Is the Fast Process at the Glass Transition Mainly due to Long Wavelength Excitations?

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Inelastic coherent neutron spectra from deuterated polybutadiene in the neighborhood of the glass transition allows one to discriminate long wavelength and other excitations. The analysis reveals the unexpected result that a dominating part of the so-called fast process in polybutadiene, commonly attributed to picosecond relaxations, rather originates from a strong softening of the sound waves. [S0031-9007(96)01603-1]

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One of the unsolved riddles of glass formation is the nature of the fast picosecond process observed in many glass formers [1–4] around the glass transition temperature. The fast process shows two typical relaxational features, namely, a quasielastic spectral shape and a strong intensity increase with increasing temperature. On the other hand, its apparent quasielastic width has been found to be essentially temperature-independent, contrary to the expectation for a thermally activated process.

While previous evaluations of neutron data concentrated on the frequency dependent spectra, following the mode-coupling result [5] of a decoupling of the Q and ω dependence (Q momentum transfer and $\hbar\omega$ energy transfer of the scattering process), the present Letter focuses on the Q dependence of the coherent inelastic scattering. For polybutadiene, a well-studied glass former [4], we find strong deviations from the decoupling prediction. While at low frequencies the inelastic spectra exhibit a pronounced sound wave like coherent form factor indicating long wavelength excitations, at higher frequencies more localized vibrations prevail.

The sample was fully amorphous deuterated (1,4)-*cis-trans* polybutadiene with a molecular weight of 100.000 atomic units. All data were taken on the spectrometer IN6 at the HFR at Grenoble with a wavelength of the incoming neutrons of 4.1 Å. At that particular wavelength one has the largest Q-range available to the instrument and an exceptionally high intensity.

Figure 1(a) shows the intensities in the elastic window (resolution width 150 μeV) at the two temperatures 20 and 293 K (the glass transition temperature is 186 K). At low momentum transfer Q, one finds a small amount of small angle scattering, possibly due to some voids and essentially temperature independent. Around 1.5 Å^{-1}, there is a pronounced peak due to interchain correlations (correlations between *different* chains lying side by side and attracted towards each other by van der Waals forces). The continuous line through the 20 K data points is a fit with a six-parameter form, describing the peak at 1.5 Å^{-1} by the three parameters of a Lorentzian.

It turned out to be possible to describe the elastic window data at higher temperatures by the same form, adapting only the three parameters of the Lorentzian and the exponent $2W = \langle u^2 \rangle Q^2$ of a Debye-Waller factor. The

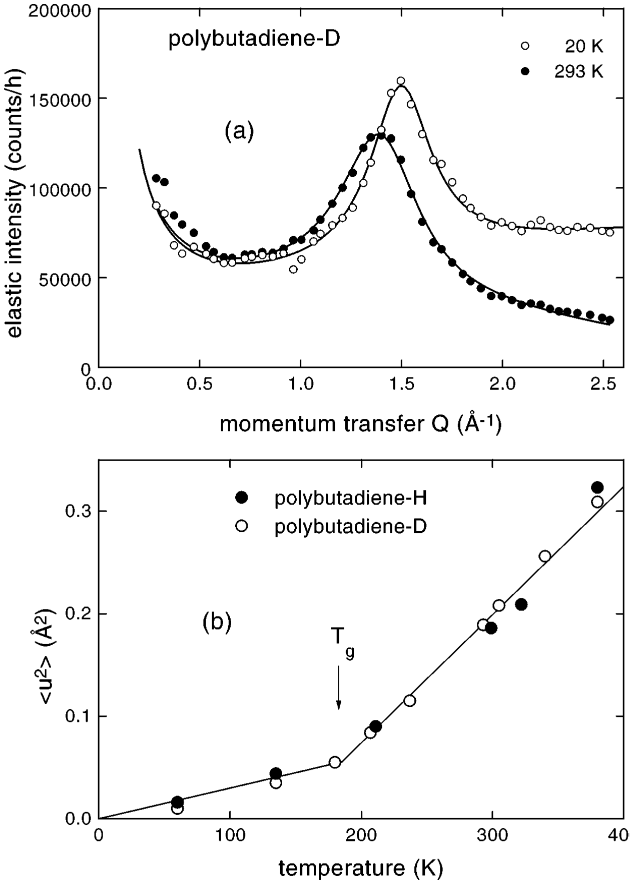

FIG. 1. (a) Q dependence of the elastic window scattering from polybutadiene at 20 and 293 K, together with the fits described in the text; (b) comparison of mean square displacements from the Debye-Waller factors $2W = Q^2\langle u^2 \rangle$ of protonated and deuterated polybutadiene. The line is a guide to the eye, emphasizing the change in slope at the glass temperature.

continuous line through the 293 K data shows the fit at room temperature. The Debye-Waller factors determined in this way agree within experimental error with those determined from the incoherent scattering of protonated samples [Fig. 1(b)]. This shows that one has a reasonable quantitative description of the elastic window intensity $S(Q,0)$, which will be needed for the quantitative treatment of the inelastic scattering.

