Brillouin scattering investigations of fast dynamics in glass forming systems

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Abstract

We review the results of recent Brillouin light and x-ray scattering investigations of the dynamic structure factor of three fragile glass forming systems: ortoterphenyl, polybutadiene, and diglycidyl ether of bisphenol-A. In these systems, evidence is given of three processes responsible for the acoustic loss at high frequencies: the α relaxation, a secondary relaxation of intramolecular nature and an "instantaneous" process. New data for the intermediate glass former glycerol are also presented and compared with literature ones, suggesting the absence of the intramolecular relaxation in this system.

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I. INTRODUCTION

The dynamical processes that lead to the supercooling of a liquid have been successfully interpreted by the mode coupling theory (MCT) in a number of real and simulated systems [1]. The MCT describes the slowing down of the structural dynamics of a liquid in terms of the development of non-linear coupling between density fluctuations, that, in the idealized version, is responsible of the structural arrest at a critical temperature T_c. The MCT has motivated an extensive experimental and numerical work, which has typically shown a remarkable agreement between the predictions of the theory and experimental results on the dynamics of supercooled systems probed by different techniques in different momentum and frequency ranges. Some recent work is collected in this same volume, and some earlier work can be found in the proceedings of previous meetings [2].

A noticeable exception is given by the dynamics of density fluctuations in the hydrodynamic regime, typically studied by Brillouin light scattering. In fact, to our knowledge, the only positive test of MCT by Brillouin light scattering has been reported in CKN, where the density fluctuation spectra were fitted using a memory function directly obtained from the depolarized light spectra measured in the same system [3]. For other systems the procedure adopted for CKN was not successful [4]. More usual is the situation where Brillouin light scattering results are apparently not consistent with MCT. This is the case of propilene carbonate (PC) [5] and salol [6], where the square root cusp in the nonergodicity parameter, predicted at T_c, has been reported at a temperature respectively $\approx$60K and $\approx$20K higher than the value of T_c derived by other techniques. This is also the case of polybutadiene, one of the first polymeric systems for which a positive test of MCT was performed by neutron scattering in the high exchanged momentum, q, limit [7]. In the low q limit of BLS, this system has shown a flat temperature behavior of the nonergodicity parameter [8,9], not consistent with the square root behavior predicted by the theory. Also Polyacrylates and diglycidyl ether of bisphenol-A (DGEBA) fitted by a single relaxation function have shown no signatures of the cusp [10].

A possible reason for this discrepancy between the results of high q and low q investigations could be found in the existence of a fast process beside the structural (α) relaxation, not taken into account in the earliest BLS studies since it requires the inclusion of a second relaxation in the density fluctuations memory function, considerably increasing the number of free parameters. For the case of PC, Brodin et al. have recently proposed both a phenomenological and a schematic MCT model to account for this fast dynamics [11]. In addition to the MCT fast process, we notice that the coupling of density fluctuations with internal degrees of freedom could be responsible for this fast dynamics, whose effect might be of major relevance in the BLS frequency region. It turns out that a meaningful generalization of the high frequency memory function calls for a careful experimental investigation of the nature of such fast relaxation channels.

In the present paper we review experimental evidences recently obtained from Brillouin light scattering and inelastic x-ray scattering of the existence of an intramolecular contribution in the spectrum of density fluctuations of three fragile glass formers of different molecular weight: i) the low molecular weight ortotherphenyl (OTP); ii) the intermediate DGEBA, and iii) the high molecular weight PB. Concerning the microscopic origin of this fast contribution, our results point to the intramolecular nature of this process. Interestingly enough, we also show acoustic loss data of the intermediate glass former glycerol which, different from previous systems, does not show any signature of this fast relaxation.

II. EXPERIMENTAL

Brillouin light scattering experiments have been performed at the GHOST laboratory of Perugia [12] by means of a Sandercock type $(3 + 3)-$pass tandem Fabry - Perot interferometer. As an example, polarized $I_{\parallel}$ and depolarized $I_{\perp}$ spectra of DGEBA recorded in the back-scattering geometry at T=223K are reported in Fig.1. From these spectra, it is possible to derive the isotropic spectrum $I_{\rho\rho}(\omega)$ as: $I_{\rho\rho}(\omega) = I_{\parallel}(\omega) - r^{-1}I_{\perp}(\omega)$, where r is the depolarization ratio. The contribution of the isotropic spectrum to $I_{\parallel}(\omega)$ usually

goes to zero at frequencies higher than about 40 GHz. In the reasonable assumption that the isotropic induced effects have a negligible weight to $I_{\rho\rho}(\omega)$, this spectrum is actually proportional to the dynamic structure factor. By taking spectra up to frequencies higher than 40 GHz and multiplying $I_{\perp}(\omega)$ by an appropriate factor (full line in the figure), it is thus possible to overlap the high frequency tails of $I_{\perp}(\omega)$ and $I_{\parallel}(\omega)$ and obtain $I_{\rho\rho}(\omega)$ by a direct subtraction procedure. More details on the measurements performed on DGEBA, OTP and PB are reported in Ref.s [13–15]. The results of new measurements on glycerol are also reported in this paper, performed in the temperature range 247-445K.

