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Local motion in the β-transition range of partially crystalline polyethylene studied by neutron scattering*)

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*) *Dedicated to Prof. E. W. Fischer on the occasion of his 65th birthday*

Abstract: We have performed inelastic neutron scattering experiments on protonated and fully deuterated partially crystalline polyethylene. Using a high-resolution, three-axes spectrometer with an energy resolution of 80 μeV, it was possible to detect a quasielastic process in the dynamic structure factor with a FWHM of 0.3 meV. This process was shown to be active above $T_0 = 260$ K and its FWHM was nearly independent of temperature and scattering vector. The spatial extent of the underlying motional process was determined from the corresponding Debye-Waller factor. The mean squared displacement increases strongly with T above T_0 up to 4 Å^2 at $T = 380$ K. Comparison with results from similar work on fully amorphous polymers suggests to relate T_0 to the glass transition of the amorphous phase in partially crystalline polyethylene. The coherent structure factor shows no evidence for a significant contribution of correlated motion to the process. A speculative explanation of the observed phenomenon as a non-equilibrium soft-mode is proposed.

Key word: Glass transition – quasielastic neutron scattering – polyethylene

I. Introduction

The complex structure of macromolecules in the melt provides the basis for a wide range of dynamic phenomena. On short time scales the bonds in the polymer backbone are found to exhibit oscillatory, librational motion in a potential essentially defined by the chain structure. This process is complemented by a comparatively slow diffusion of chain segments and, finally, the whole chain. Whereas the fast dynamics are conceptually similar to oscillatory excitations in crystalline solids the diffusional part carries several extraordinary characteristics. The temperature dependence of the typical times involved in segmental diffusion is very strong and phenomenologically described with the Vogel–Fulcher equation. This leads to a freezing phenomenon at low temperatures, the glass transition.The liquid melt is transformed into a glassy transition. The liquid melt is transformed into a glassy state which no longer supports large scale segmental diffusion. The glass transition is observed in amorphous polymers as well as in non-polymeric materials.

Whereas the main effect of the glass transition is related to the slow segmental dynamics, there is recent experimental evidence for a correlation of the transition with the short time dynamics of the system [1–3]. Neutron scattering experiments revealed the existence of an anomaly in the dynamic structure factor in the frequency range of 10^{-12} s which appeared in the regime of the glass transition of the material. This effect has been observed in polymeric as well as non-polymeric glass forming liquids but its nature is still widely unknown [4].

In a preceding publication [5], we have demonstrated the existence of the fast process in a partially crystalline polymer: polyethylene. The emphasis there was on a separation of the dynamics in the crystalline and the amorphous regions of the material. Using the combination of several high-resolution neutron scattering techniques, it was possible to measure the slow segmental dynamics as well as the fast component of the dynamic structure factor. It was characterized as a quasielastic contribution with a full width at half maximum (FWHM) of 300 μeV.

The present work now extends this investigation to study the properties of the fast process in partially crystalline polyethylene in more detail. We have used neutron scattering experiments in a range of energy transfers that allow to resolve the structure factor in the meV regime. In addition to the incoherent scattering from polyethylene, we have used a fully deuterated sample in order to separate the contribution of correlated motion to the scattering.

II. Experimental

The polyethylene (PE) sample *A* used in the incoherent scattering experiment was the same as sample II of our previous study [5]. It was a linear, high molecular ($M > 10^6$) weight PE obtained from Hoechst AG. The sample was melt-crystallized at 125 °C resulting in crystallinity of 0.62 as obtained by DSC.

Sample B was a fully deuterated PE obtained from Promochem GmbH/Germany. It was further purified by dissolving it in hot toluene and precipitating with methanol. The sample exhibited a rather broad melting regime and had a crystallinity of 0.62 after slow cooling.

Thin sheets were prepared of the samples and contained between the walls of two hollow aluminum cylinders of 1.4 cm diameter and a height of 4.9 cm. The sample thickness was 0.1 mm for the protonated and 0.5 mm for the deuterated material. The transmission of these samples was larger than 0.9 and no absorption corrections were necessary. A cryostat was used for the low T measurements $-100\,^\circ\mathrm{C} < T < 50\,^\circ\mathrm{C}$ and an oven for elevated temperatures.

