

## Change of the vibrational dynamics near the glass transition in polyisobutylene: Inelastic neutron scattering on a nonfragile polymer

B. Frick\*

*Institute Laue-Langevin, BP 156X, F-38049 Grenoble, France*

D. Richter

*Institut für Festkörperforschung, Kernforschungsanlage Jülich G.m.b.H., D-517 Jülich, Germany*

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Incoherent-inelastic-neutron-scattering studies were carried out on polyisobutylene, presumably the least-fragile polymeric glass former known so far. A fast dynamical process on a frequency scale of roughly 500 GHz is measured for temperatures higher than the glass transition essentially without being influenced by the  $\alpha$  relaxation. The present data show that this fast dynamical process can be inelastic and thus has no relaxational, i.e., quasielastic character. This strongly underlines the importance of changes in the vibrational behavior of glasses near the glass-transition temperature. We propose a librational model relating steric hindrance with the observed inelastic scattering.

### INTRODUCTION

The transition from the glassy state to the melt, usually referred to as the glass transition, is a major, incompletely understood phenomenon in solid-state physics. Past research often concentrated on a rather long time scale corresponding to the slowing down of the structural relaxation, i.e., the  $\alpha$  relaxation. More recently it was found by inelastic neutron scattering that a fast dynamical component might be of interest, which appears with increasing temperature near  $T = T_g$  and on a time scale that is fast compared to the diffusional relaxation modes, but slow with respect to phonon or librational modes and thus is located on the time scale slower than a few picoseconds.<sup>1,2</sup> Mode coupling theories<sup>3</sup> had predicted a fast relaxational component in this frequency range and on a microscopic scale ( $\beta$  relaxation) and also have made predictions about its connections to the  $\alpha$  relaxation. Alternative models attribute the observed fast dynamical component rather to a vibrational property of the softening glassy structure.<sup>4</sup> Unusually high spin-lattice relaxation times  $T_1$  have been measured as well on several polymers by <sup>13</sup>C-NMR and were ascribed to librational modes.<sup>5</sup>

Our recent experiments on the backbone polymer polybutadiene<sup>6</sup> had shown rather good agreement with some predictions of the mode coupling theory.<sup>3</sup> Also, experimental results from low molecular glasses,<sup>7</sup> ionic glasses<sup>8</sup> and even proteins<sup>9</sup> support the mode coupling picture. The observation of a fast dynamical process seems to be general for glass forming materials near  $T_g$ . A common assumption in the evaluation of most of these experiments is that the nature of the observed "fast dynamical processes" is quasielastic, i.e., one is dealing with a relaxation phenomenon. In fact, there was no reason to assume an inelastic character of this fast process, as even with the best energy resolution available the additional intensity appeared to be quasielastic. A separation of the elastic scattering and the fast dynamical

process was also hampered by the observed broadening of the elastic line at temperatures slightly higher than  $T_g$  ( $T \sim T_g + 40$  K) which one can attribute to the  $\alpha$  relaxation.

In this paper we study polyisobutylene (PIB):  $(-\text{CH}_2-\text{C}(\text{CH}_3)_2)_n$ . PIB is known for its comparatively slow onset of the  $\alpha$  relaxation with increasing temperature. This can be ascribed to steric hindrance with respect to skeletal bond rotations. The substitution of the small hydrogen atoms in a simple hydrocarbon chain by large methyl groups leads to a strong steric repulsion and can dominate the rotational potentials,<sup>10</sup> which are thought to be essential for the  $\alpha$  relaxation. Nonbonded interactions might lead to considerable steric strain forces, that open the valence angle at the  $\text{CH}_2$  group.<sup>11,12</sup> It is also known that the packing efficiency in PIB is quite high, compared, e.g., to polyethylene. In spite of steric hindrance PIB shows a low glass-transition temperature ( $T_g \approx 200$  K). Recently, based on Brillouin<sup>13</sup> and NMR<sup>5</sup> data, Angell, Monnerie, and Torell<sup>14</sup> have proposed that polyisobutylene might be the least-fragile<sup>15</sup> polymer ( $D \sim 16$ ) documented so far; i.e., its shear viscosity or the relaxation times for the  $\alpha$  relaxation show a less pronounced Vogel-Fulcher behavior than fragile glasses. Comparing the temperature behavior of the  $\alpha$  relaxation times plotted versus  $T_g/T$  ("Angell plots"<sup>14</sup>), one finds that PIB seems to be less fragile than, e.g., glycerol, a hydrogen bonded network glass. On the left-hand side (lhs) of Fig. 1 we have plotted literature data for the  $\alpha$  relaxation times of PIB. The data show a pronounced Vogel-Fulcher behavior. Also shown [right-hand side (rhs) of Fig. 1] are the correlation times for the methyl group rotation, which follow a simple activated temperature behavior. The dashed lines on the lower rhs of Fig. 1 mark the dynamical ranges of the neutron spectrometers under the conditions where we have used them. Our experiments extend over a large temperature range,  $2 \text{ K} < T < 300 \text{ K}$ , but barely reach the temperature and frequency range where  $\alpha$  relaxation might be observed.

