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High-frequency collective excitations in a molecular glass-former

J Mattsson¹, A Matic², G Monaco³, D Engberg⁴ and L Börjesson²

¹ Department of Experimental Physics, Chalmers University of Technology,
SE-412 96 Göteborg, Sweden

² Department of Applied Physics, Chalmers University of Technology,
SE-412 96 Göteborg, Sweden

³ European Synchrotron Radiation Facility, BP 220, F-38043, Grenoble Cedex, France

⁴ The Studsvik Neutron Research Laboratory, SE-611 82 Nyköping, Sweden

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Abstract

The high-frequency dynamics of the molecular glass-former propylene carbonate has been investigated by the use of inelastic x-ray scattering (IXS) spectroscopy. The inelastic contribution to the spectra was analysed with a damped harmonic oscillator model. Up to a momentum transfer of $Q_c \simeq 5 \text{ nm}^{-1}$ and an energy of $\Omega_c \simeq 8 \text{ meV}$, acoustic-like excitations with a Q^2 -dependence of the linewidth and a linear dispersion, consistent with the low-frequency sound velocity as measured by means of Brillouin light scattering, were found. At Q_c , a clear change in the excitation behaviour is found, which is characterized by a bending of the dispersion and a deviation from the Q^2 -behaviour of the linewidth. A comparison with reported IXS data for other glass-formers reveals a common tendency to bend upon approaching a pseudo-Brillouin zone boundary defined at $Q_{FSDP}/2$. The comparison also shows that the energy of the acoustic excitations, relative to that of the boson peak (Ω/E_{BP}), extends to larger values for glasses without a strong directional bonding topology.

1. Introduction

The behaviour of acoustic-like excitations in disordered materials at high frequencies and at wavevectors in the mesoscopic range is much debated at present [1–9]. A particular issue that has attracted considerable attention recently is the connection between short-wavelength acoustic-like modes and the origin of the so-called boson peak. The latter, regarded as a generic feature of disordered systems, is the excess vibrational density of states (VDOS) in glasses observed as a broad peak in inelastic neutron or Raman scattering experiments in the energy range 1–10 meV. Its origin is far from understood, even though it is well known that it is related to the characteristic low-temperature properties of glasses [10]. Most models, suggesting an

explanation to the boson peak, consider the behaviour of acoustic modes in the disordered structure at mesoscopic wavelengths. The excess in VDOS has been suggested to arise from phonon localization [2], strong scattering caused either by structural inhomogeneities [7] or by the presence of low-frequency excitations [9, 11, 12], a marked bending of the transverse mode dispersion relation [13] or a disorder-induced version of a van Hove singularity [14, 15]. It is of interest to note that the excess in the VDOS, and the corresponding low-temperature anomalies in the thermal conductivity and specific heat, are observed also in crystalline systems which show orientational disorder [16, 17].

Investigations of short-wavelength acoustic excitations in glasses were long hampered by the lack of suitable experimental techniques for studies of the relevant momentum transfer–energy space. For example, inelastic neutron scattering, which has been so successfully used in investigating acoustic dispersion relations in crystals, can normally not be used for glasses because the kinematic conditions of neutrons require studies of acoustic modes, for most condensed systems, to be performed in higher-order Brillouin zones. However, recently, inelastic x-ray scattering (IXS) became a feasible technique for use in studies of acoustic modes in glasses and liquids with the development of high-resolution spectrometers at the European Synchrotron Radiation Facility in Grenoble [5]. A number of experimental investigations of the acoustic-like short-wavelength excitations in glasses using IXS have been reported [2, 5, 7–9, 18–20].

The general finding is that at low momentum transfers ($\sim 1\text{--}5\text{ nm}^{-1}$) there is a more or less linear dispersion and an approximate Q^2 -dependence of the width of the excitations. The slope of the dispersion relation generally corresponds well to the low-frequency sound velocity, confirming the acoustic-like nature of these modes. In a few studies, concerning covalently bonded network glasses, a strong bending of the dispersion relation is found within the regime investigated [7, 9]. Such behaviour has not been reported for non-network, molecular or ionic glasses. It is important to understand whether this difference is due to the different mesoscopic structure and connectivity or whether it is due to the fact that for molecular glasses, data at higher Q have so far not been reported.

