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Brillouin and Umklapp scattering in polybutadiene: Comparison of neutron and x-ray scattering

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We report a comparison of high resolution inelastic x-ray Brillouin scattering to coherent inelastic neutron scattering for amorphous deuterated polybutadiene, done for one temperature in the glass phase and another one in the melt. The x-ray scattering proves to be by far the better technique for such a polymer within its present resolution bounds. The neutron scattering allows one to extend these measurements to a much better resolution, showing an additional quasielastic signal in the melt. The results suggest x-ray measurements at higher momentum transfer, to see whether they are complementary to neutrons. [S1063-651X(99)50109-8]

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The most pronounced difference between the vibrational properties of crystals and glasses appears at low energies E $\approx 2-5$ meV. In ordered crystals, this region is usually dominated by acoustic vibrations which show a Debye-like density of states $g(E) \sim E^2$. However, the vibrational spectra in all disordered systems have a $g(E)$ which significantly exceeds the one expected in the Debye model [1]. The excess $g(E)$ appears as a peak, the so-called boson peak, in the dynamic structure factor $S(Q,E)$ in neutron and Raman scattering spectra of glasses [2]. The nature of these excess vibrations is at present a subject of intense discussion.

Significant information about the nature of the atomic motion at the boson peak can be obtained from an analysis of $S(Q,E)$, accessible by neutron and x-ray scattering. However, each technique has its characteristic limitations. Inelastic neutron scattering (INS) spectroscopy has a kinematic limitation at small Q which is related to the velocity of neutrons: if the latter is lower than the longitudinal sound velocity, then one cannot reach Brillouin conditions. Due to that reason INS is mainly used for an analysis of $S(Q,E)$ at higher Q ranges, the so-called Umklapp scattering around the first and the second diffraction peak, i.e., at 0.5–5 Å^{-1}. The recent developement of high-resolution inelastic x-ray scattering (IXS) allows to measure the Brillouin spectra of glasses without any kinematic limitation. However, up to now these measurements were restricted to the Brillouin Q range, i.e., to $Q<1$ Å^{-1}, and still have only a resolution of about 1.5 meV, which does not allow one to analyze $S(Q,E)$ below this frequency. Nevertheless, these data clearly demonstrate the presence of a strong soundlike contribution to $S(Q,E)$ at energies around and above the boson peak [3].

In the present Rapid Communication we report combined IXS and INS measurements on deuterated 1,4-polybutadiene (PB) in the liquid and in the glassy state. This combination enabled the measurement of the dynamic structure factor for both Brillouin and Umklapp scattering. In our experiment, the former is significantly weaker than the latter. We present a quantitative analysis, which gives an estimate of the soundlike contribution and demonstrates the way one can check different model approaches using both IXS and INS.

PB, a well-known glass forming polymer, was chosen due to its relatively low sound velocity, which is important for the kinematic limitation of INS. Deuterated 1,4-polybutadiene with a molecular weight of 2.5×10^4 a.u. was prepared by anionic polymerization. Inelastic x-ray scattering was measured using the ID-16 high resolution spectrometer at the ESRF in Grenoble. The neutron scattering measurements were done on the cold neutron time of flight spectrometer IN5 at the ILL Grenoble. Two wavelengths, 5 and 2 Å, were used. The neutron scattering spectra were treated in the usual way, with normalization to vanadium, empty container subtraction and multiple-scattering corrections. The latter were done assuming isotropic multiple scattering and a multiple scattering probability of 15% after the first scattering process (the sample was a hollow cylinder with a transmission of 90%). The neutron spectrometer IN5 at 2 Å has roughly the same resolution as the ID-16 and a kinematic limitation to a sound velocity $v_l = 2$ km/s. Also, data of a previous IN6 measurement [4] have been used.