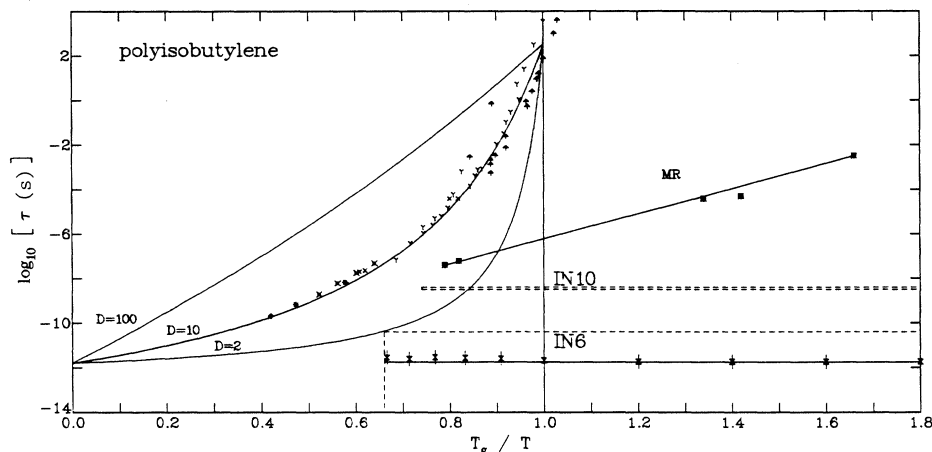


FIG. 1. Plot of the  $\alpha$ -relaxation times of PIB vs normalized inverse temperatures. A simple activated behavior shows up as a straight line ("strong" glasses and large  $D$ ), Vogel-Fulcher behavior as an extremely curved line ("fragile" glasses and small  $D$ ); see Ref. 14. The data points are read off from literature (see Ref. 16 and references therein): ( $\diamond$ ) Brillouin scattering (Ref. 13); ( $\boxtimes, \otimes$ ) NMR (Refs. 5 and 17); ( $\nabla$ ) dielectric experiments (Refs. 17–19); ( $\blacktriangle$ ) mechanical experiments (Refs. 13 and 17–19); and ( $*$ ) incoherent neutron scattering at  $Q=0.5 \text{ \AA}^{-1}$  (Ref. 20). The line through these data corresponds to a fragility of  $D=10$ ,  $T_g=200 \text{ K}$ ,  $T_0=154 \text{ K}$ , and a high-temperature limit of  $\tau$  fixed to the librational mode observed on IN10 in the elastic window mode and on IN6 as well as the investigated temperature range (horizontally). The dashed lines on the rhs show the limits of the accessible time regime (vertically) on IN10 in the elastic window mode and on IN6 as well as the investigated temperature range (horizontally). The data points on the lower rhs mark the position of the observed inelastic peak positions of the torsional oscillation mode (this work). The horizontal straight line through these data is an extrapolation of the observed low-temperature excitation to higher temperatures. The value of  $\tau$  in the high-temperature limit was fixed to this value. Literature data for methyl group reorientation times are added (MR).

The experiments are limited to frequencies above roughly 10 GHz, but can investigate the vibrational behavior in the temperature range  $0.66 > T^* = T_g/T < 100$ , thus sufficiently wide around the glass transition  $T_g$ . This feature makes it attractive to study this polymer by neutron scattering, as the fast relaxation process observed so far for many glass forming systems is expected to be well separated from the  $\alpha$  relaxation. Furthermore, the relaxation times for methyl group rotations show that these should also not contribute to the observed scattering intensity. The main aim of this study is to characterize the dynamical structure factor of the fast relaxation process as a function of temperature, when the polymeric system passes from the frozen glassy state to the undercooled melt.

Inelastic-neutron-scattering studies have been reported on PIB at temperatures below  $T=50 \text{ K}$ . A broad inelastic excitation around 2.6 meV was found and interpreted as being due to phonon-assisted tunneling of molecular units in an asymmetric double-well potential.<sup>21</sup> We will comment on this in the discussion. High-energy resolution neutron-scattering experiments on PIB at much higher temperatures ( $T > T_g + 140 \text{ K}$ ) were carried out earlier to investigate the local motion in the melt.<sup>20</sup> These data are included in Fig. 1 and are discussed below.

#### EXPERIMENTAL AND THEORETICAL DETAILS

The incoherent-scattering law  $S^{\text{inc}}(Q, \omega)$  may in many cases<sup>22</sup> be separated into an elastic, a quasielastic, and an inelastic part. Taking only one species of the scattering atom into account (valid here in first approximation due

to the strong incoherent scattering of hydrogen) one can write the incoherent-scattering law as

$$S^{\text{inc}}(Q, \omega) \approx \text{DWF} \left\{ f_0(Q) \delta(\omega) + \sum_{i=1}^n f_i(Q) L_i(Q, \omega, \Gamma_i) + \frac{Q^2}{8\pi M} [n(\omega) + 1] \frac{g(\omega)}{\omega} \right\}, \quad (1)$$

with  $\delta(\omega)$  being the delta function and  $L_i(Q, \omega, \Gamma_i)$  the normalized spectral functions.  $f_i(Q)$  is the elastic and inelastic structure factors for which a sum rule holds:

$$\sum_{i=0}^n f_i(Q) = 1. \quad (2)$$

DWF is the Debye-Waller factor

$$\text{DWF} = \exp\left[-\frac{1}{3} Q^2 \langle u^2(T) \rangle\right],$$

$n(\omega)$  is the Bose factor, and  $g(\omega)$  is the vibrational density of states. The temperature dependence comes in by (i) the mean-squared displacement (MSD),

$$\langle u^2(T) \rangle \approx \langle u_0^2 \rangle + (\delta \langle u_1^2 \rangle / \delta T) T + \dots,$$

being in harmonic approximation linearly dependent on temperature, (ii) the temperature-dependent linewidths of the spectral functions due to the onset of the motion of scatterers having, e.g., an activated temperature behavior [ $\Gamma \sim 1/\tau \sim \Gamma_0 \exp(-E_a/kT)$ ], and (iii) the Bose factor for the inelastic part. Different molecular motions, like methyl group rotation and rotational or translational diffusion might contribute to the elastic and quasielastic

terms in Eq. (1) thereby exhibiting different  $Q$  dependencies.<sup>23,24</sup>

In a fixed elastic window scan, which will be discussed below, we measure only the elastic part of the model scattering function Eq. (1). Thus, if we convolute with the instrumental resolution function  $R(\omega)$ , for the observed intensity  $I_{el}(Q, T, \omega \sim 0)$  holds:

$$I_{el}(Q, T, \omega \approx 0) \approx \int_{-\infty}^{+\infty} S^{inc}(Q, \omega') R(\omega) d\omega' |_{\omega=0}. \quad (3)$$

In the low-temperature limit, as long as the linewidths are small with respect to the width of the instrumental resolution function  $R(\omega)$ , the total elastic and quasielastic intensity is measured. Thus, due to the sum rule [Eq. (2)] and because the zero-point motion should be the only relevant term:

$$S^{inc}(Q, \omega) \approx \sum_{i=0}^n f_i(Q) \delta_i(\omega) = \text{DWF}(T=0) \quad \text{for } T \rightarrow 0. \quad (4)$$

Below we will report first on the “fixed window” experiments,<sup>23</sup> using the high-resolution neutron backscattering instrument IN10 at the ILL Grenoble. Due to the energy resolution of  $1 \mu\text{eV}$  we are sensitive to the presence of molecular motions in the frequency range above  $\sim 0.2$  GHz. The available  $Q$  regime on IN10 ranged from  $0.2$  to  $2 \text{ \AA}^{-1}$ . As we did not use partially deuterated samples, the experiment is not selective for the dynamics of special atoms within the polymer chain, but the scattering is dominated by the dynamics of all hydrogens, and for PIB by the methyl group hydrogens (see Table I).

