_{\text{app}} = \omega_{\text{app}}/q$ is larger than $c_{\alpha\infty}$. This shows once more that, already at the small q values explored in BLS experiments, the sound velocity does not probe the α process solely, but is also affected by a faster dynamics.

The D_o parameter, representing the contribution to the Brillouin linewidth coming from the instantaneous process, is found to be temperature independent and is reported in Fig. 2. For the sake of comparison, in the same figure we also report the analogous quantities $D_{\text{BLS}} = 2\Gamma_{\text{BLS}}/q^2$ ($D_{\text{IXS}} = 2\Gamma_{\text{IXS}}/q^2$), obtained from the BLS (IXS) FWHM $2\Gamma_{\text{BLS}}$ [$2\Gamma_{\text{IXS}}$] [14] [$2\Gamma_{\text{IXS}}$] [9]. The D_{IXS} data are found to be temperature independent from the glass up to the normal liquid phase, $D_{\text{IXS}} = (5 \pm 1) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. Conversely, in the low- q range, D_{BLS} shows a considerable temperature

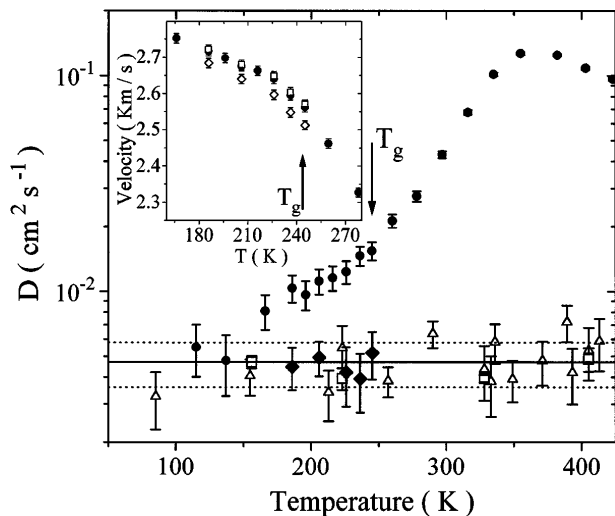


FIG. 2. Apparent longitudinal kinematic viscosities obtained from (i) the instantaneous process contribution, D_o , to the FWHM of the BLS peaks (full diamonds); (ii) $2\Gamma_{\text{BLS}}/q^2$, where the linewidth (FWHM), $2\Gamma_{\text{BLS}}$, of the BLS peaks has been derived by fitting them to the DHO ansatz in the peak region (full circles) [14]; (iii) $2\Gamma_{\text{IXS}}/q^2$, where the FWHM, $2\Gamma_{\text{IXS}}$, of the IXS Brillouin peaks has been obtained using the DHO ansatz on single spectra (open triangles) and averaging the results obtained at different q 's along the dispersion curves (open squares) [9]. The solid (dotted) line represents the average value (the $\pm 1\sigma$ confidence bands) of the D_{IXS} data, $D_{\text{IXS}} = (5 \pm 1) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. In the inset, the sound velocities c_∞ (open squares) and c_{app} (open diamonds) are reported. The apparent velocities, c_{app} (full circles), have been obtained by fitting the Brillouin peaks with the DHO ansatz [14].

dependence. In the liquid phase this dependence is mainly due to the α process which, however, is expected to have no influence on D_{BLS} below T_g . Here, however, D_{BLS} is still temperature dependent, and, at the lowest probed temperatures, tends towards a limiting value which compares very well to both D_o and D_{IXS} . This behavior provides an internal consistency to our initial assumption that two separate relaxations are active in the glassy phase. They are as follows: (i) A temperature dependent process, which comes from a "fast" dissipative dynamics, and (ii) a T -independent process that, as derived from the equivalence of the D_o and D_{IXS} values, gives rise to a q^2 dependence of the Brillouin linewidth in the whole $0.04\text{--}6 \text{ nm}^{-1}$ range.

In conclusion, we have presented dynamic structure factor spectra ($q \approx 0.04 \text{ nm}^{-1}$) of the OTP glass obtained from BLS measurements. These spectra show, independently of any specific model, the characteristic signatures of a secondary relaxation process active in the GHz range: (i) a Mountain-like, central component and (ii) a T dependence in the Brillouin widths. Such a relaxation process is clearly separated from the α one which, at the probed temperatures, is completely buried in the instrumental resolution function. Moreover, the $S(q, \omega)$ spectra can be well modeled in terms of a phenomenological memory function with a Debye (single-exponential) contribution representing this secondary relaxation, and an

instantaneous one which approximates the microscopic dynamics. The former process is found to be slightly temperature dependent, and has a characteristic time in the 10^{-11} s range, consistently with the fast process observed in glassy OTP by other experimental techniques [2–5]. Conversely, the latter process is found to have a temperature independent effect on the Brillouin line shape and is able to explain, beside the low- q BLS data, also the $S(q, \omega)$ spectra measured by IXS in the high q region [9]. This analysis gives clues on the connection between the fast relaxational dynamics and the microscopic transient, a topic which is still not fully addressed by the current theories on the glass transition. It will therefore be of great interest to see whether the results reported here can be understood within a well-defined theoretical framework.

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