Figure 1 compares typical IXS spectra of PB with 2 Å neutron spectra at two temperatures: 324 K, deep in the liquid state, and 140 K, deep in the glassy state ($T_g = 180$ K). The IXS data could be analyzed in terms of a damped harmonic oscillator (DHO) model with a soundlike dispersion up to $Q = 0.4$ Å^{-1} for the inelastic contribution with the sound velocity $v_l = 1.92$ km/s at 324 K and $v_l = 2.64$ km/s at 140 K. These results are similar to findings in other glass forming systems [3] and are presented in more detail elsewhere [5]. For the quantitative comparison of the IXS and INS data, we assumed that the coherent structure factor $S(Q)$ in the Q range 0.3–1.5 Å^{-1} is the same for x-ray and neutron scattering (in fact, the first sharp diffraction peak at 1.5 Å^{-1} looks quite similar in both techniques). The neutron data, even for a deuterated sample, have an additional Q-independent incoherent signal, partly from an incoherent cross section of the deuterium atoms and partly from incom-

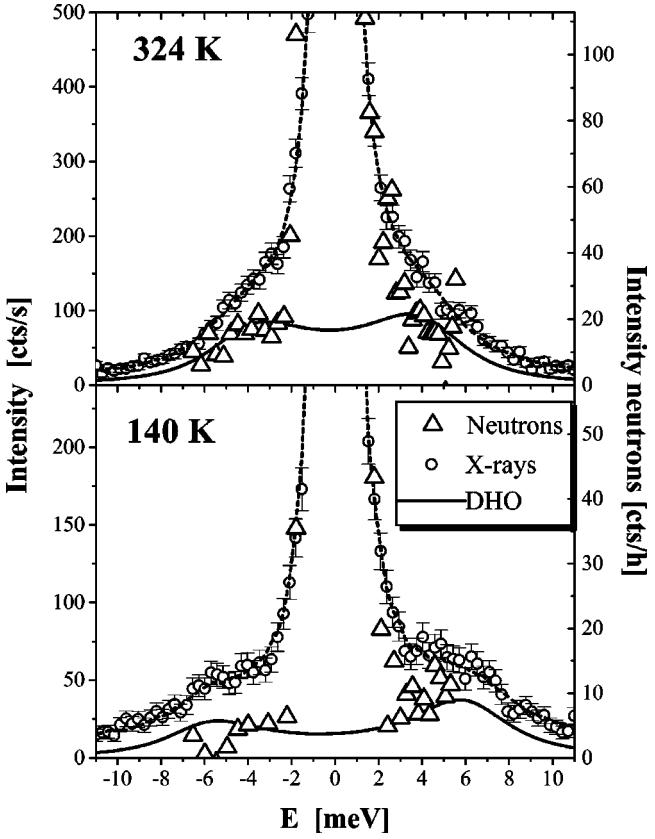

FIG. 1. X-ray and neutron spectra at $Q=0.4$ Å^{-1}.

plete deuteration. For the x-ray measurements, the form factor correction for a carbon atom was taken into account. The comparison showed good agreement between the two $S(Q)$ assuming about 37% of the neutron scattering to be incoherent, corresponding to 96% deuteration of the sample. Using the same factor in the inelastic range, one obtains the neutron data points in Fig. 1. They agree within statistical error with the x-ray fit in terms of the DHO model (the neutrons in that case do not suffer from such broad resolution tails as the x rays). So, using that normalization, the two measurements show a very satisfactory quantitative agreement with each other. As we will see below, this comparison normalization agrees within 10% with an independent neutron normalization using the Carpenter-Pelizarri equations [6].

The comparison shows several disadvantages of the neutron spectroscopy relative to IXS in the Brillouin region: (i) the Brillouin spectra are measured in a limited energy range (smaller than 6 meV) due to the kinematic limitation; (ii) very poor statistics (cts/h instead of cts/s for IXS); (iii) strong multiple scattering contribution at small Q (it is nearly half of the signal; see Fig. 2); (iv) presence of an incoherent contribution even in a deuterated sample.