We also report on neutron “time-of-flight” (TOF) experiments performed on IN6 at the ILL Grenoble. Using this instrument we measure the incoherent-scattering law Eq. (1) over a wide energy range but, due to the modest energy resolution, we do not separate the elastic contributions well. The TOF data were taken with an incident wavelength of  $\lambda = 5.12 \text{ \AA}$  resulting in an elastic resolution of about  $80 \mu\text{eV}$  and a  $Q$  range between  $Q = 0.2$  and  $2.1 \text{ \AA}^{-1}$ . The dynamic structure factor could be measured in the energy range between  $E = -1.5 \text{ meV}$  (energy loss) and about  $E = 80 \text{ meV}$  (energy gain of the neutron). The data were corrected for detector efficiency, self-screening, sample container and cryostat scattering in the standard way and normalized to a Vanadium standard. Multiple scattering or multiphonon corrections were not applied.

Very thin, flat samples (thickness about  $0.06 \text{ mm}$ ) were used for the TOF experiment on IN6 and a transmission of  $T = 96\%$  was measured; the transmission in the case of the IN10 experiment was about  $85\%$ . The sample was

TABLE I. Coherent and incoherent neutron-scattering cross sections (Ref. 25) for the methine and methyl groups and a monomer unit of polyisobutylene.

Subgroup	$\sigma_{\text{coh}} (10^{-28} \text{ m}^2)$	$\sigma_{\text{inc}} (10^{-28} \text{ m}^2)$
$-\text{CH}_2-$	9.07	159.8
$-\text{C}(\text{CH}_3)_2-$	27.21	479.4
Total monomer	36.28	639.2

prepared by cationic polymerization and a molecular weight of  $M_w \sim 53\,000$  with a polydispersity of about 1.8 was determined by gel permeation chromatography. The literature value for the calorimetric glass-transition temperature of polyisobutylene is  $T_g \sim 200 \text{ K}$ .

## EXPERIMENTAL RESULTS

In Fig. 2 we show the results from a fixed window scan on PIB as measured on the neutron backscattering spectrometer IN10. The natural logarithm of the elastic-scattering intensity is plotted as a function of the sample temperature. The curves for different momentum transfer values  $Q$  are normalized to the scattering intensity at  $T = 4 \text{ K}$ , where we assume that the dynamics of the system are frozen [see Eq. (4)], thus dividing out the DWF due to zero-point motion. The observed decrease of the intensity at low temperatures is ascribed to the Debye-Waller factor [see Eq. (1)]. In harmonic approximation we expect the logarithm of the measured elastic intensity to decrease, linearly both in temperature and in  $Q^2$  due to a linear increase of the mean squared displacement with temperature. The situation becomes more complex if the displacements result from contributions of different atoms or molecular groups (i.e., in our case of methine group protons and of methyl group protons, respectively) as well as from local heterogeneities like from vibrations within different local potentials. The observed elastic intensity deviates clearly from a linear temperature dependence for all  $Q$  values (Fig. 2). A linear behavior of  $\ln(I)$  versus temperature might be present up to  $T \approx 100 \text{ K}$ , but certainly not above  $T \approx 150 \text{ K}$ . Reasons could be anharmonic contributions to the MSD or form-factor contributions from different types of molecular reorientations, which should result in a deviation from a  $Q^2$  dependence of the elastic scattering.

We investigate the  $Q$  dependence of the elastic intensity in Fig. 3, where we present data from Fig. 2 at several temperatures as  $\ln(I)$  vs  $Q^2$ . The solid lines are fit results for

$$\ln[I(T)] = a - \frac{1}{3} [\delta \langle u^2 \rangle^*(T) / \delta T] T Q^2,$$

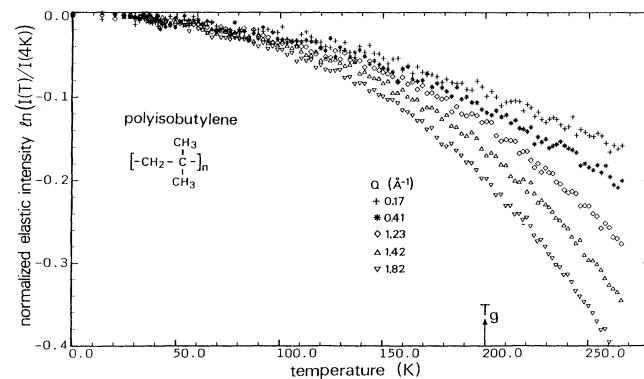


FIG. 2. Fixed window scan for polyisobutylene measured on IN10, ILL Grenoble. The onset of dynamics in the frequency range above  $0.2 \text{ GHz}$  is seen as a decrease of the measured elastic intensity.

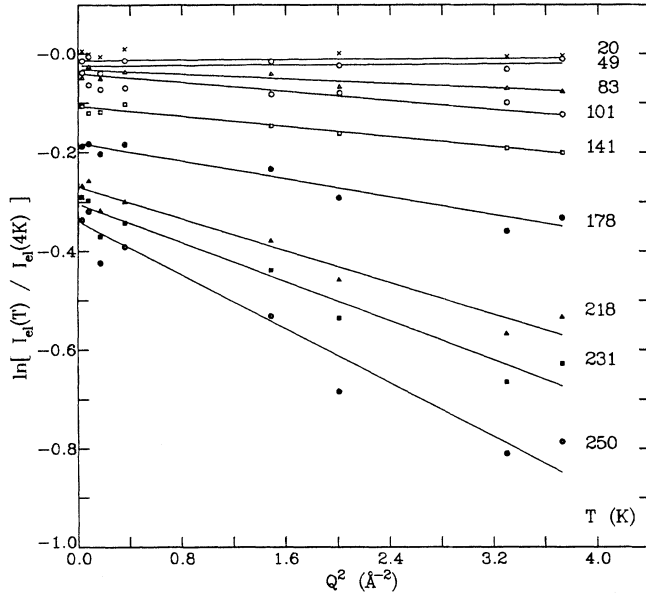


FIG. 3. Elastic intensity  $\ln[I(T)/I(4K)]$  vs  $Q^2$  for PIB at several temperatures. A straight line is expected for harmonic vibrations. The results of the least-squares fits for the straight line are shown as solid lines (see text).

and the constant factor  $a$ , represents a  $Q$  independent loss of elastic intensity, which could account for multiple-scattering processes. The factor  $a$  will be temperature dependent as elastic-scattering processes are the dominating multiple-scattering events at low temperatures, but with increasing temperature they are gradually replaced by inelastic-scattering events. The observed linearity in  $Q^2$  justifies the interpretation that a growing mean-squared displacement of the scattering hydrogen causes the observed intensity loss with increasing temperature.