In this paper, we present IXS data on the molecular glass-former propylene carbonate (PC) measured at a temperature $T = 167\text{ K}$ near $T_g \simeq 160\text{ K}$ and over a wide Q -range, $1\text{--}9\text{ nm}^{-1}$. PC is one of the classic glass-forming systems and it has been thoroughly investigated as regards a range of properties of importance for the liquid-to-glass transition [21–25]. In the experiment, we observe a strongly Q -dependent inelastic scattering that, when modelled with a damped harmonic oscillator (DHO), indicates a change of character of the excitation behaviour at intermediate wavevectors. This change is characterized by a bending of the dispersion and a deviation from the Q^2 -behaviour of the linewidth. The observed transition between the two regimes occurs at length scales corresponding to a few inter-molecular distances and at an energy considerably above that of the boson peak.

2. Experimental details

PC was purchased from Sigma-Aldrich (99.7%, anhydrous) and used without further purification. All handling of the sample was performed in an argon atmosphere. The IXS experiment was performed at the high-resolution inelastic beam line (BL21-ID16) at the European Synchrotron Radiation Facility, Grenoble, France [5]. The monochromatic beam is obtained by a combination of a cryogenically cooled Si(111) double-crystal pre-monochromator and a very-high-energy-resolution monochromator operating at the Si(11 11 11) reflection in a backscattering configuration. The experiment is performed in a forward-scattering geometry and the scattered photons are collected by a spherical silicon

crystal analyser, using the Si(11 11 11) reflection [26]. Energy scans are performed by varying the relative temperature of the monochromator and analyser crystals. The total energy resolution, determined from the elastic scattering of a polymethyl methacrylate sample at the maximum of its static structure factor ($Q \simeq 10 \text{ nm}^{-1}$), is $\sim 1.5 \text{ meV}$ (FWHM). The momentum transfer, $Q = 2k_0 \sin(\theta)$, where k_0 is the wavevector of the incident photon and 2θ the scattering angle, is selected by rotating a 7 m long analyser arm in the horizontal scattering plane. The Q -resolution was set to 0.2 (0.4) nm^{-1} for $Q \leq 2 \text{ nm}^{-1}$ ($> 2 \text{ nm}^{-1}$).

IXS spectra were recorded between 1 and 9 nm^{-1} . Each scan took about 130 min, and each Q -point was obtained from the average of three individual scans. The data were normalized to the intensity of the incident beam. The IXS experiment was performed at $T = 167 \text{ K}$. The sample was placed in a cylindrical glass cuvette with an inner diameter of 4 mm, an outer diameter of 10 mm and a length of 20 mm (along the incident beam). The cell was capped with 1 mm thick diamond single-crystal windows. The cell length was chosen to be comparable to the x-ray photoabsorption length, resulting in negligible multiple-scattering effects. Measurements with the empty cell showed that the empty cell contribution was negligible.

Inelastic neutron scattering experiments were performed at the time-of-flight spectrometer IN6 at the Institut Laue-Langevin (Grenoble, France) in order to characterize the excess in the VDOS. The experiment was performed at 50 K in order to reduce the contribution from quasi-elastic scattering at low energies. A measurement at 2 K was used in order to estimate the elastic contribution. The sample was contained in a hollow cylinder with a 0.2 mm thick gap.

3. Analysis

In order to extract the spectroscopic parameters from the recorded spectra, the dynamic structure factor, $S(Q, \omega)$, was modelled with a delta function for the elastic scattering and a DHO for the inelastic scattering,

$$S(Q, \omega) = I_c(Q)\delta(\omega) + I(Q) \frac{\Omega(Q)^2 \Gamma(Q)}{(\omega^2 - \Omega(Q)^2)^2 + \omega^2 \Gamma(Q)^2} \frac{\omega/k_B T}{1 - \exp(\omega/k_B T)}, \quad (1)$$

where $I_c(Q)$ and $I(Q)$ are the intensities of the central peak and of the inelastic contribution respectively. $\Omega(Q)$ and $\Gamma(Q)$ refer to the energy and energy width of the excitation. The DHO model has previously been successfully used to describe IXS data in several different glass-forming systems [5, 7, 8, 27, 28]. The spectra were fitted to the convolution of $S(Q, \omega)$ with the instrument resolution function using a standard χ^2 -minimization routine. Figure 1 shows data for $Q = 3 \text{ nm}^{-1}$, together with the corresponding resolution function, the resulting fit as well as the deduced inelastic contribution. We note that the DHO model is not expected to give a good physical description of the excitations at sufficiently high momentum transfers, where the excitations lose their propagating character. However, for reasons of consistency, the whole Q -range has been fitted with the same function.