The neutron scattering experiments were performed at the three axes spectrometer TAS7 of Risø National Laboratory, Denmark. The incoming beam was monochromized with the (002) reflection of a Graphite crystal (PG002) and most measurements were done with an incoming energy $E_{\mathrm{in}} = 3.6$ meV. The scattered intensity was analyzed with a PG002 crystal and the range of energy transfers investigated was $-1\,\mathrm{meV} \leq \Delta E \leq 1$ meV. The scattering vector interval was from $0.5\mathrm{\AA}^{-1}$ up to $2\mathrm{\AA}^{-1}$. The instrumental resolution was determined with the incoherent scattering from vanadium as well as with the samples at low temperature. No difference was found with these two methods and the resolution was characterized by a FWHM of 0.08 meV independent of scattering angle. The quasielastic scans were performed at a fixed scattering vector q and constant energy of the incoming beam.

III. Results

A. Incoherent scattering

Polyethylene scatters essentially incoherently due to the large incoherent scattering cross-section of hydrogen. The incoherent dynamic structure factor therefore represents an average of the dynamics of all protons in the sample.

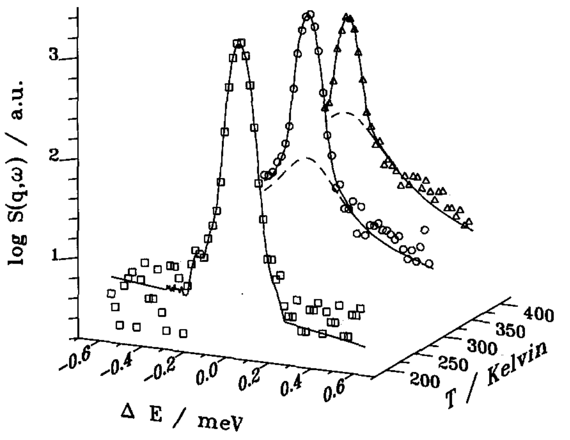

Fig. 1. The incoherent structure factor of polyethylene at a scattering vector $q = 1\mathrm{\AA}^{-1}$. The lines are fits of Eqn. (1). The quasielastic process is indicated as a broken line

The qualitative features and the development of the fast process are shown in Fig. 1. The incoherent dynamic structure factor of sample A is compared for three temperatures below and above the glass transition, respectively. At low T the structure factor consists of a purely elastic line indicating no dynamics within the spectral range of the experiment.

Increasing temperature then causes the development of a quasielastic line in addition to the elastic component. It is seen in Fig. 1 that the main effect of temperature is an increase of the quasielastic intensity at nearly constant FWHM.

A detailed description of the structure factor may be obtained within the two-phase model for the partially crystalline polymer [5] as

$$
\begin{aligned}
S_{\mathrm{inc}}(q,\omega) &= \alpha_c S_{\mathrm{inc}}^{\mathrm{cryst}} + (1-\alpha_c) S_{\mathrm{inc}}^{\mathrm{amorph.}} \\
S_{\mathrm{inc}}^{\mathrm{cryst}}(q,\omega) &= e^{-\frac{q^2 u_v^2}{3}} \delta(\omega) \qquad (1)\\
S_{\mathrm{inc}}^{\mathrm{amorph.}}(q,\omega) &= e^{-\frac{q^2 u_v^2}{3}} \left[e^{-\frac{q^2 u_r^2}{3}} \cdot \delta(\omega) + \left(1 - e^{-\frac{q^2 u_r^2}{3}}\right) \cdot \frac{\Gamma/2\pi}{\omega^2 + \left(\frac{\Gamma}{2}\right)^2} \right]
\end{aligned}
$$

The elastic part of S_{inc} therefore carries the intensity

$$A_\delta = \alpha_c \cdot e^{-\frac{q^2 u_v^2}{3}} + (1-\alpha_c) \cdot e^{-\frac{q^2 (u_v^2 + u_r^2)}{3}} \, .$$

The intensity of the quasielastic, Lorentzian, part is

$$A_L = (1-\alpha_c) \cdot e^{-\frac{q^2 u_v^2}{3}} \left(1 - e^{-\frac{q^2 u_r^2}{3}}\right) ;$$

α_c denotes the crystallinity of the sample. At low temperatures it is set to the value obtained in the DSC measurement. Its weak T dependence is taken from Ref. [5]. $\delta(\omega)$ is a delta function describing the elastic component of the structure factor. The Debye–Waller factor of the system consists of two contributions. One is caused by the vibrational excitations and leads to a mean squared displacement of the average proton denoted u_v^2. It is assumed to apply to the crystalline as well as to the amorphous part of the structure factor. The quasielastic component itself is related to a further displacement u_r^2 which weakens the elastic contribution from the amorphous phase and shifts intensity to the quasielastic line. The latter is represented in Eq. (1) as a Lorentzian with FWHM Γ.