From the slopes of the straight line fits of Fig. 3 we deduce the temperature dependence of the MSD  $\langle u^2 \rangle^*(T)$  (Fig. 4). The experimental MSD does not include the zero-point motion as this term cancels by normalizing. We find a linear increase of the mean-squared displacement  $\langle u^2 \rangle^*$  with temperature up to about  $T \sim 150$  K, with a slope

$$\partial \langle u^2 \rangle^* / \partial T \sim 8.35 \times 10^{-4} \text{ (K}^{-1} \text{ \AA}^2\text{)}$$

(fitted in the range from  $T=30$  to  $150$  K). Limiting the fits to the temperature range between  $T=4$  and  $50$  K we get  $\partial \langle u^2 \rangle^* / \partial T \sim 9.5 \times 10^{-5} \text{ (K}^{-1} \text{ \AA}^2\text{)}$ . The mean-squared displacement measured at the glass-transition temperature  $T_g \sim 200$  K amounts to  $\langle u^2 \rangle^* \approx 0.2 \text{ \AA}^2$ . This value is much larger than one would expect from a linear extrapolation of the low-temperature displacements. Also the observed average displacement  $\sqrt{\langle u^2 \rangle^*} \sim 0.44 \text{ \AA}$  turns out to be considerably smaller than for polybutadiene ( $\sqrt{\langle u^2 \rangle^*} \sim 0.6 \text{ \AA}$  at  $T_g$ ; Frick *et al.*<sup>2</sup>), and certainly reflects the steric hindrance of the skeleton motion in polyisobutylene. Most important, however, the upturn of the  $\langle u^2 \rangle^*(T)$  curves, somewhat below  $T_g$ , indicates the onset of fast dynamical processes

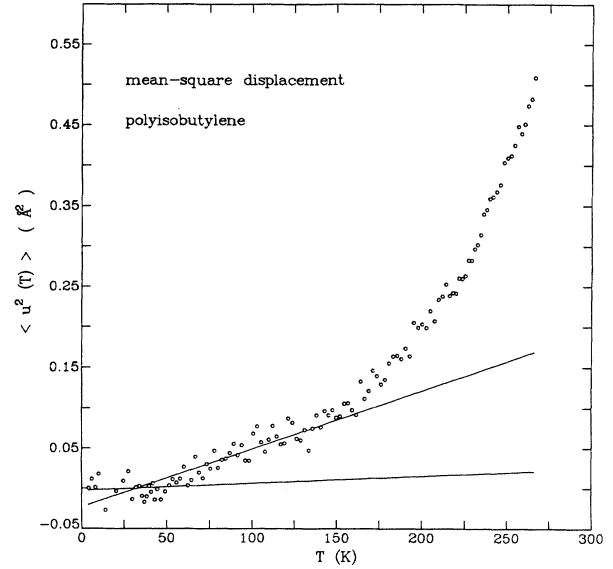


FIG. 4. Mean-squared displacements as a function of temperature, determined from the fitted slopes of straight lines to the measured data (see Fig. 3). The solid straight line is a fit for temperatures below  $T=150$  K.

near  $T_g$  in PIB, very similar to polybutadiene or non-polymeric glass forming materials.<sup>2,7,8</sup>

We will now display the dynamic structure factor  $S(Q, \omega)$  as measured with the TOF instrument IN6 with  $80 \mu\text{eV}$  energy resolution [full width at half maximum (FWHM)]. First we study the integral elastic scattering (integrated over  $\pm 100 \mu\text{eV}$ ) as a function of  $Q$  and temperature (Fig. 5). Again the elastic scattering clearly decreases with increasing  $Q$  and temperature. This decrease is stronger for large  $Q$  values and more pronounced for temperatures above  $T_g$ . Furthermore, a broad peak as a function of  $Q$  shows coherent contributions from the static structure factor  $S(Q)$  and bears witness to the amorphous character of the sample. We find

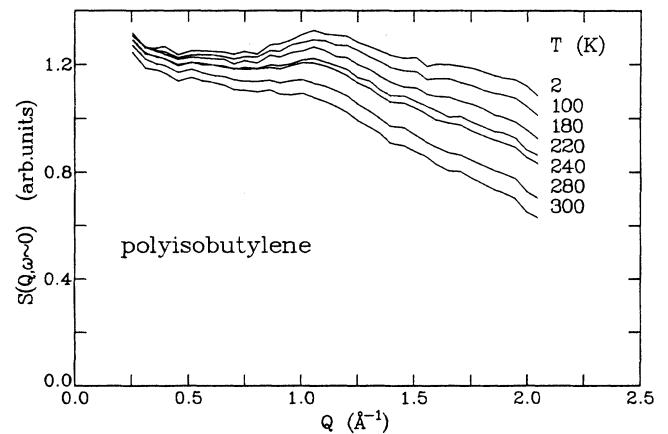


FIG. 5. Elastic scattering (integrated between  $\pm 100 \mu\text{eV}$ ) as a function of  $Q$  as measured at some temperatures on the time-of-flight instrument IN6, ILL.

that at  $T=240$  K the elastic intensity for  $Q=1.82 \text{ \AA}^{-1}$  has decreased to 64% of the intensity at 2 K. This should be compared with a decrease to 47% measured with  $1 \mu\text{eV}$  energy resolution on IN10 (Fig. 2). It is evident that we are integrating over inelastic-scattering intensity located in the low-frequency range.