4. Results and discussion

Figure 2 shows IXS data for a number of Q -values in the range $Q = 1\text{--}7 \text{ nm}^{-1}$. The inelastic contribution is clearly resolved from the elastic scattering. It is evident that in the low- Q regime the inelastic modes move out in energy with increasing momentum transfer. From the raw data we already find that at $Q \simeq 5 \text{ nm}^{-1}$ the dispersion of the inelastic contribution appears to cease and a qualitative change of the behaviour occurs.

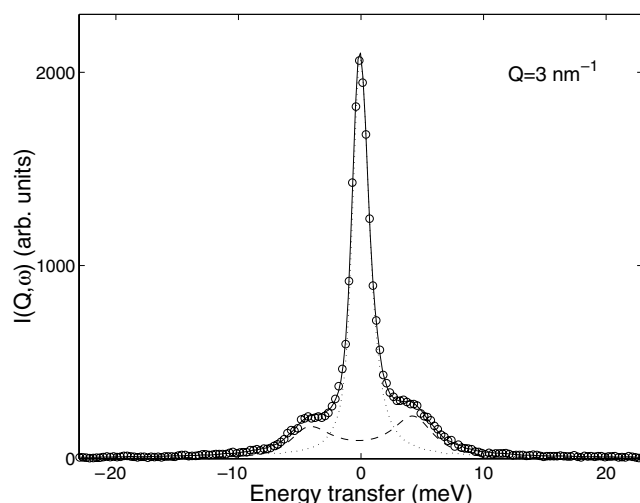


Figure 1. The IXS spectrum at $Q = 3 \text{ nm}^{-1}$ (symbols), together with the resolution function (dotted curve) and the result of fitting with the use of a DHO model convoluted with the resolution function (solid curve). The dashed curve shows the convoluted inelastic contribution.

The energy and width of the inelastic contribution were obtained from the DHO analysis, described above, and the results are shown in figure 3. We find a linear dispersion of the inelastic modes up to $Q \sim 5\text{--}6 \text{ nm}^{-1}$, where the excitation energy becomes momentum transfer independent within the accuracy of the experiment. The transition where the strong bending of the dispersion relation occurs takes place at an energy of $\Omega_c \simeq 8 \text{ meV}$. Under the assumption that the observed inelastic spectral contributions are acoustic in character within the dispersive regime, it is reasonable to calculate the corresponding longitudinal sound velocity, which corresponds to the slope of the linear dispersion. From the data in figure 3, we find a value of $v_l = 2400 \pm 50 \text{ m s}^{-1}$. This value is fully consistent with the low-frequency sound velocity as obtained by means of Brillouin light scattering (BLS) [21, 23]. This fact strongly suggests an acoustic nature of the observed excitations at small momentum transfers, in agreement with results found for several other glass-forming systems [5, 7, 8, 27, 28].

Turning to the widths of the excitations we find, consistent with the energy data, different behaviours at low and high momentum transfers. At low momentum transfers, the width increases with increasing Q following an approximate Q^2 -dependence, whereas at $Q > 5 \text{ nm}^{-1}$ the width becomes more or less momentum transfer independent; see figure 3. At the onset of the strong bending of the dispersion relation, the energy and width of the excitations become approximately equal. The excitations become ill defined, which implies that a description based on propagating excitations is no longer meaningful. For higher momentum transfers a DHO model is hence no longer physically meaningful and we therefore refrain from a detailed analysis of this high- Q regime.