In order to fit the experimental data with the model given in Eq. (1), one has to take the finite resolution of the spectrometer into account. We use the purely elastic scattering from the sample at low temperatures to obtain the normalized resolution function $R(\omega)$ independent of scattering vector q. The data were obtained at constant monochromator position and the intensity at a given energy transfer ΔE is therefore dependent on the volume of the resolution ellipsoid [7]. This effect is accounted for in the fitting procedure by a normalization factor $k_f^3 \cot\Theta_A$ with k_f denoting the wave vector of the scattered neutron and Θ_A the Bragg angle of the analyzer crystal. This factor varies by approximately 2 across the spectra. The intensity is therefore given as

$$I(q,\omega) = A R(\omega) * S_{\mathrm{inc}}(q,\omega) \cdot k_f^3 \cot\Theta_A \qquad (2)$$

with a normalization factor A.

The quality of the fits is shown in Fig. 1 and, in more detail, in Fig. 2 for the example of a measurement on sample A at 117 °C and a scattering vector $q = 1 \text{Å}^{-1}$. Although the elastic line is the dominating part in the dynamic structure factor, it is seen in Fig. 2 that the quasielastic contribution may be reliably separated.

The dependence of the FWHM of the Lorentzian on scattering vector q is displayed in Fig. 3. For the case of a diffusion process, one would

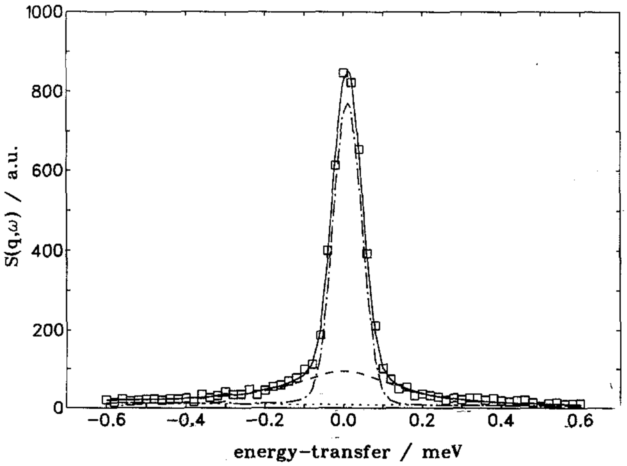

Fig. 2. Deconvolution of the incoherent structure factor into an elastic part, a quasielastic line and a flat background. This spectrum was taken at $q = 1$ Å^{-1} and $T = 390$ K

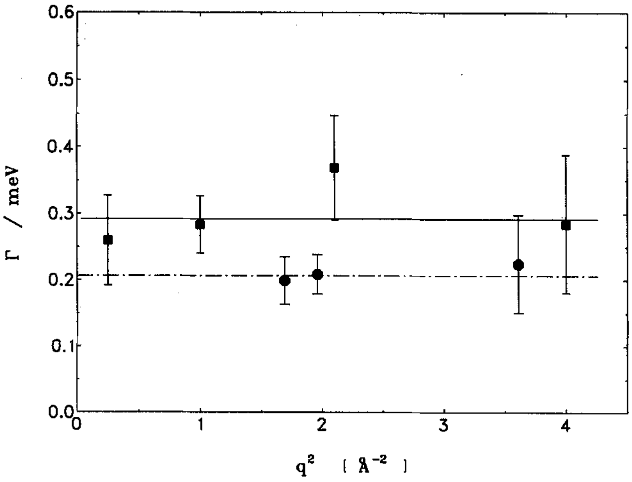

Fig. 3. FWHM of the quasielastic line in the incoherent (■) and the coherent (●) structure factor of PE. There is no dependence on q observable in both cases

