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High-frequency dynamics of the glass former dibutylphthalate under pressure

A. Mermet,[1] E. Duval,[2] A. Polian,[3] and M. Krisch[1]
[1]*European Synchrotron Radiation Facility, Boîte Postale 220, F-38043 Grenoble Cedex, France*
[2]*LPCML, Université Lyon I, UMR-CNRS 5620, 43 boulevard du 11 Novembre, F-69622 Villeurbanne Cedex, France*
[3]*Physique des Milieux Condensés, CNRS-UMR 7602, Université Paris VI, 4 place Jussieu, F-75252 Paris Cedex 05, France*
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The high-frequency dynamics of a fragile molecular glass former (dibutylphthalate) was studied through inelastic x-ray scattering (IXS), as a function of pressure and temperature. The mesoscopic structural arrest associated with the glass transition process was tracked by following upon cooling the inelastic excitations at fixed Q points in the dispersion curves, at ambient pressure and 2 kbar. The application of pressure to this system induces an offset between the *macroscopic* glass transition temperature T_g and the *mesoscopic* glass transition temperature, as determined from IXS. The concomitant fragility decrease of dibutylphthalate under pressure unveils that the stronger the glass former is, the more its mesoscopic dynamics differ from the macroscopic regime. This trend is interpreted as the signature of a nanoscopic inhomogeneous elastic network. Further aspects of this system are obtained when studying the temperature dependence of its nonergodicity factor $f_Q(T)$. The chemical specificity of the molecule is suggested to be responsible for the nonobservation of a critical temperature T_c in dibutylphthalate up to $\sim$300 K.

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I. INTRODUCTION

The cooperative character of the glass transition makes the collective dynamics of glass forming liquids an essential feature to be investigated. While techniques such as nuclear magnetic resonance or dielectric relaxation provide information on concerted molecular motions inherent to the microsecond/nanosecond time scale, inelastic scattering spectroscopies complete the picture down to the nanometer/picosecond scale. In this respect, the development of inelastic x-ray scattering (IXS) has considerably helped improve our knowledge of the acoustic dynamics in disordered systems at the mesoscopic scale. It is now well established that glass forming liquids sustain well defined terahertz harmonic excitations until the phonon wavelength matches a Q value located at about a few tenths of the first sharp diffraction peak (ca. a few nm^{-1}) [1]. Unlike crystals, the phonon mean free path in disordered systems is restricted by the topological disorder, experimentally showing up as a Q^2 dependence of the excitations broadenings.

Upon freezing through the glass transition the phonon pattern is slightly modified, though with no such change that could straightforwardly account for the salient glasses vibrational anomalies, such as the vibrational density of states excess or the so-called ‘‘boson peak.’’ This contrast between very pronounced glass vibrational properties and nearly ‘‘featureless’’ phonon dispersion curves calls for a better assessment of the vibrations detected by IXS. In particular, it is not yet clear whether the dispersion relations observed between phonon energy Ω and momentum transfer Q over the $(1-10)$-nm^{-1} range reflect a homogeneous or an inhomogeneous *elastic* disorder. Indeed, it has been argued [2] that the observation of a linear dispersion relation between Ω and Q in glasses can either well reflect propagating or nonpropagating dynamics. This yet unresolved issue deserves deeper examination as the concept of dynamical heterogeneity emerges out of several experiments [3–7], simulation works [8–11], and theories [12–15]. The common point made in these latter works is that nanoscopic privileged correlations (*clusters*) exist either as transient above T_g or as frozen below T_g, conferring the ensemble dynamics a heterogeneous character. In the supercooled state, the lifetime of the assumed clusters is predicted to compete with vibrational periods ($\omega\tau\simeq1$) and should therefore modify the collective dynamics as far as quantities related to vibrational energy propagation are concerned. Inelastic x-ray scattering appears therefore as a very adequate tool to test the relevancy of this type of assertion.

So far, most of the studies dedicated to the investigation of the acoustic dynamics in disordered systems have been performed as a function of temperature. In the aim of better characterizing the elastic network, the pressure parameter appears as an additional pertinent tool. Previous studies made on polymer glasses [16] showed that the response of the collective dynamics to the application of a hydrostatic pressure is more biphasic than monotonic, thereby giving a hint of a nonuniform elastic disordered network. It is the aim of this work to further explore this notion by studying a glass former under high pressure, below and above its glass transition temperature.

The sample chosen for this purpose is dibutylphthalate (DBP), classified as a fragile glass former. Raman and vibration density of states measurements on this material demonstrate the existence of a boson peak around 2 meV [7], thereby testifying non-Debye acoustic dynamics, a glass landmark. DBP turns out as a suitable sample for our investigation for two reasons: (i) unlike other molecular glass formers, it does not crystallize spontaneously, thus ensuring a pressure study without crystallization problems; (ii) according to pressure-temperature viscosity measurements [17], DBP shows an enhanced pressure sensitivity in comparison to another glass former, namely, glycerol.