The averaged dynamic structure factor is displayed in Fig. 6. The scattering functions measured at different scattering angles were corrected for the Bose factor and the DWF. The Bose factor corrections were performed such as to scale all spectra to the reference temperature  $T_g$ . We have chosen to extrapolate the DWF from the low-temperature behavior of the MSD (Fig. 4). After this scaling procedure and after having added up the spectra from different scattering angles, we compare runs for different temperatures. The inelastic-scattering intensity corresponding to the different temperatures should now fall onto a master curve, if its origin were due to harmonic vibrations. Obviously this is the case for *all* energy transfers at temperatures below  $T_g$ , but above  $T_g$  only for energy transfers  $\Delta E \geq 3$  meV. At temperatures below  $T_g$  we observe besides the strong elastic scattering a broad inelastic excitation near  $E=2.3$  meV. Above  $T_g$  the curves no longer collapse onto a master curve but, with increasing temperature, a considerable amount of additional scattering fills up the low-temperature minimum.

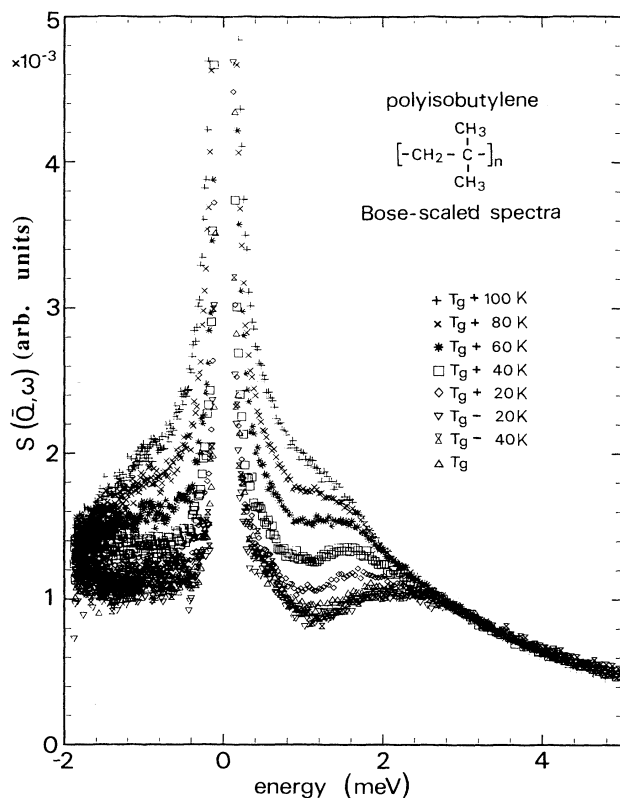


FIG. 6. Dynamic structure factor  $S(Q, \omega)$  of PIB corrected for Debye-Waller factor and Bose factor as measured on IN6, ILL. The measured curves are presented for  $T=200$  K, the glass-transition temperature of PIB, as a reference temperature.

There is no question that this scattering deviates from the temperature behavior expected for harmonic phonons. It indicates the onset of a fast dynamical process in the temperature range around  $T_g$ , analogous to recent neutron-scattering results on other polymeric and nonpolymeric glasses.<sup>1,2,4,6-9</sup> However, in contrast to previous observations, the additional scattering observed here for PIB is clearly of *inelastic* nature up to quite high temperatures, i.e., up to  $T \sim T_g + 80$  K.

In order to underline the anomalous temperature behavior and its analogy to previous neutron-scattering results (Buchenau and co-workers in Refs. 4 and 26, Frick *et al.* in Ref. 1, and Knaak in Ref. 1), we plot the inelastic intensity versus Bose factor and correct the data for the Debye-Waller factor, which is deduced from the elastic line intensity. In the high-temperature approximation the Bose factor dependence can be replaced for low-energy transfers by a linear temperature dependence. We therefore plot in Fig. 7 the inelastic intensity, integrated over different energy windows versus the relative temperature  $T - T_g$ . In agreement with Fig. 6 we observe for higher-energy transfers a linear variation of the inelastic intensity with temperature. However, in the frequency range below 3 meV a clear change of slope appears in the temperature dependence near  $T_g$  and it is more pronounced for lower-energy transfers.

In the following we will investigate the  $Q$  dependence of the inelastic scattering, or the inelastic form factor. From Figs. 6 and 7 we know that at low temperatures a broad inelastic hump is present around 2.3 meV in  $S(Q, \omega)$ . With increasing temperature the scattering at energies below and above this peak varies differently. We will therefore investigate if this goes along with a different  $Q$  dependence or inelastic form factor within the respective energy-transfer regimes [Fig. 8(a)]. Selecting

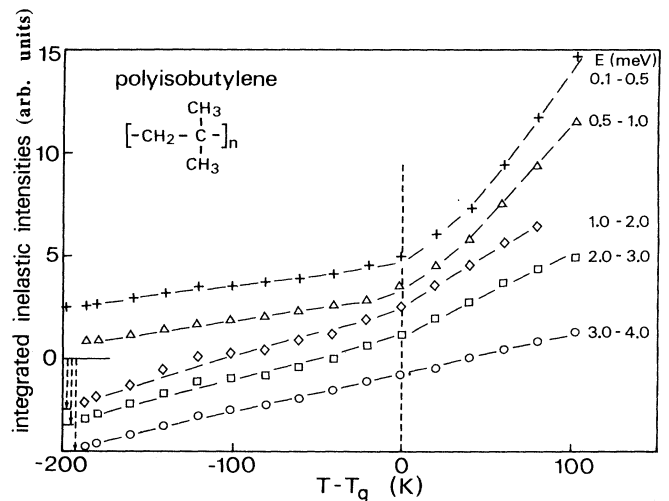


FIG. 7. Integrated inelastic intensity of PIB as a function of temperature for different energy-transfer regimes ( $T_g = 200$  K). The arrows at the lhs indicate the shift of the curves. A linear temperature dependence is observed for high-energy transfers, whereas at low-energy transfers a change of the temperature dependence is observed close to  $T_g$ .

different energy windows between 0.2 and 6 meV, we compare the  $Q$  dependence of the inelastic scattering at  $T=240$  K, a temperature where the additional low-frequency scattering shows up clearly. The data are corrected for the DWF, which was deduced from the elastic line. Obviously, up to  $Q=2.5 \text{ \AA}^{-1}$  there is a well-defined  $Q^2$  dependence within the total energy-transfer regime. We also have tested whether the  $Q$  dependence of the inelastic scattering changes with temperature. Figure 8(b) shows the  $Q$  dependence of the integrated scattering intensity between 1.0 and 1.5 meV for different temperatures (an energy window with a strong intensity increase near  $T_g$ ). Obviously the  $Q$  dependence

does not change with temperature and this holds as well for other energy-transfer regimes which are not shown here.