The Q^2 -dependence of Γ has been found for several glass-forming systems [5] and appears to be an intrinsic feature for the behaviour of acoustic modes in the mesoscopic regime. The underlying mechanism of this apparently very general behaviour is not clearly understood at present, but it appears to be of static origin [20]. To further investigate the behaviour of the widths, we have plotted the widths versus Q in a log-log plot as shown in figure 4. The Q -dependence of $\Gamma(Q)$ is indeed consistent with a Q^2 -behaviour. Data obtained from a measurement at lower energies and momentum transfers, by the use of BLS [21], have

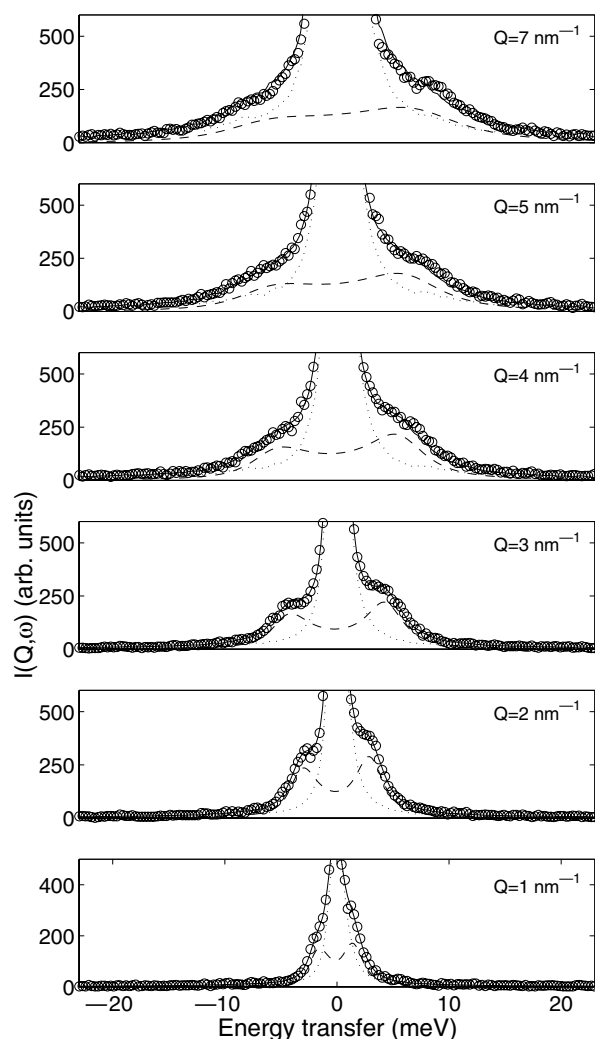


Figure 2. IXS spectra (symbols) for six different Q -values indicated in the figure. The dotted curve shows the resolution function, the solid line the DHO fit and the dashed curve the fitted (convoluted) inelastic contribution.

been included for comparison. We find that the BLS width is larger than what would be expected from a simple extrapolation of the Q^2 -behaviour found for the IXS data. This could be anticipated, since at the temperature of the measurements, $T \approx T_g$, we expect an increased broadening of the BLS widths due to the effects of structural relaxation. This suggests that at the frequencies investigated by means of IXS the acoustic modes are not significantly influenced by the structural relaxation, as expected. The results are in agreement with the proposed static origin of the IXS widths [20]. To conclusively investigate the validity of extrapolations from the IXS to the BLS regime, BLS data are needed at (low) temperatures where most effects of structural relaxation are eliminated. Unfortunately, such data are not available in the literature to our knowledge.

For a number of network glasses a Q -dependence stronger than Q^2 , approaching Q^4 , has been reported for the widths of the observed excitations [18, 30]. This Q -dependence has

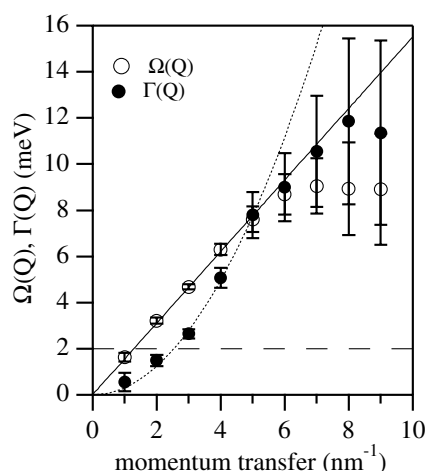


Figure 3. Results from the DHO analysis of the spectra. Unfilled and filled symbols represent the position and the width of the excitation respectively. The solid line is a linear fit to the $Q < 6 \text{ nm}^{-1}$ energy position data, whereas the dotted curve corresponds to a Q^2 -fit of the width in the same region. The dashed line, in turn, indicates the position of the maximum of the excess in the VDOS, i.e. the boson peak.