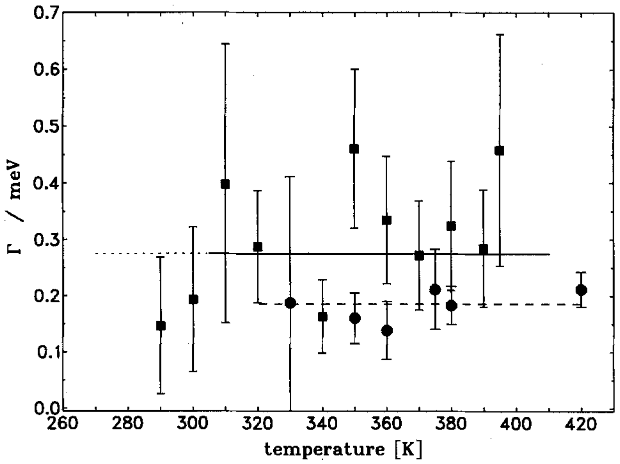

Fig. 4. Temperature dependence of Γ for the incoherent (■, $q = 2\,\text{Å}^{-1}$) and the coherent (●, $q = 1.3\,\text{Å}^{-1}$) experiment

expect a relation $\Gamma \sim q^2$ which is clearly ruled out by the results shown in Fig. 3. This finding agrees with our previous results [5]. If the microscopic type of motion is assumed to be a diffusion process, it would have to be restricted to a volume of size $2\pi q_{\max}^{-1} \approx 3\text{Å}$.

A further remarkable property of the fast process is its very weak temperature dependence as shown in Fig. 4. With the exception of the data points just above 260 K there is no significant further increase of Γ with T up to 400 K. In this respect, Γ shows a behavior that is completely different from that of the α process. The latter is strongly activated with temperature and its relaxation time decreases by several orders of magnitude within the temperature range of our experiment.

The dominant influence of temperature on the fast process lies in an increase of the intensity found in the quasielastic line with T. In Fig. 5a and 5b, we show the variation of the elastic and the quasielastic intensity, A_δ and A_L, respectively. These values are obtained from a fit of the incoherent structure factor according to Eq. (2). The scattering vector dependence of the intensities is indeed found to be well described by the assumption of an isotropic Gaussian distribution for the position of the scattering proton. This leads to the Debye–Waller factor used in Eq. (1) of the integrated intensities A_δ and A_L. The remaining prefactor in Eq. 2 is determined at low temperatures ($T = 100$ K) where the total scattering is elastic. The mean squared displacements $\langle u_v^2 \rangle$ and $\langle u_r^2 \rangle$ are consequently relative values referring to zero displacements at $T = 100$ K. Their absolute value may be obtained by adding $\langle u_v^2 \rangle_{T=100\,K} = 0.06\,\text{Å}^2$ [5, 6].

Figure 5a displays variation of the elastic intensity with q for several temperatures together with a fit of the q dependence given in Eq. (1). The only adjustable parameter for each T is the mean squared displacement $\langle u^2 \rangle$ caused by the fast process which shows up as a quasielastic line in the structure factor. The parameter $\langle u_v^2 \rangle$ referring to the vibrational part of the spectrum which is not covered by our measurement is taken from experiments [5] at larger q and used here as a fixed parameter. As a check of consistency we then use the thus obtained $\langle u^2 \rangle$ to calculate the variation of the quasielastic intensity in Fig. 5b. The agreement between Eq. (1) and the data is satisfactory.

We may then study the temperature dependence of the mean squared displacement $\langle u_r^2 \rangle$ as is done in Fig. 6. We include here also the data obtained from high resolution backscattering experiments that have been reported previously [5]. Whereas the $\langle u_r^2 \rangle$ measured on IN10 with an energy resolution of 1 μeV are clearly larger than the present results, we find exact agreement between IN13 and our results. Obviously, there is an additional process contained in the dynamics of PE with a frequency in between 1 μeV and