The invariant  $Q$  dependence at different energy transfers suggests a factorization of the  $Q$  and  $\omega$  behavior and thus after correction for the Bose factor we should be able to produce a master plot, multiplying the inelastic form factors by a  $\omega$  dependent scaling factor. The master plot is shown in Fig. 8(c), corresponding to the data from Fig. 8(a) ( $T=240$  K). The solid line through the data shows that the master plot, i.e., the inelastic form factor is proportional to  $Q^2$  ( $\sim \text{const.} + 0.003Q^2$ ). The inset in Fig. 8(c) displays the resulting  $\omega$  dependence for the scal-

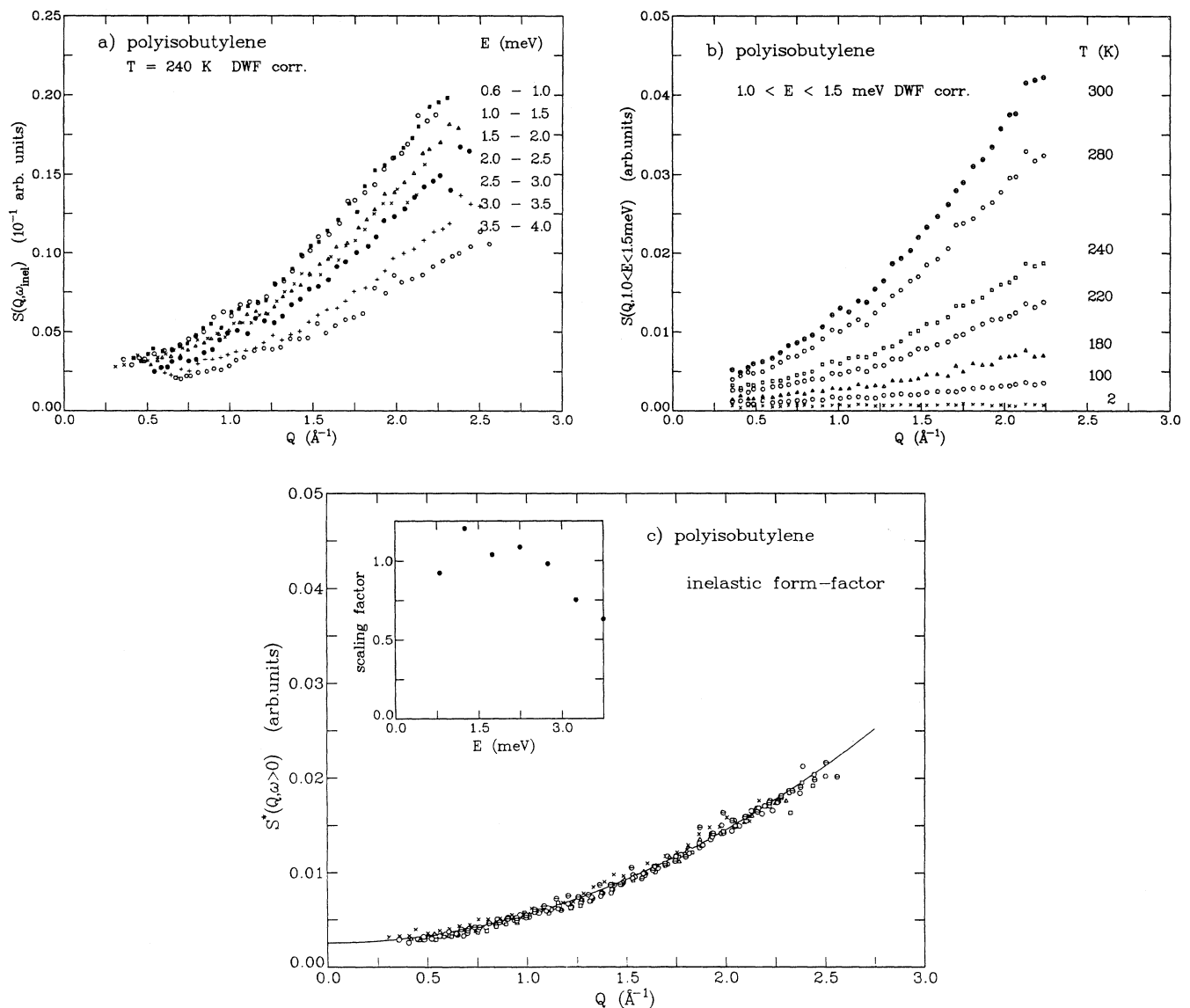


FIG. 8. (a)  $Q$  dependence of the inelastic scattering for different energy regimes measured at  $T=240$  K on IN6, ILL. (b)  $Q$  dependence of the inelastic scattering for different temperatures in the energy window from 1.0 to 1.5 meV. (c) Master curve for the  $Q$  dependence of the inelastic form factor produced from curves measured at different energy transfers. The inset shows the multiplication factors as a function of energy transfer, which were used to produce the master curve.

ing factors. If the observed inelastic-scattering intensity were due to vibrational excitations, then this scaling factor should be proportional to the vibrational density of states divided by frequency  $n(\omega)g(\omega)/\omega$ .

### DISCUSSION

We have shown that the amorphous polymer glass polyisobutylene exhibits additional low-frequency excitations when the sample temperature comes close to or exceeds the glass-transition temperature  $T_g$ . The analysis of the data (Figs. 2–4, 7, and 8) also made clear that the observed fast dynamical process in PIB is qualitatively of the same nature as the fast dynamical process observed earlier for other glass formers. However, in contrast to recent observations on more fragile glasses<sup>1,2,4,6–9</sup> the fast process reveals here to be of inelastic nature (Fig. 6). We will first discuss the influence of methyl group rotations and of the  $\alpha$  relaxation, compare the results with the predictions of the mode-coupling (MC) theory and finally try an interpretation of the low-temperature excitation and its change with temperature.