Inelastic x-ray experiments on OTP [16], PB [17] and Glycerol [18] were carried out at the very high energy resolution IXS beamline ID16 at the European Synchrotron Radiation Facility [19].

III. RESULTS AND DISCUSSION

The shape of the dynamic structure factor can be derived within the framework of the generalized hydrodynamics [20]:

$$I_{\rho\rho}(\omega) = \frac{I_0}{\omega} \frac{M''(\omega)}{[\omega^2 \rho/q^2 - M'(\omega)]^2 + [M''(\omega)]^2} \tag{1}$$

where q is related to the wavenumber of the incident light k_i and to the refractive index of the medium n by the relationship $q = 2nk_i$, ρ is the mass density, and $M(\omega) = M'(\omega) - iM''(\omega)$ is the longitudinal acoustic modulus. The two limiting cases of very low frequency or high temperature (relaxed case) and very high frequency or low temperature (unrelaxed case) are characterized by the limiting values of the longitudinal modulus M_0 and M_∞, respectively. In these limits the acoustic damping is described by $M''(\omega \to 0) \to \omega\eta_0$ and $M''(\omega \to \infty) \to \omega\eta_\infty$ where $\eta_0 = \eta_\infty + \Delta\eta$ is the longitudinal viscosity and η_∞ is the limiting longitudinal viscosity. In the relaxed limit, η_0 can be measured by quasi-static methods, like dynamic-mechanical techniques and ultrasound. In the unrelaxed case, η_∞ is a residual contribution to the damping including all processes occurring at frequencies

higher than those covered by the experimental frequency window (*instantaneous processes*). The presence of very high frequency relaxation processes in solids is known since long time and is phenomenologically described by the Voigt model of viscoelasticity, corresponding to a longitudinal modulus written as $M(\omega \rightarrow \infty) \rightarrow M_\infty + i\omega\eta_\infty$ [21]. This unrelaxed viscosity contribution is also included in the mode coupling theory of supercooled liquids as the white noise fluctuating force background (see p. 239 of Ref. [1]). Between the two considered limiting conditions, the frequency dependence of both real and imaginary part of the modulus must be considered in to take into account the effects of relaxation processes.

Some preliminary information on the nature of the relaxation processes affecting the spectrum of density fluctuations of DGEBA can be directly obtained from a visual inspection of Fig. 1. In particular, it can be noticed a non-negligible quasielastic (Mountain) contribution in the spectrum, indicating the presence of a relaxation process in the experimental frequency window. The α relaxation is the natural candidate for temperatures higher than T_g. We notice, however, that for temperatures close and below the glass transition, as in the case of Fig. 1, the characteristic time of the α relaxation becomes so long ($> 100s$) that it cannot be responsible for the hypersonic absorption. This result suggests the presence, in the GHz frequency region, of a relaxation process which remains active even in the glassy phase. Moreover, it is evident from Fig.1 that the shape of the low frequency side of $I_{||}$ is different from that of $I_\perp$ spectrum (see dotted line). Since the Mountain region of the spectrum mirrors the shape of $ImM^{-1}(\omega)/\omega$, this experimental evidence indicates that the memory function of the spectrum of density fluctuations must be different from that of the fluctuations of the polarizability anisotropy. This result points out that, in the case of DGEBA, we cannot use the strategy adopted for CKN, i.e. we cannot use the memory function extracted from wide frequency range $I_\perp$ spectra to fit the spectrum of density fluctuations.

To gain more information on the high frequency dynamics of density fluctuations in DGEBA and in the other three systems, we analyze the temperature behavior of the width

of the Brillouin peaks. Eq. 1 shows that the isotropic spectrum has a maximum close to the characteristic frequency of the longitudinal acoustic (LA) modes $\omega_{LA} = (M'(\omega)q^2/\rho)^{1/2}$, corresponding to the peak at about 20 GHz in Fig.1. Position and width of the peaks give velocity and attenuation of the longitudinal modes, i.e. real (M') and imaginary (M'') parts of the longitudinal modulus at the frequency ω_{LA}. In fact, for frequencies close to the peak, Eq. 1 can be approximated by a damped harmonic oscillator (DHO) contribution:

$$I_{LA}(\omega) = I_{LA}^0 \frac{\Gamma_{LA}\omega_{LA}^2}{[\omega_{LA}^2 - \omega^2]^2 + [\omega\Gamma_{LA}]^2} \tag{2}$$

where ω_{LA} and Γ_{LA} approximately correspond to the frequency position and to the linewidth (FWHM) of the LA peaks [13]. These parameters are related to the real and imaginary parts of the longitudinal modulus through the relations:

$$M'(\omega_{LA}) = \rho\omega_{LA}^2/q^2 \quad ; \quad M''(\omega_{LA}) = \rho\omega_{LA}\Gamma_{LA}/q^2 . \tag{3}$$

Both light and x-ray spectra have been fitted by Eq.2, convoluted with the intrumental function.