Inelastic x-ray scattering measurements were performed in a temperature interval that spans the liquid, supercooled, and glassy states of DBP for applied pressures ranging between 0 and 4 kbar. Following the temperature evolution of IXS spectra at fixed Q points in the dispersion curve, we observed the splitting of the *mesoscopic* glass transition temperature from its *macroscopic* counterpart between 0 and 2 kbar. This result is put in relation with the lower fragility of this material under pressure, thereby suggesting that the stronger the glass former is, the more the mesoscopic dynamics deviate from the macroscopic dynamics. Fixed-temperature variable-pressure measurements were also achieved. Quite similarly to the effect of cooling, the dependences of the IXS excitations upon pressure increase show a crossover between two linear regimes; such crossover is identified as a glass transition pressure, which there again does not seem to scale with macroscopic evaluations of P_g. Finally, the quantitative analysis of the elastic and inelastic components of the $S(Q,\omega)$ allowed us to point out the unusual temperature behavior of the nonergodicity factor, $f_Q(T)$, in DBP. Arguments based on the chemical specificity of the molecule are given in order to explain this behavior.

II. EXPERIMENT

A. Inelastic x-ray scattering

The experiment was carried out in two different runs at the two inelastic x-ray scattering beamlines of the European Synchrotron Radiation Facility (ID16 and ID28). In the first run (ID16), measurements were made at room temperature and variable pressure, while in the second run (ID28) the additional use of a cryogenic setup allowed to vary both temperature and pressure. In both cases, pressure was applied using a piston-and-cylinder device using DBP itself as pressure transmitting medium. The cell consisted in a 20 mm long cylinder sealed at both ends by 1 mm thick diamond windows. For constant temperature measurements, data were collected upon pressure increase. In the constant pressure case, data were collected upon cooling, while manually keeping the pressure constant at the desired value, compensating for the sample thermal shrinkage (*isobaric* conditions). Pressure was measured with a piezoelectric gauge located outside the cryogenically cooled cell; the pressure gradient between the inside of the cell and the pressure gauge was checked to be negligible.

The inelastic scans were made using the five-analyzer setups of both instruments, at the Si(11,11,11) energy resolution (i.e., $\simeq 1.6$ meV full width at half maximum). In this configuration, each inelastic scan yields five Q points spaced off $\simeq 3\ \mathrm{nm}^{-1}$. Further details on the beamline operation can be found in Refs. [18–20]. The typical statistics of one inelastic scan required adding up several of them, with a final mean integration time of 150 s per point.

B. Brillouin light scattering

Brillouin light scattering (BLS) measurements were made at room temperature as a function of pressure. A 5+4 tandem Fabry-Perot interferometer in combination with the 514.5 nm radiation of an ion argon laser was used in backscattering geometry. DBP was inserted into a diamond anvil cell and pressure was controlled with the classical ruby luminescence technique. Brillouin spectra consisted of a longitudinal doublet, from which the longitudinal sound velocity was deduced using the equation

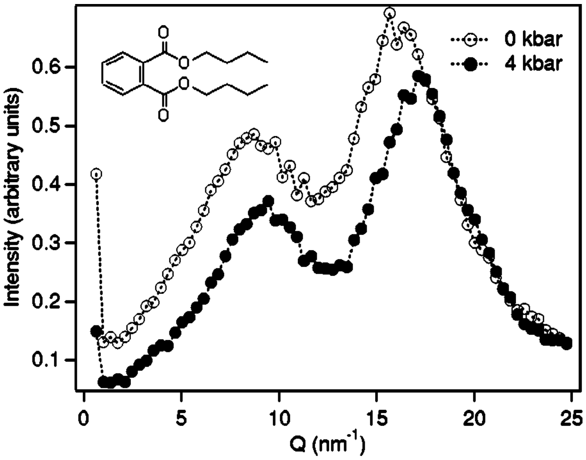

FIG. 1. Static structure factor of dibutylphthalate (DBP), $S(Q)$, at ambient pressure (○) and 4 kbar (●). The molecular structure of DBP is depicted in the inset.

$$v = \frac{\lambda c \Delta\sigma}{2n}, \tag{1}$$

where λ is the wavelength of the incident radiation, c the speed of light, $\Delta\sigma$ the wave number spacing of the Brillouin doublet and n the index of refraction of the sample. BLS data as a function of temperature at ambient pressure were retrieved from already published works [21].

C. Data

1. Chemical presentation

Dibutylphthalate is a well known, large molecule (Fig. 1, inset) often used as plasticizer in the polymer industry. As a glass former, it has been the focus of many investigations including viscosity [22], shear modulus [23], and dielectric measurements [24]. The glass transition temperature of DBP is $T_g \simeq 176$ K, while its melting point is 238 K. The temperature dependence of the viscosity (η) of DBP can be described by a single Vogel-Fulcher-Tammann law $(\ln(\eta/T) = A\exp[B/(T-T_0)])$ [22] throughout the temperature interval $T_g - T_g + 220$ K, with $T_0 \simeq 150$ K. Unlike the vast majority of glass-forming liquids, the observation of a "critical temperature" T_c is not straightforward in the high-temperature regimes of both the dielectric relaxation spectra and viscosity curves of DBP. Recent optical Kerr effect measurements report, however, an indirect estimation of $T_c \simeq 226$ K [25].