However, the neutron spectroscopy has also some advantages: (i) the results can be presented in absolute values due to a well established procedure of the normalization to vanadium. In the present case, the normalization constants are 5093 counts per hour for the coherent scattering and 1890 counts per hour for the incoherent scattering. The normalization enables a quantitative comparison of different measurements (Fig. 2) and with different model predictions (see below); (ii) combining the measurements performed at

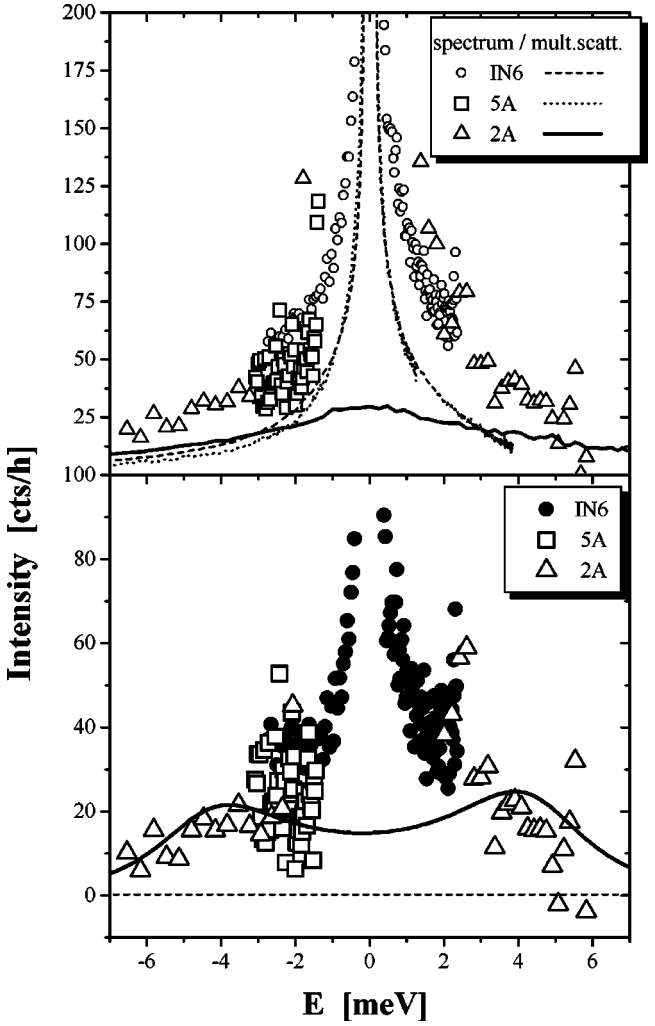

FIG. 2. Combined neutron spectra at $Q=0.4$ Å^{-1} and 324 K. Top: data before multiple scattering correction (lines show the estimated multiple scattering); bottom: data after multiple scattering correction (line shows DHO fit).

different wavelengths one can reconstruct $S(Q,E)$ with very high energy resolution, in our case down to 0.1 meV (Fig. 2).

The upper part of Fig. 2 shows INS spectra at 324 K in the interval $Q=0.3$–0.5 Å^{-1} using neutrons of different wavelengths, together with the calculated multiple scattering. The spectra resulting after subtraction of the multiple scattering are presented in the lower part of Fig. 2. For all three wavelengths together, the spectrum consists of a central quasielastic line with a broad inelastic shoulder in the range of 2–4 meV. A similar analysis was not possible for the spectra measured at $T=140$ K because of their bad statistics.

In order to check whether the quasielastic signal is real and not the artifact of an insufficient multiple scattering correction, we plotted its Q dependence (Fig. 3), together with that of an earlier experiment which did not reach down to such low Q [4]. The intensity decrease at the smallest accessible Q corroborates the existence of an unexpectedly strong inelastic signal below the Brillouin line at 0.4 Å^{-1}.

Figure 4 shows constant energy scans of $S(Q,E)$ for the energies around the boson peak at the two temperatures. At 324 K the neutron spectra reach the Brillouin condition; the arrow marks the expected position. The main result in Fig. 4

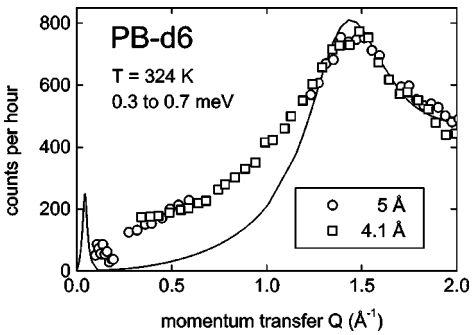

FIG. 3. Q dependence of the quasielastic scattering at low frequency for neutron wavelengths of 5 Å (this work) and 4.1 Å (Ref. [4]). The line shows the expected Brillouin scattering plus a contribution proportional to $Q^2S(Q)$.

is that the Brillouin scattering is much harder to measure than the Umklapp scattering at higher Q. This is not new, but it has never been so clearly demonstrated before.