The linewidths obtained for the four investigated samples using this procedure are reported in Fig. 2 as a function of temperature. Their values are divided by q^2, giving the so called *apparent longitudinal kinematic viscosity*. These values correspond to the longitudinal kinematic viscosity η_0/ρ and to η_∞/ρ in the relaxed and unrelaxed limits, respectively. The unrelaxed limit of the longitudinal modulus can be reached either for a given temperature at very high frequency or for a given frequency at very low temperature. This second condition is met by x-rays in the whole examined T ranges and by light-scattering only in the low temperature limit, as can be observed in the OTP, PB and Glycerol data reported in Fig. 2. In this figure, the dotted lines show the plateau level which is reached by Γ/q^2 at low temperature and/ot high frequency. An interesting phenomenon is evidenced in glycerol. The BLS data of Γ/q^2 are almost constant in a range of about 80K below T_g. At lower temperatures, i.e. below 100K, they start to decrease again, suggesting a scaling of Γ with a power of q higher than 2. A possible interpretation of this phenomenon has been given

in terms of a dynamic contribution to the sound attenuation affecting the low frequency (<100GHz) density fluctuations [22].

When increasing the temperature, the three fagile samples OTP, DGEBA and PB, show a common trend of the BLS values of Γ/q^2. They increase with temperature, and become noticeably higher than the unrelaxed limit, even for $T < T_g$. In this temperature region we cannot expect any significant contribution to the acoustic loss coming from the α relaxation. This "excess" of damping can be explained in terms of the coupling of the LA modes with internal degrees of freedom of the molecules constituting the system. We have independent confirmations for this interpretation coming from the comparison of different measurements performed on the same systems. *i)* In the case of OTP this idea is supported by the finding of the same relaxation process in the glassy, the liquid and the single crystal phases [23]; by the absence of its effect on the transverse dynamics [23]; and by a molecular dynamics study of a flexible molecule model of OTP [24]. *ii)* In DGEBA the intramolecular nature of this relaxation was proven by a direct comparison of dielectric and BLS spectra in the Mountain region [13]. *iii)* In the case of PB a joint analysis of ultracoustic, BLS and IXS spectra and the comparison with MD simulations suggest that this relaxation can be attributed to the torsional dynamics of segments of the polymer backbone [9,15]. It is important to emphasize that the possible influence of fast intramolecular relaxations in the damping of the LA modes has been recognized since the fifties in ultrasonic studies of the dynamics of normal liquids, as reported in the extensive work of Herzfeld and Litovitz [25]. These relaxations are described in terms of coupling among the acoustic modes and one or more intramolecular vibrations. In these studies, the liquids affected by intramolecular relaxations were classified as "Kneser". Revisiting the list of the Kneser liquids, one easily recognizes that it almost coincides with that of the liquids which are called - using a modern terminology - fragile [26]. Unfortunately, the body of knowledge resulting from those ultrasonic studies seems to be almost forgotten in the recent literature.

A different case is that of glycerol, as can be deduced from the Γ/q^2 data (Fig.2). In this case, BLS data show no excess of damping up to the glass transition temperature. For

temperatures higher than T_g, the α relaxation comes into play, giving rise to the intense acoustic loss in both glycerol and the other systems; however, below T_g only the instaneous process remains active and there is no signature of excess damping which could be attributed to a vibrational relaxation. As a matter of fact, glycerol is neither a fragile nor a Kneser liquid: it is an intermediate system (or associated liquid, in the old classification scheme) for which ultracoustic works gives no evidence of the presence of vibrational relaxations [25]. We can imagine that the vibrational relaxations are pushed towards much higher frequencies by the network character of glycerol related to the presence of hydrogen bonds.

In conclusion, three processes have been evidenced to be responsible for most of the acoustic loss around and above the glass transition temperature in the considered three fragile systems: the α relaxation, a secondary relaxation of intramolecular nature and an "instantaneous" process. It is useful to make clear that, in our opinion, the presence of this secondary relaxation is not an evidence against the MCT; however, this process can play a major role in determining the spectral features in the GHz region and, possibly, it may mask the high frequency side of the spectrum as predicted by the MCT. Conversely, the data obtained on glycerol suggest the absence of such an intramolecular relaxation, encouraging a quantitative test of the MCT predictions on the BLS spectrum of this system.

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FIGURE CAPTIONS

FIG. 1 - Log-log plot of polarized $I_\parallel$, and depolarized $I_\perp$, spectra of DGEBA at $T = 223K$. The two spectra have been normalized in the high frequency tail. The dotted line is the $I_\perp$ spectrum multiplied by a constant. The small peak at ≈ 20 GHz in the $I_\perp$ spectrum is due to leakage of the LA Brillouin peak.

FIG. 2 - Apparent longitudinal kinematic viscosity of OTP, DGEBA, PB and Glycerol as obtained from x ray scattering at $q = 2$nm^{-1} (triangles), $q = 2.5$nm^{-1} (diamonds) and $q = 4$nm^{-1} (squares) and

from light scattering (circles). Unrelaxed values obtained from fitting the BLS spectra are shown as open circles. The dotted lines are guides for the eye.