The structure factor $S(Q)$ of DBP is very similar to that of other aromatic liquids (Fig. 1): it is characterized by a "prepeak" at $8.7\ \mathrm{nm}^{-1}$ and a more prominent peak at

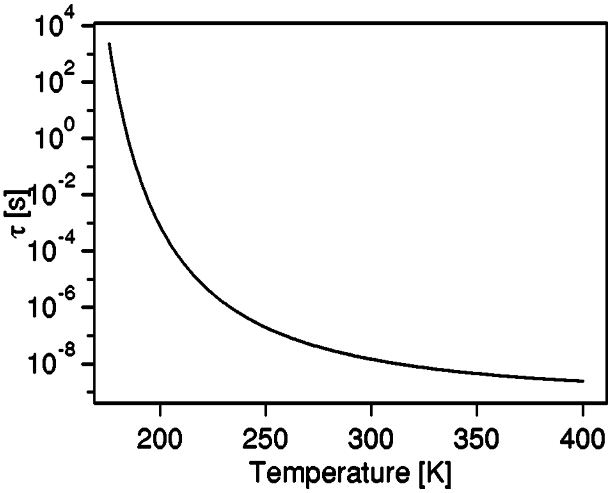

FIG. 2. Temperature dependence of the α-relaxation time in DBP as deduced from $\tau_\alpha = \eta(T)/G_\infty(T)$. $\eta(T)$ was extracted from the Vogel-Fulcher-Tammann law $\ln(\eta/T) = A\exp[B/(T-T_0)]$ with $A = 2.4\times10^{-4}$ P/K, $B = 995$ K, and $T_0 = 147$ K [22]. $G_\infty(T)$ was deduced from the reported law $(G_\infty)^{-1} = (G_0)^{-1} + C(T-T_0)$ with $G_0 = 4.8\times10^9$ Pa, $C = 1.9\times10^{-11}$ Pa/K, and $T_0 = 151.3$ K [23].

16 nm^{-1}, at ambient pressure and ambient temperature. While the position of the main peak can be correlated to the van der Waals diameter of the molecule (first coordination shell), the origin of the prepeak is more debated. In non-H-bonded phenylene-based glass formers, it is often related to orientational correlations between phenylene groups of neighboring molecules [26]. The change of the static structure factor upon applied pressure mainly affects the low-Q region: the prepeak and the main peak, respectively, move up by 6% and 7% upon a 4 kbar pressure increase. More striking is a substantial reduction of the scattered signal over the whole region $2 < Q < 17$ nm^{-1}. This latter behavior reflects the decrease of density fluctuations as the system is densified. It could be considered as the tail manifestation of a more dramatic reduction of an ultra small angle x-ray scattering, which in the case *o*-terphenyl (OTP) was ascribed to scattering by fractal aggregates of nanometric domains [27].

The relaxation time characteristics associated with the α process can be deduced from the temperature dependences of the viscosity and of the limiting shear rigidity modulus (G_∞), with $\tau_\alpha = \eta(T)/G_\infty(T)$. Combining experimental determinations of both quantities [22,23], one gets the evolution of $\tau_\alpha = f(T)$ displayed in Fig. 2. This figure indicates that the macroscopic relaxation time in DBP, at ambient pressure, is of the order of several nanoseconds in the high-temperature regime, becoming doubtlessly larger under applied pressure. Therefore the vibrational dynamics probed with IXS, which lie in the picosecond time domain, can be considered as uncoupled from the relaxational dynamics, the condition $\omega\tau \gg 1$ being verified throughout the investigated temperature-pressure range. The fragility index ($m = [d\ln\langle\tau\rangle/d(Tg/T)]_{T=Tg}$) [28] deduced from this curve is estimated at 85, a value comparable to that of OTP, a typical fragile glass-forming liquid.

2. IXS spectra and dispersion curves

Figure 3(a) displays typical inelastic x-ray spectra of dibutylphthalate at 244 K, for the selected Q values of 1, 2, 3, and 5 nm^{-1}. All spectra consist of a strong elastic peak and a Brillouin doublet. For the lowest Q value the inelastic peaks hardly emerge out of the elastic footline because of the unfavorable Lorentzian-like line shape of the energy resolution function. Still, one can clearly observe the shifting of an inelastic signal towards high energies with increasing Q. Figure 3(b) shows the corresponding $\Omega = f(Q)$ dispersion relation derived from a three-component fit of the corresponding $S(Q,\omega)$, using a Lorentzian line shape for the deconvoluted elastic and inelastic peaks. All data fits performed within this study yielded a negligible elastic broadening.

The obtained dispersion curve reveals a linear Ω-Q relationship, which ceases to hold for $3 < Q < 5$ nm^{-1}. On deviation from the linear regime, the excitation broadening Γ severely increases with Q [Fig. 3(c)]. As observed for all glass formers investigated so far by IXS, such Q dependence appears to be quadratic within the error bars. Such behavior is known to originate from the topological disorder. The departure of the $\Omega(Q)$ variation from a linear relationship is often referred to as the signature of "structural effects," meaning that on approaching the first peak in the static structure factor ($Q_{prepeak} \simeq 9$ nm^{-1}, Fig. 1) the dynamical correlations more and more feature the detailed molecular arrangement of the vibrating units.