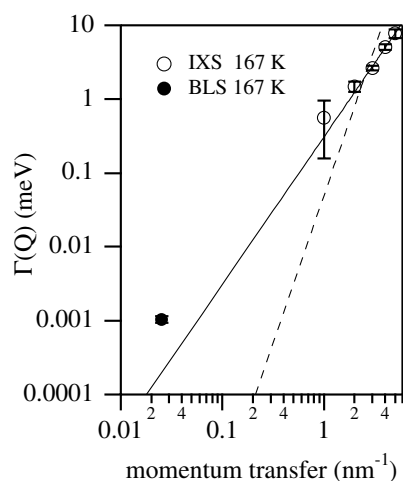


Figure 4. Comparison between the width obtained from IXS in this work (unfilled symbols) and from BLS (filled symbol) from [21]. The solid line shows the Q^2 -dependence of the widths found in the IXS experiment. The dashed line indicates a Q^4 -dependence of the width.

been interpreted as being due to strong scattering of the longitudinal modes. In figure 4, a Q^4 -dependence of the width is indicated by a dashed line. It is evident that such behaviour is not consistent with the present data, and accordingly we find no evidence for an onset of strong scattering within the IXS regime for PC.

As discussed in the introduction, the dynamics of disordered materials shows a number of archetypal features, among which one of the most general is the so-called boson peak, i.e. the excess in VDOS compared with the VDOS expected from the Debye model. Figure 5 shows the excess in VDOS for PC derived from inelastic neutron scattering. In PC, the maximum of the boson peak is found at $E_{BP} \approx 2 \text{ meV}$. Turning again to figure 3, the approximate

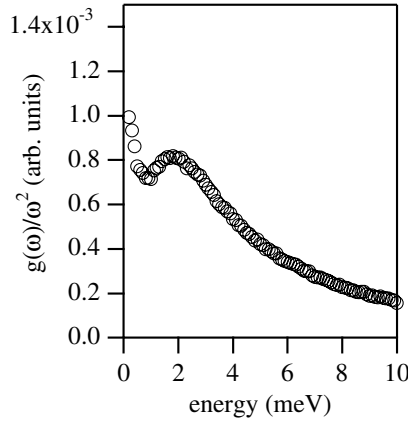


Figure 5. The excess in VDOS, $g(\omega)/\omega^2$, for PC at 50 K. The maximum of the excess in VDOS is found at ≈ 2 meV.

boson peak energy is marked by the dashed line. We find that the linear dispersion shows no observable deviations throughout this dynamic range and that the dispersion relation instead changes character around $\Omega_c \approx 4E_{BP}$. Thus, the end of the longitudinal branch occurs at considerably higher energies than that of the boson peak.

We can also consider the momentum transfer range where the dispersion relation changes character, $Q \approx 5\text{--}7 \text{ nm}^{-1}$. For PC, at 167 K, the main peak in the static structure factor, $S(Q)$, is found at $\sim 14 \text{ nm}^{-1}$ [22]. Thus, it is noticeable that the strong bending of the dispersion relation occurs around $\sim Q_p/2$, where Q_p is the Q -value of the main peak in $S(Q)$. From the perspective of crystalline solid-state physics, this Q -regime might be visualized as the end of the acoustic branch at the Brillouin zone boundary. The first peak in the static structure factor in glasses can in this picture be regarded as the first reciprocal quasi-lattice point and $Q_p/2$ might thus be seen as the boundary of a pseudo-Brillouin zone (p-BZ) [31].