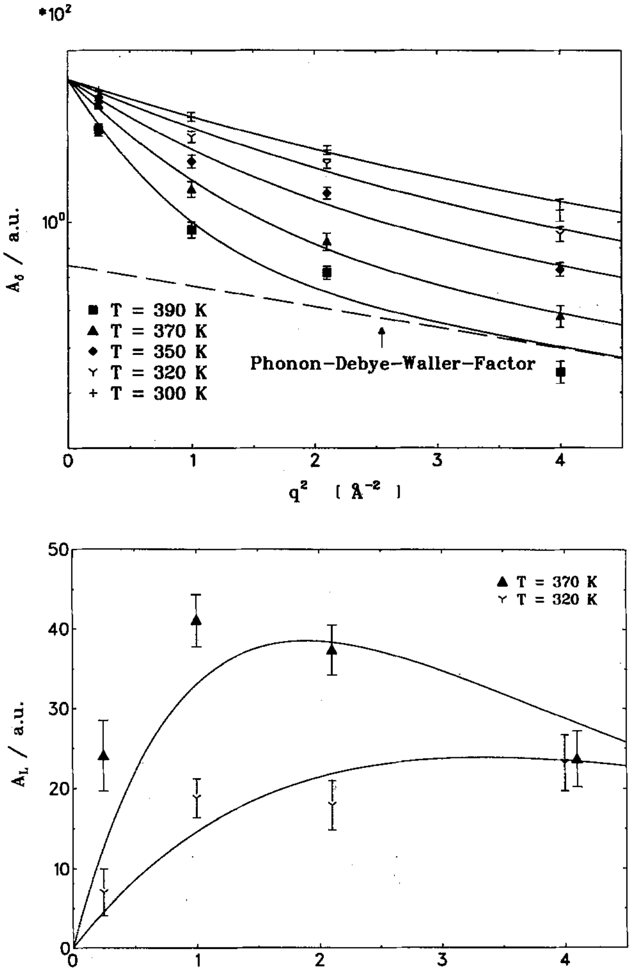

Fig. 5. Intensity of the elastic (a) and the inelastic (b) part of the incoherent structure factor. The lines are fits of the q dependence given in Eq. (1) and allow us to determine the mean squared displacement $\langle u_r^2 \rangle$

10 μeV. This processes has been identified as the β/γ process [5, 6].

The agreement between IN13 and our results demonstrates the correctness of the data-evaluation procedure applied to the backscattering data which do not cover the full width of the fast quasielastic process at all temperatures. $\langle u_r^2 \rangle$ there was obtained from fixed window scans measuring the elastic intensity within the resolution of the instrument. It shows further that there is no additional contribution to the dynamics in between 8 μeV and 80 μeV, the resolution of both experiments.

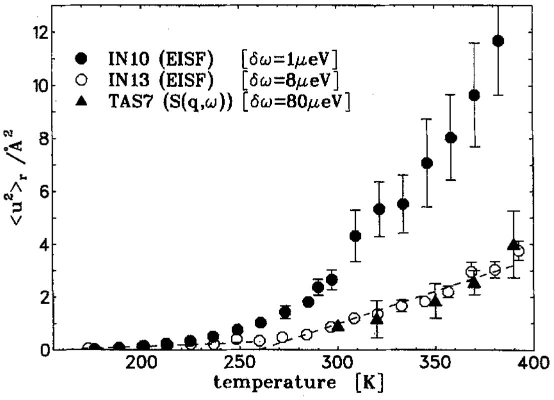

Fig. 6. Temperature dependence of $\langle u_r^2 \rangle$. Above 260 K the mean squared displacement of the average proton increases strongly with T. The broken lines are guide lines for the eye

The temperature dependence of the mean squared displacement of the average proton in the amorphous phase changes drastically at $T = 260$ K. This temperature also marks the appearance of the fast process in the dynamic structure factor. Work on noncrystalline polymers has shown that this temperature is located just above the glass transition temperature of the material. $\langle u_r^2 \rangle$ gains an additional temperature dependence and increases up to 4Å² at 390 K.

In partially crystalline linear PE the glass transition temperature is not well defined by thermal or mechanical experiments. There is no mechanically active process in PE that shows a clear WLF behavior and thus leads to a determination of T_g. In branched PE samples with low crystallinity one observes the β process which has the properties of a glass transition, with a T_g around 250 K. It is interesting to note that our experiment on a highly crystalline material now locates the onset of a local mode in exactly the same temperature range.