The detailed study of the pressure-temperature dependences of the collective dynamics in DBP was achieved by following the evolution of IXS scans at only three Q points in the dispersion curve (because of a limited availability of beam time). Several checks of the overall shape of the dispersion curves, in both the glassy and liquid/supercooled phases, were achieved. Apart from density driven stiffening effects, no significant change upon pressure or temperature was detected, as far as the linear dependence of $\Omega(Q)$ and the quadratic behavior of $\Gamma(Q)$ are concerned [Fig. 3(c), inset]. From the latter observation, it should be noted that besides being temperature independent, the disorder induced sound attenuation process ($\Gamma = \alpha Q^2$ with $\alpha = 0.147 \pm 0.005$ $\mathrm{meV\,nm}^{-2}$ in the present case) is found here to be also *pressure independent*.

3. Temperature dependence of the collective dynamics in DBP at fixed pressure values

Previous IXS investigations on various glass formers demonstrated the existence of a slope discontinuity in the temperature dependence of the excitations' frequencies at the fixed Q value of ≈ 2 nm^{-1} [29–31]. The occurring temperature T_x of this slope change was associated with the liquid-glass transition, at the *mesoscopic* level. Figure 4(a) reports the T dependences of Ω_Q and Γ_Q at the fixed Q values of 2 and 5 nm^{-1}, for DBP at ambient pressure. Also reported in this figure is the frequency shift at 2 nm^{-1} expected from the BLS speed of sound [21].

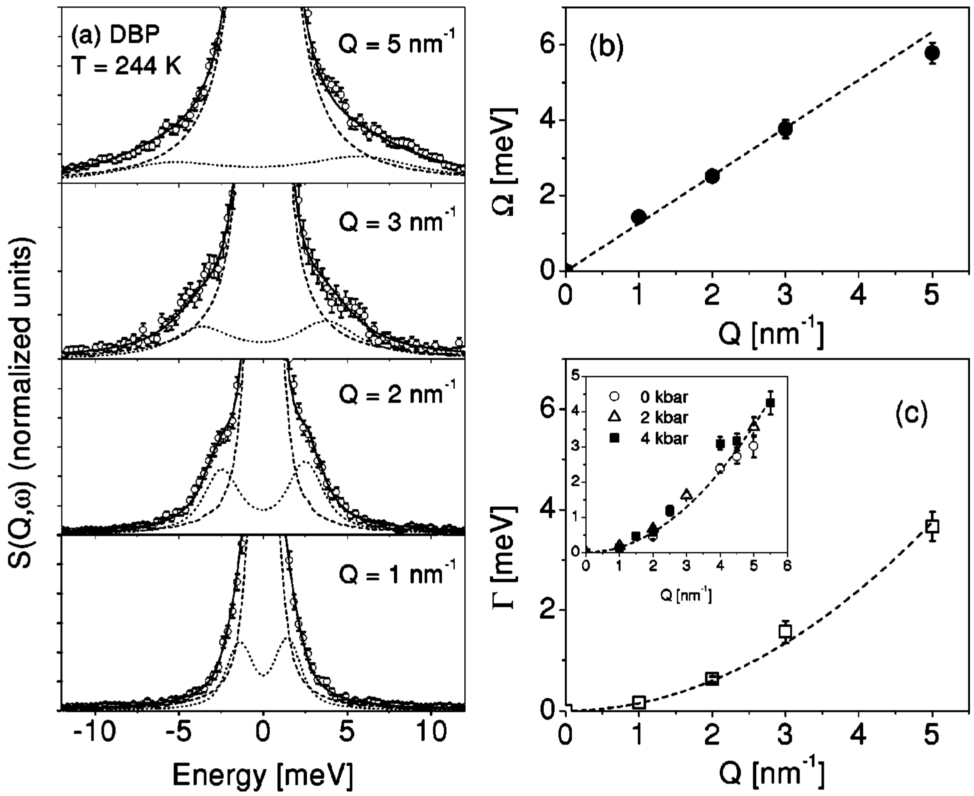

FIG. 3. (a) Inelastic x-ray spectra of DBP at $T = 244$ K, recorded at different Q values. The data (○) are shown together with the total fit (solid line), the elastic contribution (dashed line), and the inelastic contribution (dotted line), as modeled by Lorentzian functions. (b) Dispersion curve $\Omega(Q)$ of DBP at $T = 244$ K (error bars correspond to $\pm 1\sigma$ statistical error). The dashed line represents a linear fit of the data, from which the deduced speed of sound $V_{IXS} = 1930 \pm 50$ m/s. (c) Q dependence of the excitations' broadenings $\Gamma(Q)$. The dashed line is a fit function $\Gamma = \alpha Q^2$ with $\alpha = 0.147 \pm 0.005$ meV nm^{-2}. The inset shows the $\Gamma(Q)$ dependences obtained at ambient pressure ("0 kbar"), 2 kbar, and 4 kbar.

The general increase of the excitations' frequencies upon cooling, with a steeper variation in the liquid phase than in the glassy phase, is the microscopic counterpart of an increase of the bulk modulus (and less importantly of the shear modulus) with decreasing temperature. Although the BLS data follow the same trend as the IXS data, one observes a quantitative disagreement between the two sets of values for $T < 250$ K. The most likely explanation for this is that what is satisfactorily well described by a linear regime in the IXS dispersion relations may in fact be an already bending end portion of a lower Q-region linear relationship. Such a scenario can be viewed as the manifestation of an inhomogeneous elasticity network of the disordered structure [2,6], along some interpretations of the boson peak (the frequency position of the boson peak in DBP matches that of the excitations detected at $Q = 2$ nm^{-1}).