For PC, the acoustic-like excitations lose their character at rather high momentum transfers and energies. A similar behaviour is found in ortho-terphenyl (OTP) [28] and CKN [8], where, as in the case of PC, a relatively weak boson peak is found [32, 33]. The microstructure in these glasses is characterized by non-directional bonds between the molecules (or ions in CKN) and hence it is difficult to envisage any large-scale inhomogeneities or low-frequency modes that can give rise to scattering of acoustic excitations at low momentum transfers. The situation is quite different in glasses with strong covalent bonds, governing the mesoscopic structure. Archetypical examples are silica and borates. Here, the transition in the dispersion relation occurs at lower momentum transfers and at energies much lower compared with that of the boson peak, $\Omega_c/E_{BP} \sim 1$. The latter systems accordingly show strong boson peaks, suggesting a link between a stronger boson peak and a bending of the dispersion behaviour near the boson peak energy.

The scenario discussed above is illustrated in figure 6, where the excitation energy determined from IXS is shown versus momentum transfer for several different systems [7, 8, 27, 28] including both network and non-network glasses. The excitation energy scaled by the boson peak energy, Ω/E_{BP} , is plotted versus Q/Q_{FSDP} , where Q_{FSDP} is the position of the first sharp diffraction peak (FSDP) in $S(Q)$. In this plot a value of $Q/Q_{FSDP} = 1/2$ hence indicates the location of a p-BZ boundary [31]. We find a common tendency of the dispersion to bend upon approaching the p-BZ boundary. However, as discussed above, one can note that the energy of the excitations relative to that of the boson

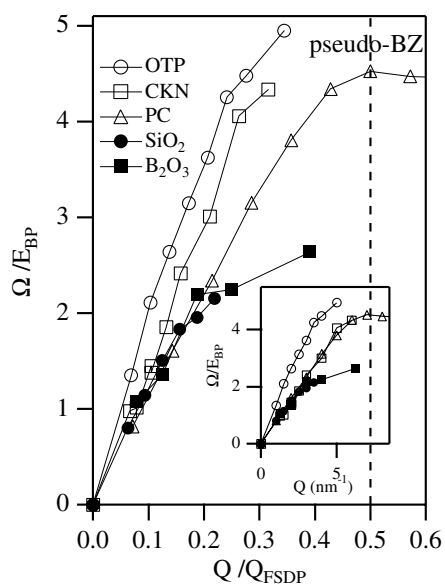


Figure 6. The excitation energy scaled with the boson peak energy versus the momentum transfer scaled with the momentum transfer at the main peak in the static structure factor for five different glasses. The figure is described in detail in the text. The inset shows the same plot without the scaling of the momentum transfer.

peak (Ω/E_{BP}) extends to considerably larger values for non-network glasses compared to that for network glasses.

These qualitative relations suggest a direct connection between the mesoscopic structure, the extent of the dispersion relation and the excess in the VDOS. It is difficult to relate the boson peak in systems such as PC, CKN and OTP to a regime of strong scattering of acoustic modes, such as that reported for covalently bonded oxide glasses [9, 12, 18]. Another scenario has been suggested by computer simulation studies [1, 13], where the mode character is gradually distorted and displays a complex behaviour with increasing momentum transfer in the mesoscopic regime. The resolution and count rate of the present IXS experiments are, however, not sufficient to reveal the details of such a complex behaviour.

5. Conclusions

In this work we have investigated the high-frequency dynamics of the molecular glass-former PC, by the use of IXS spectroscopy. The results of the experiment show:

- (i) a linearly dispersive regime at small momentum transfers, with a slope corresponding to the longitudinal sound velocity determined from Brillouin light scattering, that continues to energies far above the boson peak energy;
- (ii) a width of the excitation that shows a Q^2 -dependence in the dispersive regime; and
- (iii) a transition at intermediate Q ($\sim 5 \text{ nm}^{-1}$) characterized by a strong bending of the dispersion and a deviation from the Q^2 -behaviour of the linewidth.

A comparison with reported IXS data for other glass-formers reveals a common tendency of the dispersion to bend upon approaching a p-BZ boundary defined at $Q_{FSDP}/2$. The comparison also shows that the energy of the acoustic excitations, relative to that of the boson

peak (Ω/E_{BP}), extends to larger values for non-network glasses compared with those found for network glasses.

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