B. Coherent scattering

In order to study the contribution of correlated motion to the fast process in the dynamic structure factor of PE, we have investigated the coherent scattering from a fully deuterated PE (sample B). The static scattering from this sample displays an amorphous halo in addition to the Bragg reflections from the crystalline part of the sample (see Fig. 7). The halo is caused by interchain as

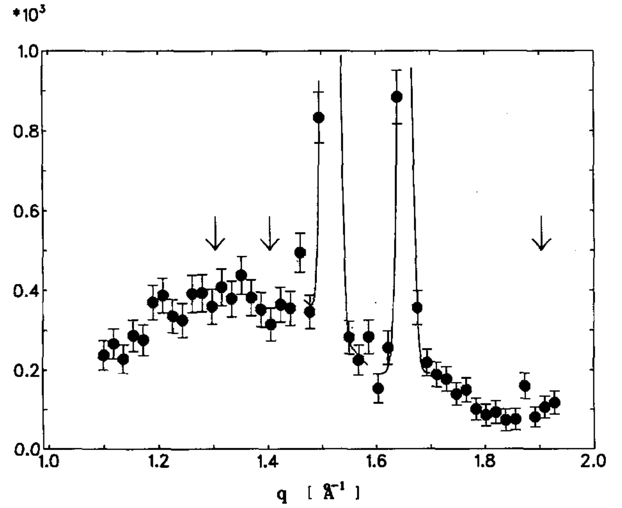

Fig. 7. Static scattering from deuterated PE. The arrows mark the q positions of the inelastic measurements. The lines indicate the positions of the (110) and (200) Bragg reflections

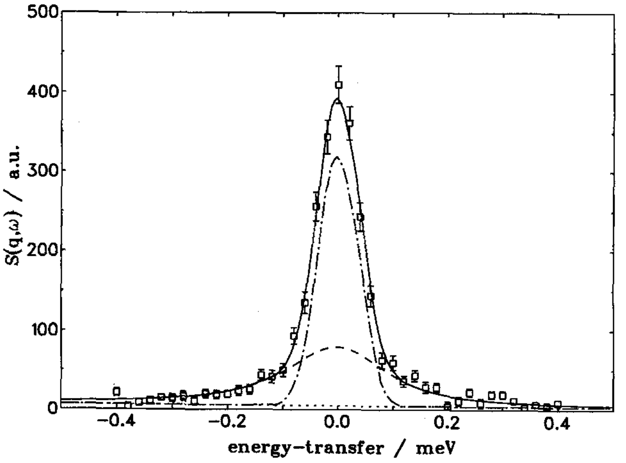

Fig. 8. Dynamic structure factor of deuterated PE. The deconvolution into elastic and quasielastic intensity is indicated

well as intrachain correlations . The arrows in Fig. 7 indicate the scattering vectors at which the dynamic structure factor was measured.

Whereas the incoherent scattering is given by the self correlation function G_s of the scattering particles alone, the coherent experiment adds correlations between pairs of distinct scatterers and thus provides access to the full pair correlation function. The experimental spectra as shown for the example of a scattering vector $q = 1.3$ Å^{-1} at $T = 380$ K in Fig. 8 look very similar to the incoherent case of Fig. 2. Again, one observes a fast inelastic process which is described by the Lorentzian line as in Eq (1).

The results for the FWHM and its dependence on q and temperature are included in Fig. 3 and 4. The coherent scattering contains a fast process with the same characteristics that were determined for the incoherent case. The fact that the FWHM Γ is about 30% smaller may be attributed to the contribution of pair correlations along the polymer chain that decay slower than the self-correlation part. There was no difference in the q dependence of Γ between the incoherent and the coherent experiment.

IV. Discussion

Our results have shown that the amorphous phase of partially crystalline PE possesses a local mode of motion which is related to the glass transition, although it is essentially different from the glass process itself. It appears at $T_0 \approx 260$ K and then gives rise to a strong increase of the mean squared displacement of the average proton with T above T_0. The FWHM of the mode is nearly independent of temperature up to 390 K and corresponds to a characteristic time $\tau \approx 10^{-11}$ s.

It seems impossible to envisage a type of motion with these characteristics for an isolated PE chain. The conformational and dynamic properties of such a molecule are described within the rotational isomeric state (RIS) model. The potential for rotations around a C–C-bond is schematically depicted in Fig. 9. It is obvious from the figure that relaxation processes like kink or crank-shaft motions would have to cross the potential barrier of 10 kJ/mol. Their corresponding relaxation time would therefore have to show a clear temperature dependence which is not present in our experiment.