At 140 K, due to the kinematic limitation, one expects to see only the tail of the Brillouin scattering. The signal in this Q range is once again much weaker than the one from the Umklapp scattering. Thus the Brillouin scattering gives minor contributions to $S(Q,E)$ at the boson peak energy. The main contribution comes from the Umklapp scattering.

In order to do a quantitative analysis of the Umklapp and Brillouin INS we use the model suggested by Carpenter and Pelizari in 1975 [6]. They calculated $S(Q,E)$ for the long-wavelength sound waves in disordered systems using the plane wave approximation (written in terms of $\omega=E/\hbar$)

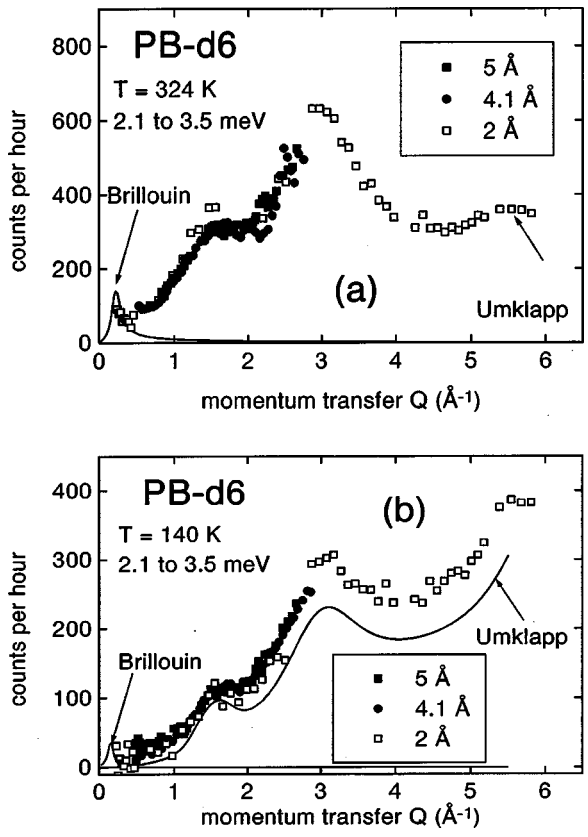

FIG. 4. Brillouin and Umklapp scattering at the boson peak for three different neutron wavelengths, including IN6 data from Ref. [4].

$$S(Q,\omega)=S_{Brill}(Q,\omega)+S_{coh}^{long}(Q,\omega)+S_{coh}^{trans}(Q,\omega), \quad (1)$$

where the Brillouin scattering is given by

$$S_{Brill}(Q,\omega)=\frac{k_BTQ^2}{2\bar{M}\omega^2}\delta(\omega\pm v_lQ), \quad (2)$$

with k_B Boltzmanns constant, $\bar{M}$ the average atomic mass, and v_l the longitudinal sound velocity. For a damped harmonic oscillator, the two δ functions have to be replaced by the DHO equation

$$F(\omega)=\frac{2}{\pi}\frac{\Omega^2\Gamma}{(\omega^2-\Omega^2)^2+\omega^2\Gamma^2}, \quad (3)$$

with the characteristic frequency Ω and a broadening Γ [3].

The Umklapp scattering from longitudinal sound waves is given by

$$S_{coh}^{long}(Q,\omega)=S_{lq}(Q,\omega)\frac{k_BTQ^2}{12\pi^2\rho v_l^3}, \quad (4)$$

where ρ is the mass density and $S_{lq}(Q,\omega)$ is given by the following average over the elastic scattering $S_{el}(Q)$

$$S_{lq}(Q,\omega)=\frac{3}{2}\int_{-1}^{1}d\mu\mu^2S_{el}[(Q^2+q^2-2Qq\mu)^{1/2}], \quad (5)$$

with $q=\omega/v_l$ and μ the integration variable.