The temperature dependences of $\Omega_{2nm^{-1}}(T)$ and $\Omega_{5nm^{-1}}(T)$ both feature a change of slope at a certain temperature T_x. From the intersection of the linear extrapolations of the high- and low-temperature regimes, one finds $T_x \approx 175$ K. The data collected at $Q = 1$ nm^{-1} require a careful analysis since for such low excitation energies the inelastic signal shows up as a quasielastic deformation of the elastic footline. By fixing the broadening of the excitations observed at $Q = 1$ nm^{-1} to a value evaluated from the experimentally found Q^2 law [Fig. 3(c)], one obtains a similar cusp behavior as that found for the two other Q settings, with a T_x value lying within an acceptable uncertainty range of $T_x = 175$ K. Recent works from Mossa *et al.* [32] suggested that the temperature T_x follows a Q dependence, at least in the case of OTP. No such behavior could be found in our data from $Q = 1,2$, and 5 nm^{-1}. It is nonetheless fair to mention that the experimental check for this predicted behavior may require a finer temperature grid than the one used in this study, in combination with a more favorable sample than DBP for which the inelastic-to-elastic intensity ratio is rather poor. Obviously, for DBP at ambient pressure, the value of T_x coincides with that of T_g.

The pressure dependence of the behaviors depicted in Fig. 4(a) was evaluated by repeating the same measurements at $P = 2$ kbar. Figure 4(b) reports the temperature variations of $\Omega_{2nm^{-1}}(T)$ and $\Omega_{5nm^{-1}}(T)$ at 2 kbar, together with the corresponding variations of the excitations' broadenings. Again, one observes a change of slope in the temperature evolutions of the excitations' frequencies for both Q values. The crossover temperature T_x is now found at $\simeq 225 \pm 5$ K. According to literature data [17], the macroscopic glass transition of DBP at 2 kbar is $T_g^{2kbar} \simeq 191$ K. Therefore, unlike the ambient pressure case, one finds $T_x / T_g \approx 1.18$ at 2 kbar.

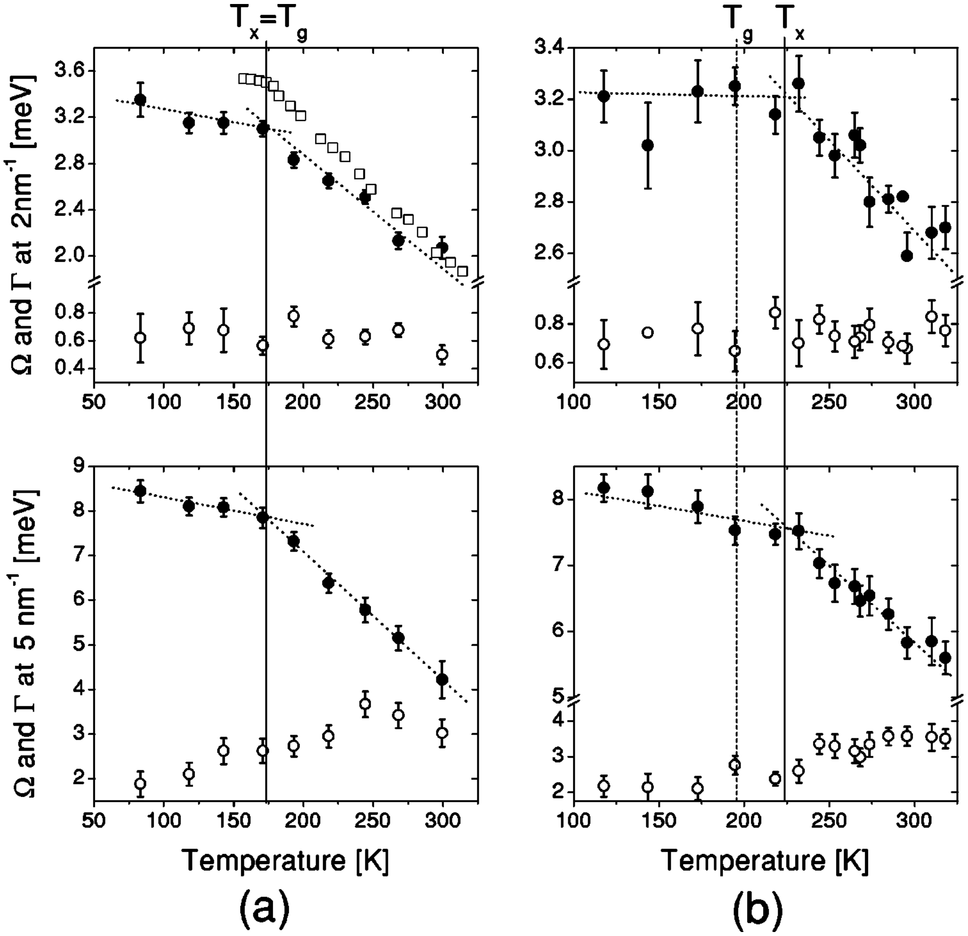

FIG. 4. Temperature dependences of the excitations' frequencies $\Omega_{2nm^{-1}}(T)$ and $\Omega_{5nm^{-1}}(T)$ (●) together with the corresponding broadenings $\Gamma_{2nm^{-1}}(T)$ and $\Gamma_{5nm^{-1}}(T)$ (○) at (a) ambient pressure and (b) 2 kbar. Square symbols show the frequency shift at $Q=2$ nm^{-1} expected from Brillouin light scattering measurements [21]. Vertical lines indicate the respective locations of the *mesoscopic* glass transition temperature T_x and the *macroscopic* glass transition temperature T_g (see text).