An alternative mechanism underlying the observed mode could be based on low frequency vibrational excitations. They correspond to collective oscillations around the positions of the minima in Fig. 9. Although PE chains in the melt are coiled, we turn for the moment to a discussion of all-trans chains. The qualitative picture will also hold for the melt. Experimentally, these modes have been studied using Raman spectro-

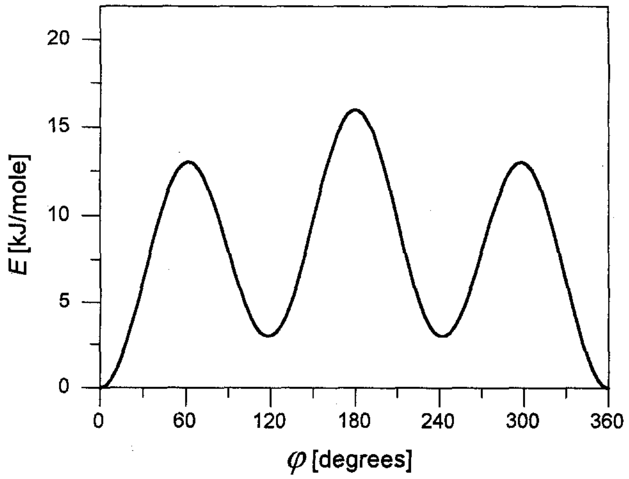

Fig. 9. Schematic graph of the potential E for rotations around C–C-bonds. ϕ is the rotation angle

scopy. For the out-of-plane torsional and bending modes, one finds a dispersion relation [8],

$$\omega = \sqrt{2\Omega} \sin\delta \cos\delta/2 , \quad (3)$$

where δ is the phase angle between successive bonds and ω the frequency of the oscillation. The value of Ω has been found to be $5 \cdot 10^{12}\ \mathrm{s}^{-1}$. In order to account for the observed line width in the incoherent dynamic structure factor, one needs to use values of δ in Eq. (3) that are very close to 0 or π, respectively. Approximately 40 successive bonds would have to oscillate collectively in order to support such a low-frequency excitation. The observed mode, however, is of local character, and does not show this high degree of collectivity.

We are therefore led to conclude that neither relaxational nor vibrational types of motion of a PE chain in its RIS equilibrium conformation are in accordance with the properties of the observed dynamics. In the following we propose a speculative explanation of the phenomenon, a non-equilibrium soft-mode. Consider again as an example an all-trans PE chain with a RIS potential as depicted in Fig. 9. If the chain is subjected to an external torque the torsion angle φ may be transferred to a value near the point of inflection of the potential. Oscillations around this position will be controlled by an effective spring constant which is extremely small as it is given by the second derivative of the potential. Large amplitudes will become possible, and the effect seen in the incoherent dynamic structure factor will be the sum of a large number of soft modes, effectively summing up to a quasielastic line.

We are left with the problem of the origin of the external forces. They may be a result of a possible heterogeneous dynamic structure of the liquid in the temperature regime above T_g. As has been discussed in the literature [9–11] the system may be considered as consisting of solid-like and liquid-like regions. The liquid-like chain segments then could be subjected to constraints due to their frozen environment and are thus forced into a configurational state that lies far out of the RIS equilibrium.

In conclusion, we suggest the quasielastic line in the dynamic structure factor of the amorphous phase in PE to be caused by non-equilibrium soft modes of the liquid-like chain segments.

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References

1. Kanaya T, Kaji K, Inoue K (1991) Macromolecules 24:1826
2. Frick B, Richter D, Petry W, Buchenau U (1988) Z Phys B 70:73
3. Buchenau U, Monkenbusch M, Stamm M, Maikrzak CF, Nücker N (1988) in Polymer Motion in Dense Systems, Springer, Berlin, p 138
4. Frick B, Richter D (1993) Phys Rev B 47:47
5. Hohlweg G, Holzer B, Petry W, Strobl G, Stühn B (1992) Macromolecules, 25:6248
6. Peterlin-Neumaier T, Springer T (1976) J Polym Phys Ed 14:1351
7. Dorner B (1972) Acta Cryst A28:319
8. Szigeti B (1961) Proc Roy Soc A264:198
9. Fischer EW (1993) Physica A 201:188
10. Cohen MH, Grest GS (1979) Phys Rev B20:1077
11. Grest GS, Cohen MH (1981) Adv Chem Phys 48 455

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