Methyl group librations could possibly contribute to the increase of the mean-squared displacement in PIB near  $T_g$  and jump rotations could give rise to quasielastic scattering. On the basis of the NMR experiments displayed in Fig. 1, however, we can exclude quasielastic scattering originating from  $\text{CH}_3$  reorientations, while the librations giving rise to a broad inelastic peak in the spectra around 40 meV (Ref. 27) may be responsible for the steeper increase of the MSD above 50 K compared to that below 50 K (Fig. 4). This would result in an even smaller contribution to the MSD from the backbone hydrogens and thus indicate an even stronger hindrance of the backbone motion. In addition, for polyisoprene<sup>28</sup> we could find a clear steplike decrease of the elastic intensity in recent neutron fixed window scans due to the methyl group reorientations, whereas for PIB there is no indication of it. And finally, we find no support for methyl group reorientations from the observed structure factors (Figs. 4 and 8). Thus we conclude that the observed excess scattering around  $T_g$  results not from specific atomic groups but from vibrations or librations of all the protons.

We furthermore exclude strong contributions from the  $\alpha$  relaxation to the observed low-frequency scattering as the elastic line is not broadened in the investigated temperature and  $Q$  range (with the energy resolution of IN6). This point of view is supported by the high-energy resolution (1  $\mu\text{eV}$ ) experiments of Allen and co-workers<sup>20</sup> on PIB, which show that the elastic line broadens only at temperatures above  $T_g + 140$  K. Taking other literature data into account (Fig. 1) we conclude that the  $\alpha$  relaxation contribution must be located within the elastic line. The absence of  $\alpha$  relaxation broadening in a fairly wide temperature range around  $T_g$  might be one explanation why the fast relaxation process is found to be inelastic. The fact that the inelastic vibrational excitation in PIB is located at somewhat higher energy (2.3 meV) than in the other, mostly fragile glass formers studied so far by neutron scattering might be another reason. The tempera-

ture range around  $T_g$ , where changes of the vibrational behavior can be studied without having considerable contributions from the  $\alpha$  relaxation, is much narrower for fragile glasses (see Fig. 1 for  $D=2$  as an extreme case) and therefore the minimum between the vibrational excitations and the elastic line (see Fig. 6) is filled up more rapidly with increasing temperature. On the other hand, we cannot exclude the possibility that the relaxation behavior changes from fragile to strong glasses. For a strong glass former, vitreous silica,<sup>26</sup> the inelastic coherent neutron-scattering experiments have shown inelastic structural relaxation far below  $T_g$  ( $T \sim T_g - 1000$  K). Buchenau *et al.*<sup>26</sup> have shown that the inelastic form factor can be understood by coupled rotational jumps of  $\text{SiO}_2$  octahedra in an asymmetric double-well potential and inelastic relaxation features were found by Raman scattering on glycerol.<sup>29</sup>

The inelastic nature of the additional scattering leads us to suppose that the vibrational behavior in PIB changes near  $T_g$ . On the other hand, earlier neutron-scattering results on fragile glasses<sup>1,2,4,6–9</sup> show strong similarities with the temperature dependence of the dynamical scattering function in PIB. These results were often interpreted comparing them to the mode coupling (MC) theory,<sup>3</sup> which predicts a fast quasielastic relaxation ( $\beta$  relaxation) accompanying the  $\alpha$  relaxation. Thus the quasielastic term in Eq. (1) would consist out of two power laws (“ $\alpha$  relaxation” and “MC  $\beta$  relaxation”) with fractional exponents  $a$  and  $b$ , which are related via a coupling strength parameter  $\lambda$ . The dynamic scattering law is predicted to show a characteristic temperature dependence towards a critical temperature  $T_c > T_g + (30 \dots 50$  K). Below  $T_c$  the  $\alpha$  relaxation arrests (without taking hopping terms into account); the  $\beta$  relaxation, however, persists. Certainly, the mode coupling theory has not been conceived to describe *inelastic* low-frequency excitations in the neighborhood of the glass transition and thus cannot account for the very pronounced inelastic feature observed for PIB. Thus the question may be asked differently: Can a change in vibrational behavior near  $T_g$  account for the “fast quasielastic relaxation” observed previously for other fragile glasses,<sup>1,2,6–9</sup> i.e., are the additional “relaxational excitations” in fragile glasses unresolved inelastic processes?

At this stage a conclusive answer cannot be given. But in order to dwell more on the similarities with earlier experimental observations we present the data for PIB as dynamic susceptibilities  $\chi'' = n(\omega)^{-1}S(Q, \omega)$ , and display the spectra for different temperatures in Fig. 9. Again, as in Fig. 6, the data were scaled by Bose factors and corrected for the DWF, and also the elastic line was subtracted. In order to display more clearly the additional low-frequency scattering, we have subtracted the phonon scattering taking the intensities at  $T=100$  K as reference. We have thereby assumed that the phonons do not change when passing  $T_g$ , an assumption which is correct at least above 3 meV. The resulting susceptibility spectra turn out to be qualitatively very similar to susceptibility spectra from other glasses, but show a much sharper peak around  $E \sim 2$  meV. One could be tempted to interpret this peak as the MC- $\beta$ -relaxation peak, but we know

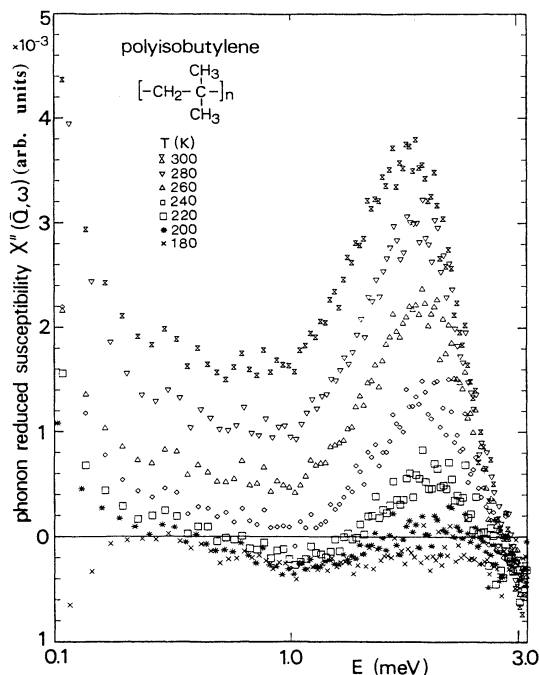


FIG. 9. Dynamic susceptibility  $\chi''(Q, \omega)$  calculated from Fig. 6. Phonon contributions extrapolated from the low-temperature behavior are subtracted after correcting for DWF and Bose factor. The elastic line was subtracted as well.

that the relaxation contribution is inelastic (Fig. 6) and thus this would be an unreasonable explanation.