The Umklapp term for the transverse sound waves, which provides most of the Umklapp scattering, is

$$S_{coh}^{trans}(Q,\omega)=S_{tq}(Q,\omega)\frac{k_BTQ^2}{6\pi^2\rho v_t^3}, \quad (6)$$

where $S_{tq}(Q,\omega)$ is given by a different average over $S_{el}(Q)$,

$$S_{tq}(Q,\omega)=\tfrac{3}{4}\int_{-1}^{1}d\mu(1-\mu^2)S_{el}[(Q^2+q^2-2Qq\mu)^{1/2}], \quad (7)$$

with $q=\omega/v_t$, v_t transverse sound velocity. This is the classical scattering; to introduce the detailed balance one has to asymmetrize the spectral function. One possibility is to replace k_BT by $\hbar\omega/[\exp(\hbar\omega/k_BT)-1]$.

It must be understood that this model is much too crude. We know already that we do not deal with perfect plane waves at the boson peak. Nevertheless, it is a good starting point for comparison to theory.

The calculation of the Brillouin scattering was done with the sound velocity and the damping known from the IXS data [5]. Otherwise, only the comparison to the vanadium sample enters the calibration. The reasonable agreement at higher frequencies in Fig. 2 shows that one gets practically the full intensity expected for these high frequency longitudinal sound waves at the measurement temperatures. The comparison with the x-ray fit in Fig. 1 shows that the two different calibrations agree within 10%, as stated above.

The calculation of both Brillouin and Umklapp scattering with the known density and sound velocities is shown in Fig.

4. It is limited to the low temperature glass phase, where the transverse sound velocity is known. Additional broadening of the Brillouin lines estimated from IXS was taken into account. The agreement at the first sharp diffraction peak is poor, as pointed out earlier [4], but at the second peak the calculation agrees again astonishingly well with the data.

The result suggests that the Umklapp scattering should be well observed also by inelastic x-ray scattering spectroscopy, for which the expressions should hold as well. X-ray measurements in combination with the Umklapp neutron scattering can bring new information about the motion at the boson peak, because neutrons and x-ray scattering are generally sensitive to different atoms. For example, in the case of SiO_2 neutrons are scattered mostly by oxygen and x rays by the heavier silicon atoms.

Another important result is the spectral shape of $S(Q,E)$ at energies below the Brillouin resonance (Fig. 2). The spectra clearly shows a presence of extra intensity at low energies, much higher than the one expected for the sound waves. This result is consistent with the presence of a quasielastic peak in the inelastic x-ray spectra recently obtained in the same system [5]. This quasielastic contribution could be due to the presence of a structural relaxation and of a faster secondary relaxation process in the viscoelastic liquid, evidenced also in previous neutron spin echo [7] and Brillouin light scattering [8,9] data from deuterated and protonated polybutadiene.

The presence of extra intensity in $S(Q,E)$ at low energies has also been seen in a simulation of model glasses [10]. The harmonic analysis of the low frequency modes showed a superposition of a random-phase atomic motion with the plane wave of the Brillouin peak. This intensity at low energy, predicted in the harmonic approximation at very low temperature, is expected to survive also in the hot glass and in the liquid phase. It has been also seen in a recent light and x-ray Brillouin scattering study of ortho-terphenyle [11]. At present we cannot tell whether the observed quasielastic feature is the signature of the fast relaxation process or of the random-phase vibrational motion or of any other mechanism. A temperature study could give hints to the origin.

In conclusion, the combined analysis of the IXS and inelastic neutron scattering data demonstrates that the main contribution to $S(Q,E)$ at the boson peak energy comes from the high-Q range (Umklapp scattering) and the Brillouin scattering gives only a weak contribution. The ratio of these two contributions agrees reasonably well with the theoretical expectations for the soundlike contribution [6]. Therefore, one expects that the Umklapp scattering should be also seen in the IXS measurements, and these measurements are planned. It is also shown that a combination of neutron spectra measured with different wavelengths gives the possibility to reconstruct the Brillouin spectra with high resolution. The latter is crucial for different model predictions, because it opens the range of $S(Q,E)$ to energies below the Brillouin resonance.

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