4. Pressure dependence of the collective dynamics in DBP at fixed temperature

Figure 5(a) compares the pressure dependences of the sound velocities deduced from BLS measurements and from the IXS data collected at $Q=2$ nm^{-1}, at 300 K (i.e., in the liquid phase). Both quantities follow a smooth behavior as a function of increasing pressure, showing a quantitatively good agreement throughout the 0–4 kbar range, as can be expected from Fig. 4(a), in the region of 300 K. Figure 5(b) reports the pressure dependences of $\Omega_{2nm^{-1}}(P)$ and $\Omega_{5nm^{-1}}(P)$ at 210 K. In contrast to the room temperature data, one observes a break in both variations at a value P_x lying around 1.5 kbar. Similarly to T_x, P_x can be considered as the pressure value that marks the mesoscopic structural arrest associated with the glass transition process. From published data of isothermal calorimetric measurements on DBP [33], the macroscopic glass transition pressure P_g of DBP at 210 K is evaluated at 6.4 kbar, a value that appears considerably larger than P_x.

5. Nonergodicity factor

The determination of the $S(Q,\omega)$ through inelastic x-ray scattering allows to evaluate the so-called nonergodicity factor f_Q, as given by the ratio of the quasielastic peak to the integrated $S(Q,\omega)$. According to the mode coupling theory (MCT) [34], the temperature dependence of $f_Q(T)$ shows a cusp behavior at a critical temperature T_c. Previous investigations on OTP [29] and polybutadiene [30] have indeed provided strong indication that such break could be found in the IXS-$f_Q(T)$, at a temperature consistent with the corresponding T_c's of the samples.

The temperature dependence of the nonergodicity factor was evaluated for DBP at $Q=1$,2, and 5 nm^{-1}, using the quasielastic and inelastic components derived from the fits of the data. Figure 6 displays the results obtained at ambient pressure. Unlike the cases of OTP and polybutadiene, these curves unveil a *monotonic* decrease with no significant slope change throughout a temperature interval that encompasses T_g (175 K) and T_c (226 K) (80–300 K). The same observation holds for the 2 kbar data, up to 320 K (not shown in Fig. 6). It is also worth noting that this ratio does not change appreciably as a function of pressure (0–4 kbar), in the fixed temperature measurements.

III. DISCUSSION

The investigation of the high-frequency collective dynamics in dibutylphthalate under pressure has led to several observations that on the one hand meet those reported for other glass formers, while on the other hand appear to feature specificities of the DBP molecule.