The failure of the decoupling scheme is demonstrated in Fig. 2, which shows raw data in two detector groups, the first at an angle corresponding to the peak in $S(Q)$ at 1.5 Å^{-1} and the second at an angle corresponding to 2.4 Å^{-1} for elastic scattering. The scattering at the peak in $S(Q)$ looks much more quasielastic than the scattering at the higher Q value.

Figure 3 shows the Q dependence of the inelastic scattering for two different frequencies, one near to the elastic window and the other one at a slightly higher frequency, around 5 meV. One sees again that the decoupling approximation is not valid: The Q dependence near to the elastic line reproduces the peak at 1.5 Å^{-1} and the one at higher frequency does not. This holds for all three sets of data in Fig. 3, from well below the glass temperature up to high above.

Even without quantitative analysis, the data in Fig. 3 demonstrate the existence of two different kinds of low frequency motion. The first is a correlated motion of neighboring polymer chains and dominates at low frequencies. The second is an uncorrelated motion of different polymer chains which prevails at frequencies above 2 to 3 meV.

While the idea of two different kinds of low frequency motion is new in the field of undercooled liquids, it is a well-established concept for amorphous solids [6–9]. The understanding of the low temperature properties of glasses requires sound waves interacting with localized excitations. These localized excitations appear as tunneling states [6], localized vibrations [7], or low-barrier relaxations, depending on the local details which determine their mode potentials [8]. In this picture, well-defined sound waves exist only at frequencies up to about 2 meV. At higher frequencies, they get overdamped by the rising number of localized vibrations [9].

Sound waves have a linear dispersion relation $\omega = vq$ between frequency ω, sound velocity v, and wave vector q. In polybutadiene with a longitudinal sound velocity of 3000 m/s, a longitudinal sound wave at 1 meV has a wave vector of 0.05 Å^{-1}—much smaller

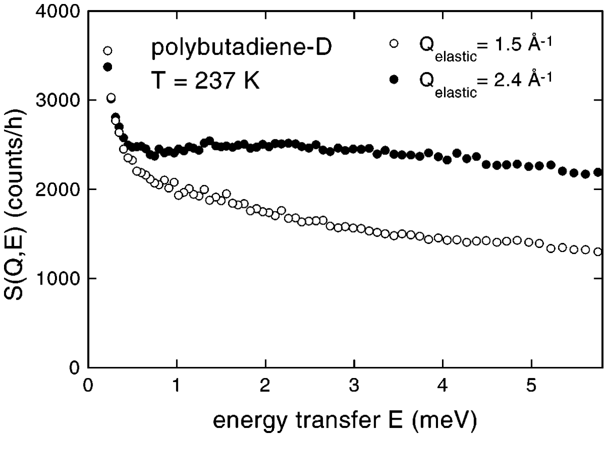

FIG. 2. Inelastic scattering from polybutadiene at 237 K at two different scattering angles.