We discuss now the nature of the low-temperature ( $T < T_g$ ) inelastic hump, which is observed at 2.3 meV in PIB and in different kinds of glass formers between 1 and 3 meV. There are not many detailed investigations about the microscopic origin of this usually broad peak. It was often ascribed to vibrational excitations, because its intensity was found (i) to be proportional to  $Q^2$  and (ii) to increase with temperature proportional to the Bose occupation factor.<sup>1,2,7</sup> In one case, vitreous  $\text{SiO}_2$ , a detailed microscopic motion was deduced from coherent inelastic neutron data.<sup>26</sup> For PIB, based on incoherent inelastic neutron data, which did not increase proportional to  $Q^2$ , but leveled off at higher  $Q$  values, Inoue *et al.*<sup>21</sup> had argued that tunneling motions lead to the observed peak. Our data also appear to level off for  $Q \sim 2 \text{ \AA}^{-1}$  but only before we have corrected for the DWF, thereafter the inelastic incoherent structure factors follow an excellent  $Q^2$  behavior up to  $Q \sim 2.2 \text{ \AA}^{-1}$  (Fig. 8).<sup>30</sup> Furthermore, the spectra precisely follow a Bose occupation factor excluding thereby the possibility of tunneling motion, which would require quite different statistics.

Another noteworthy point is the factorization of the incoherent-scattering function  $S_{\text{inc}}(Q, \omega)$  into a  $Q$ - and a frequency-dependent term at all temperatures [see Fig. 8(c)]:

$$S_{\text{inc}}(Q, \omega) \sim f(Q)n(\omega, T)F(\omega),$$

$F(\omega)$  being a normalized spectral function, and  $n(\omega, T)$  a

temperature factor. Such a factorization was found recently for ortho-terphenyl<sup>7</sup> and was taken as a confirmation of this prediction by the mode coupling theory.<sup>3</sup> This conclusion is certainly premature as a similar behavior is expected for incoherent phonon scattering, with  $n(\omega, T)$  being the Bose factor and  $F(\omega) = g(\omega)$  the vibrational density of states [see Eq. (1)]. Similarly local molecular motions can exhibit the same feature (e.g., jumps between two sites).<sup>31</sup>

In the remaining discussion we offer an alternative explanation for the observed low-frequency scattering. Tentatively we presume that the significant changes in the inelastic spectrum close to  $T_g$  are caused by changes in the vibrational properties of the chain backbone, most likely the torsional modes. We speculate that the observed inelastic hump around 2.3 meV at low temperatures corresponds to a torsional mode involving several carbon chain atoms, whereby a single atom might undergo only a small displacement. The shift of the peak with increasing temperature could now be caused by a change in the boundary condition for this torsional mode. Let us define a length scale  $\xi$  as the distance between two points of strong steric hindrance. Then, for distances shorter than  $\xi$  torsional excitations along the chain could be excited, while for exceeding length scales those modes are blocked or frozen. The distribution in local environments, i.e., distances between blocking points, is then reflected by the width of the observed inelastic peak and by the steepness of its low-frequency tail. With raising temperature, more and more of the steric blocking is removed and the length scale  $\xi$  increases. The longer wavelength torsional excitations increase the inelastic scattering at frequencies lower than the inelastic low-temperature excitation at 2.3 meV. Finally, increasing the temperature further the spectrum becomes overdamped and shows quasielastic character. At even higher temperatures above  $T_g$  (not investigated here), all atoms will undergo translational motion and the elastic line will broaden. This corresponds to the temperature range where the  $\alpha$ -relaxation is observed and happens closer to  $T_g$  for fragile glass formers than for strong glass formers.

This interpretation gets some support from the observed temperature behavior of  $S(Q, \omega)$  in Fig. 6 or from the inelastic intensities plotted as a function of temperature in Fig. 7. Both figures show that above  $T_g$  the inelastic intensities increase with a steeper slope, but are still linearly in temperature. In Fig. 6, where the intensities are divided by Bose occupation factors, thereby scaling all scattering due to harmonic phonons to a common master curve, excess scattering occurs in between the elastic line and the low-frequency excitation at 2.3 meV. Scrutinizing the high-frequency part of this extra intensity, we observe that the high  $\omega$  flank of the shifting peak establishes a new master curve in the sense that the data at consecutively higher temperatures follow the curve performed by the preceding lower  $T$  spectra. The range of the "anomalous" intensity increase is progressively pushed towards the elastic line. Relating this to the ideas above we propose that the characteristic chain length  $\xi$  on which torsional vibrations appear increases steadily



above  $T_g$ , thus the vibrating mass increases and the vibrational frequencies become lower. Once the vibrations on a certain length scale are unfrozen, the observed intensity increase with temperature follows in the corresponding energy range the Bose statistics for even higher temperatures.

### CONCLUSION

The investigations of the vibrational behavior on the polymer glass polyisobutylene, presented above, show that, as in other glasses, an additional low-frequency process appears close to  $T_g$ . This is the first time, that the inelastic character of such additional excitations above  $T_g$  has been shown. This observation became possible due to the less fragile, i.e., more sterically hindered microstructure of this polymer, which leads to a larger temperature distance between the glass transition temperature  $T_g$  and the appearance of the  $\alpha$  relaxation. We tentatively interpret this additional scattering as an unfreezing of torsional excitations of the chain backbone which are blocked in the glass. The mode coupling theories in their present form, predicting a dynamical phase transi-

tion at  $T_c > T_g$ , assume that the vibrational properties do not change and consequently can not account for the observed inelastic excitations. The identification of the features below 2 meV in polyisobutylene as arising from truly inelastic low-frequency excitations casts some doubt on the interpretation of similar observations in other polymers and molecular glass formers at similar frequencies as due to the  $\beta$ -relaxation process of the mode coupling theory. The fragility of those substances may have masked the inelastic nature of the so-called "fast relaxation process."

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\*Present address: National Institute of Standards and Technology, Reactor Radiation Division, Gaithersburg, MD 20899.

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