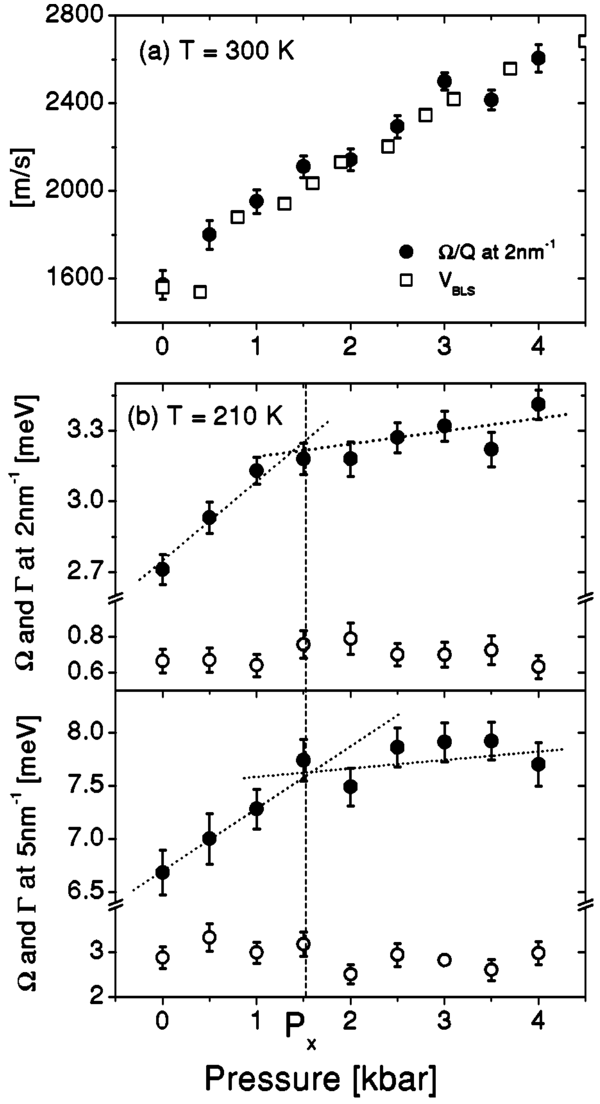

FIG. 5. (a) Pressure dependences of the sound velocities deduced from the ratio Ω/Q at $Q=2\ \mathrm{nm}^{-1}$ (●) and from Brillouin light scattering (square symbols), at $T=300$ K. (b) Pressure dependences of the excitations' frequencies $\Omega_{2nm^{-1}}(P)$ (top graph) and $\Omega_{5nm^{-1}}(P)$ (●) together with the corresponding broadenings $\Gamma_{2nm^{-1}}(P)$ and $\Gamma_{5nm^{-1}}(P)$ (○) at $T=210$ K. The vertical dashed line locates the *mesoscopic* glass transition pressure P_x.

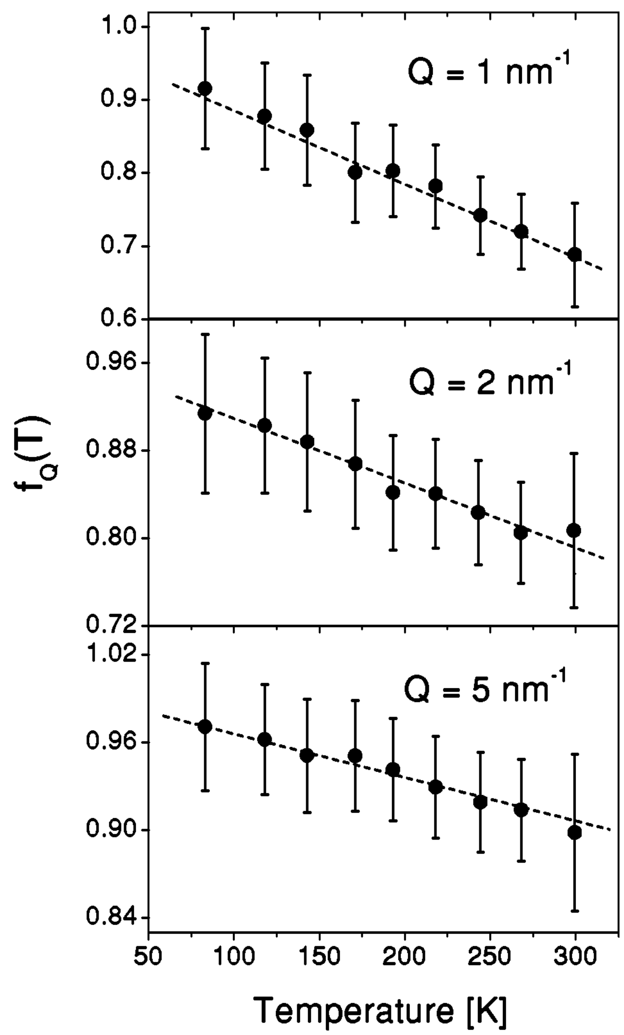

FIG. 6. Temperature dependence of the nonergodicity parameter $f_Q(T)$ at different Q-values, as determined from the ratio of the quasielastic intensity to the integrated $S(Q,\omega)$ intensity (± 14 meV). The dashed lines are guides to the eye.

As far as propagation characteristics are concerned, the acoustic dynamics in DBP are typical of those of disordered systems: one observes an acoustic excitation of frequency Ω that disperses with wave vector Q, with a speed of sound close to that found from Brillouin light scattering. As for most glass formers, the broadening of this excitation Γ appears to follow a unique Q^2 dependence, whether in the liquid phase or in the glassy state, at either ambient pressure or up to 4 kbar. The evolution of these dynamics on cooling the liquid through the glass transition is also qualitatively similar to that found for other glass-forming systems: the stiffening rate of the collective dynamics upon temperature decrease shows a marked slowing down on crossing a narrow temperature range indexed as T_x, which can be considered as the *mesoscopic* glass transition temperature. The comparison of T_x with the *macroscopic* glass transition T_g reveals that both values coincide at ambient pressure, while they significantly split as the system is submitted to a pressure of 2 kbar. From this observation one concludes that the densification of the disordered structure of DBP leads to a separation of the mesoscopic and macroscopic regimes: the more compact the system is, the more the "freezing" point of the local (nanoscopic) structure is off the macroscopic structural arrest. It is interesting to relate this finding to results obtained from viscosity measurements under pressure [17]. According to this latter study, DBP displays an unusual behavior in the low-pressure range: its fragility index (there defined as $m_T=[\partial \ln \eta/\partial(T_g/T)]_{T\to T_g}$) decreases rapidly as applied pressure is increased from ambient up to 4 kbar, then it follows a monotonic increase as a function of pressure, in a similar fashion to that of glycerol. Between 0 and 2 kbar, the value of m_T of DBP decreases by $\approx 25\%$, thereby meaning that DBP turns from a fragile to an intermediate glass former within this pressure range. Combining this observation with our IXS results leads to the conclusion that the concept of fragility is connected to a decoupling of the *macroscopic* dynamics ($\Leftrightarrow T_g$) from the *mesoscopic* dynamics ($\Leftrightarrow T_x$): the stronger the glass is the more the local scale collective properties separate from the macroscopic behavior. Such trend goes well along descriptions that associate the degree of fragility with an inhomogeneity of the glass nanometric scale [2,35]: the stronger the glass former is, the greater the fluctuations within the elasticity inhomogeneous network. It may also be considered as a support of computer simulations evidencing a breakdown of continuum elasticity in amorphous structures [8,9]: local elastic inhomogeneities, with characteristic sizes lying in the nanometer range, possess their own dynamics which are mainly dominated by size effects, and which therefore do not scale with those of larger length scales. We have to point out that although the *elastic* disorder appears to be more inhomogeneous as the system is submitted to pressure, it does not imply an increased inhomogeneity of the *static* disorder. Such is indicated by the marked decrease of elastic scattering under the application of pressure, thereby revealing a reduced level of *density* fluctuations over the mesoscopic range. This behavior strongly shows up in the pressure dependence of the $S(Q)$, as displayed in Fig. 1.