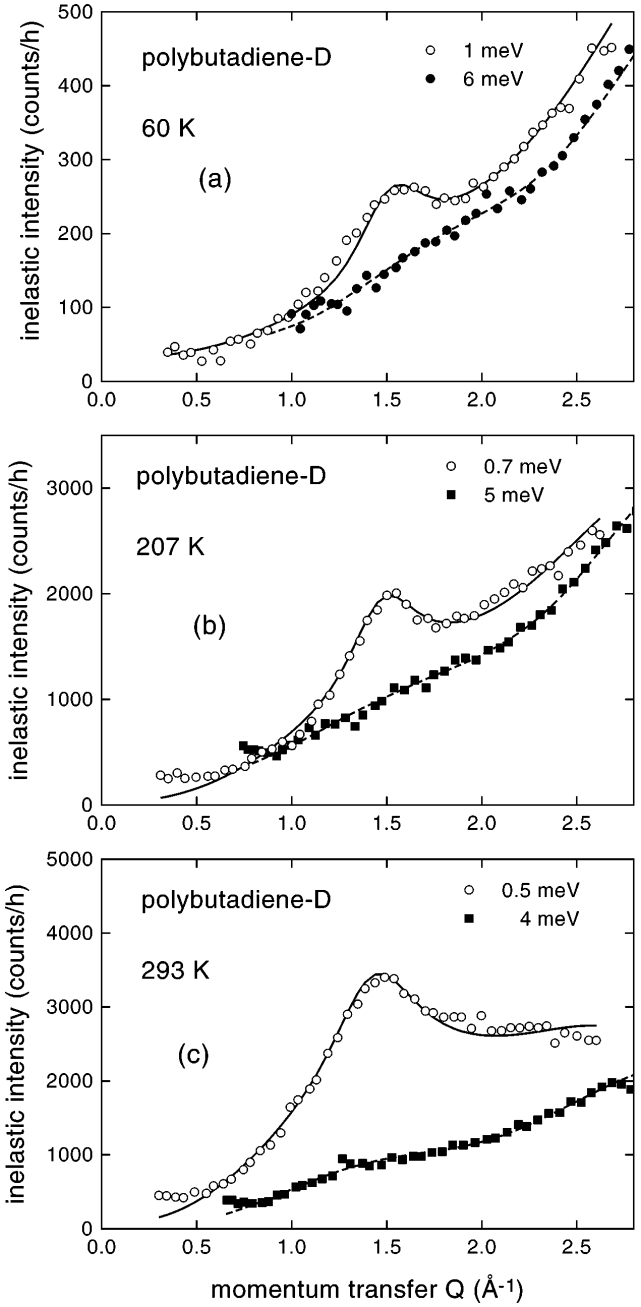

FIG. 3. Q dependence of the inelastic scattering from polybutadiene at different frequencies (a) at 60 K, (b) at 207 K, (c) at 293 K, together with the fits described in the text.

than the Q values of the time of flight experiment. There are two different ways to see such a sound wave in coherent neutron scattering (i) Brillouin scattering at $Q = q$ [10,11] (ii) Umklapp scattering at higher Q. In the present paper, we focus on the second possibility. In crystals, one measures a phonon at an energy transfer $\pm\hbar\omega$ and at a momentum transfer $\mathbf{Q} = \mathbf{G} \pm \mathbf{q}$. Carpenter and Pelizzari [12] showed one has these Umklapp processes in glasses as well, replacing the sharp lattice vectors of the crystal by the diffuse peaks of $S(Q)$. As long as $q \ll Q$, the sound wave scattering has a $Q^2S(Q)$ structure factor, reproducing the peaks in $S(Q)$. Thus the peak at low frequencies in Fig. 3 can be taken to be a fingerprint of sound waves, while its absence at higher frequencies indicates additional modes.

Naturally, the existence of the peak at 1.5 Å^{-1} in the coherent inelastic scattering does not prove inequivocally that one deals with sound waves. Any other motion in which neighboring polymer chains move in phase would give the same dynamic structure factor. Nevertheless, an analysis of the scattering in terms of a sum of sound waves and localized modes seems to be a reasonable starting point. The continuous and broken lines in Fig. 3 represent a fit of the data in terms of that picture. Basically the Q dependence of the sound wave part was assumed to follow a $Q^2S(Q,0)$ curve, while the dynamic structure factor of the additional excitations was chosen to be close to a simple Q^2e^{-2W} dependence. In detail, the fit was more complicated, taking the explicit formulae of Carpenter and Pelizzari [12] for the sound wave part and assuming a frequency-dependent Debye-Waller factor to account for the influence of multiphonon scattering effects [13]. For the purpose of the present Letter, the important feature of that analysis is that it allows one to determine in a reasonably quantitative way a frequency-dependent density of sound waves as well as a frequency-dependent density of additional excitations.

Figure 4 shows the result of this analysis for three temperatures. As in the case of the Debye-Waller factors, the total temperature-dependent effective density of states agrees within experimental error with the one determined from incoherent spectra of protonated polybutadiene [4], showing the internal consistency of the analysis. Here, however, that density of states is decomposed into sound wave and additional parts. In the low temperature glass phase [Fig. 4(a)], the sound wave part first rises for frequencies below the boson peak and then decreases for frequencies above, in qualitative agreement with expectation for sound waves interacting with a broad distribution of local resonant modes. At the glass transition [Fig. 4(b)], the decrease sets in at considerably lower frequencies, consistent with a sizable vibrational softening of both the sound waves and the additional vibrations.

In the undercooled liquid at 237 K [Fig. 4(c)], the sound wave signal looks like a broad quasielastic line and does in fact account for a large part of the intensity previously attributed to the famous fast picosecond process. Note that the sound wave part extrapolates accurately to the Debye density of states calculated from acoustic [14] and Brillouin data [15] for longitudinal and transverse sound waves [the arrows in Fig. 4].