The quantitative analysis of the scattered elastic and inelastic intensities, as obtained from the fits of the experimental $S(Q,\omega)$, brings complementary details on the viscoelastic behavior of this molecular glass former. As mentioned above, the temperature dependence of the IXS nonergodicity factor $f_Q(T)$ of DBP does not show any marked transition up to surprisingly high temperatures (~ 300 K), at variance with other glass formers [29,30]. In fact, the nonobservation of a pronounced crossover between the high- and low-temperature dynamical regimes of DBP can also be noticed from viscosity or dielectric loss spectroscopy data [22,24]. A closer inspection of published BLS data on DBP [21] provides further understanding on how both the longitudinal and transverse dynamics behave as a function of temperature. From these results, it appears that in this material shear wave excitations can be observed up to $\simeq 250$ K, i.e., up to temperatures *above* the melting point ($T_m = 238$ K). This means that DBP maintains a solidlike behavior up to rather high temperatures, in comparison with other fragile glass formers. A possible explanation for this can be found by examining the chemical structure of dibutylphthalate (Fig. 1). The DBP molecule consists of two hydrocarbon flexible butyl chains bonded to a phthalic nucleus. Obviously, the interaction between neighboring DBP molecules may feature two origins, one being ascribed to the interaction between adjacent phtalic groups while the other arises from the interaction between hydrocarbon chain portions. Surely, the former interactions are rather strong in comparison with the latter ones, that most likely dominate the α-relaxation dynamics if one considers the rather low glass transition temperature of DBP (in accord with its use as plasticizer). As suggested in a recent study on the orientational dynamics in DBP [25], it is very plausible that the phthalic groups interactions lead to a ‘‘nanoscopic organization,’’ analogous to pseudonematic domains in liquid crystals.

From these considerations, it follows that the temperature variation of the nonergodicity factor reflects atomic motions that arise both from ‘‘strongly’’ interacting molecular entities (within phthalic ‘‘clusters,’’ that can be considered as the source of solidlike behavior at high temperature) and from ‘‘weakly’’ interacting species (butyl chains). Upon cooling, it is expected that the breakdown of ergodicity be driven by the onsets of solidlike effects (or so-called ‘‘cage effects,’’ according to the MCT) that deprive molecular segments from their translational degree of freedom. The BLS data indicate that such definitely occurs from temperatures as high as 250 K; therefore, the breakdown of ergodicity in DBP may already set in at ambient temperature. Further IXS experiments over a temperature region that would extend from ~ 400 K down to T_g will help checking the validity of this scheme.

IV. CONCLUSION

The use of inelastic x-ray scattering has allowed us to probe the collective dynamics inherent to the *mesoscopic* scale as a function of pressure and temperature, in the molecular glass former dibutylphthalate. Benefitting from the high sensitivity of DBP dynamical properties to pressure, we have observed a significant upshift of the ‘‘IXS glass transition temperature’’ (T_x) on going from ambient pressure to 2 kbar. The comparison of T_x with the macroscopic glass transition T_g reveals that whereas both values are equal at ambient pressure, they differ by a factor 1.18 at 2 kbar. On the grounds that the degree of fragility of DBP decreases with increasing pressure, we straighforwardly demonstrated that a lower fragility index is connected to an offset between macroscopic and mesoscopic dynamics. This observation can be considered as a sign of dynamical inhomogeneity at the nanoscopic scale, along the lines of the inhomogeneous elastic network of glasses.

On a more molecular level, we have shown that dibutylphthalate behaves differently from somewhat comparable fragile glasses like OTP, in the view of the temperature dependence of its nonergodicity parameter $f_Q(T)$. We propose that this peculiarity may be due to the existence of relatively strong interactions between phthalic groups of neighboring molecules, which are screened by the comparatively weaker butyl chains interactions. In this sense, the aliphatic parts of the molecule act as plasticizing agents, thus explaining the relatively low glass transition temperature of DBP in comparison to other aromatic molecules. However, the relatively long-lived phthalic groups interactions lead to a local freezing of the translational degree of freedom quite early in the supercooled state. Such scenario meets conclusions drawn from a study on the orientational dynamics in DBP [25], thereby establishing the net originality of this molecule.

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