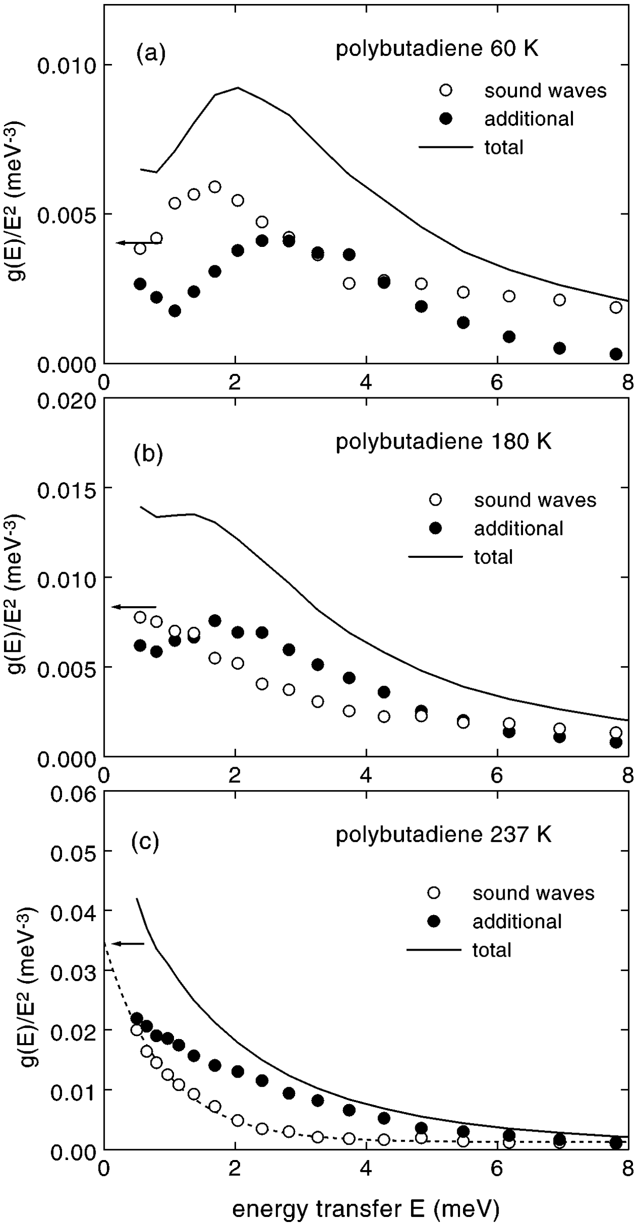

FIG. 4. Fit results in terms of a total effective density of states vs frequency, plotted as density of states over frequency squared and decomposed into a sound wave and an additional excitation part (a) at 60 K, (b) at 180 K, (c) at 237 K. The arrows denote the Debye density of states calculated from acoustic [14] (at 77 K) and Brillouin [15] data.

Thus using the inelastic coherent formfactors as a fingerprint, we have found that a sizable part of the low frequency dynamic structure factor stems from correlated, in-phase molecular motions related to the sound waves. The correlation range ξ of this cooperative motion may be estimated from the width in Q of the sound wave form factor $\xi = 2\pi/\Delta Q \approx 15$ Å.

Superimposed there is a vibrational pattern whose form factor does not deviate significantly from the conventional $Q^2 e^{-2W}$ incoherent phonon form factor within the Q range of the measurement. In principle, one must reckon with a frequency dependence of such a vibrational form factor. Moreover, there might be an interference term between sound wave like and additional excitations. However, since it turned out to be possible to fit all spectra at different temperatures and frequencies with a sum of the sound wave form factor and just one additional contribution, we assumed that these other features are weak and could be disregarded.

To show experimentally the essential role of long range correlated motion in the low frequency inelastic scattering from glasses and undercooled liquids is the novel result of this communication. It raises questions on the models commonly applied to the phenomenon of the dynamic glass transition:

(i) The mode coupling theory of the glass transition [5] predicts the already mentioned decoupling of the frequency dependent spectral function from the Q dependent form factors, at least for the frequency window of the fast process in simple liquids. In polybutadiene, Figs. 2 and 3 demonstrate that such a window could exist only for frequencies below 0.5 meV.

(ii) In a recent approach following the coupling model of Ngai [16], Colmenero *et al.* [4,17] interpreted the short time dynamics of undercooled polymer melts in terms of local conformational transitions unaffected yet by the interaction with other chains. The picture is supported by the activation energies for the time scale of the fast process which agree with local rotational barriers in different polymers. Such a local picture of the fast process, however, will have difficulties in explaining the cooperativity of the low frequency motion expressing itself in terms of a pronounced sound wave form factor.

(iii) Finally, also the vibration-relaxation model [4], which starting from the soft potential model [8] assumes double minimum potentials providing possibilities for soft vibrations and at the same time for over barrier jumps, cannot easily account for the observed cooperativity.

Although the strong decrease of the longitudinal and transverse sound velocities has been well known from Brillouin data [18], its consequence for the dynamic response of a glass forming material in the meV regime has never been realized before. The experimental results displayed here require the inclusion of the sound waves and their interaction with other excitations in any future attempt to understand the anomalous low frequency dynamics of glass forming polymers and probably that of other glass formers as well.

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