Temperature Dependence of the Nonergodicity Parameter in Polybutadiene in the Neighborhood of the Glass Transition

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Using neutron-spin-echo and time-of-flight spectroscopy we have investigated the precise temperature dependence of the elastic (nonergodic) fraction in the spectrum of density fluctuations of the glass-forming polymer polybutadiene. With increasing temperature we found a critical decrease of the normalized elastic intensity following closely the $(T_c-T)^{1/2}$ behavior predicted by the mode-coupling theory. The critical temperature was determined to be $T_c=216\pm1$ K, i.e., 35 K above T_g.

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The freezing of a liquid into a glass is essentially a transition from an ergodic to a nonergodic state. Recently, it was discovered that mode-coupling theories of liquids exhibit a dynamical transition to nonergodicity if the strength of the nonlinear coupling surpasses a critical value.[1-4] This transition displays characteristics similar to that of the liquid-glass transition. In particular, nonergodicity shows itself by the appearance of a nondecaying part in the spectrum of the density fluctuations. For the liquid-glass transition at a critical temperature $T_c > T_g$, as one of its essential results, the theory predicts spontaneous ergodicity breaking followed by a subsequent $(T_c-T)^{1/2}$ increase of the nonergodic spectral contribution or the nonergodicity parameter $f(Q,T)$, where Q denotes the spatial Fourier components.

Neutron scattering couples directly to the density fluctuations and, therefore, is uniquely suited to scrutinize the theoretical predictions. In a neutron spectrum the frozen correlations display themselves as an elastic spectral component. Above T_c in the supercooled-liquid state, as a result of structural relaxation processes, the elastic fraction broadens. Its spectral contribution is described by $f^0(Q)$, the value of the nonergodicity parameter at T_c-0, and should only be weakly dependent on temperature. Several experimental attempts to determine $f(Q,T)$ have been reported.[5-8] They are consistent with the mode-coupling predictions, but no detailed study has been performed so far.

Here we present coherent quasielastic neutron-spin-echo (NSE) and neutron time-of-flight (TOF) experiments on the temperature and Q dependence of the nonergodicity parameter. They were performed on polybutadiene, a polymer consisting only of a backbone without sidegroups. The results are in quantitative agreement with the theory. We find a cusplike behavior of $f(Q,T)$ which evidences a $(T_c-T)^{1/2}$ singularity with $T_c=216$ K, i.e., 35 K above $T_g=181$ K. This value is in good agreement with what is obtained from a power-law fit of viscosity data at higher temperatures. The observed Q dependence mirrors the static structure factor $S(Q)$.

Mode-coupling theory deals with equations of motion for density fluctuations

$$\phi(Q,t)=\langle\delta\rho^*(Q,t)\delta\rho(Q,0)\rangle/\langle\delta\rho^*(Q,0)\delta\rho(Q,0)\rangle\,, \tag{1}$$

where $\delta\rho(Q,t)$ is the time-dependent Fourier component to the wave vector Q of a deviation from the mean density. The mode-coupling equations are solved under the assumption that the memory function can be written in the form of a polynomial of ϕ. Increasing the coupling strength then leads to structural arrest of the density fluctuations. It has been shown that the resulting dynamical transition corresponds to a certain class of bifurcation singularities.[9] This result indicates that the transition to nonergodicity is expected to exhibit universal features largely independent of the specific material investigated. For the nonergodicity parameter $f(Q)=\phi(Q,t\to\infty)$ the following predictions are made:

$$f(Q,T)=f^0(Q)+\begin{cases} h(Q)\sqrt{\epsilon}+O(\epsilon), & T\to T_c-0\,,\\ O(\epsilon), & T\to T_c+0\,,\end{cases} \tag{2}$$

where $\epsilon=(T_c-T)/T_c$. Thereby, T_c lies in the supercooled-liquid region above the glass transition characterized by T_g. Thus, if one approaches T_c from below, the elastic fraction in the spectrum of density fluctuations decreases critically with $\sqrt{\epsilon}$, while above T_c, where $f^0(Q)$ measures the spectral contribution of the structural or α relaxation, only regular weak temperature dependences should occur. The $\sqrt{\epsilon}$ singularity is a consequence of the underlying fold bifurcation.[9] Its validity, therefore, is essential for the applicability of the theory to the glass-transition problem. Concerning Q dependences one has to keep in mind that in the mode-coupling approach the interactions are not described in terms of potentials, but the coupling coefficients are written in terms of the static structure factor $S(Q)=\langle\delta\rho^*(Q,0)\delta\rho(Q,0)\rangle$, which implicitly contains the interatomic potentials. Consequently, Q dependences are governed by $S(Q)$: $f(Q)$ is found to oscillate in phase with $S(Q)$ while $h(Q)$ oscillates in antiphase. Considering $S(Q)/kT$ as a generalized compressibility, this result is also physically plausible: In Q regions of high compressibility at the peak positions of $S(Q)$ density fluctuations easily arrest and $f(Q)$ becomes maximal. On the contrary, the nonarrested fluctuations will be strongest where $S(Q)/kT$ is minimal.

The experiments were performed on deuterated *cis-trans*-vinyl (47:46:7) polybutadiene (PB) of molecular weight $M_w = 93000$ with $M_w/M_n = 1.03$. This polymer is built up by a hydrocarbon backbone essentially without sidegroups $(-CH_2-CH=CH-CH_2-)_n$. The randomness in the chain structure is provided by the random distribution of *cis*- and *trans*-configurations with respect to the double bond. With differential scanning calorimetry (DSC) the glass transition was determined to occur at $T_g = 181$ K.

The neutron-spin-echo experiments were performed using the NSE spectrometer IN11 at the Institute Laue Langevin (ILL) in Grenoble. In a NSE experiment the difference of the neutron velocities before and after scattering is measured directly in terms of the Larmor precessions of the neutron spin in an external magnetic field B.[10] This leads to the normalized intermediate scattering function $S(Q,t)/S(Q,0)$, where the Fourier time t is proportional to the traversed field integral $\int B\,ds$. In order to obtain a large range of variation for $f(Q)$ we measured at $Q = 1.88$ Å^{-1} in the first valley of the structure factor where the structural arrest should be less pronounced. Using a double-spin-echo setup[11] at a wavelength of $\lambda = 4.72$ Å, we accessed the time range $3.2\times 10^{-3} \leq t \leq 1.35$ ns. Below 220 K the normalized scattering function does not decay with time but stays at a time-independent plateau, the level of which decreases with increasing temperature. The plateau level signifies a time-independent "elastic" spectral contribution; the difference between the plateau level and 1 (the scattering function is normalized) evidences inelastic components with frequencies above the shortest detectable time ($\nu \geq 5\times 10^{10}$ Hz) and less than a limiting frequency of about 1 THz given by the bandpass of the spectrometer.

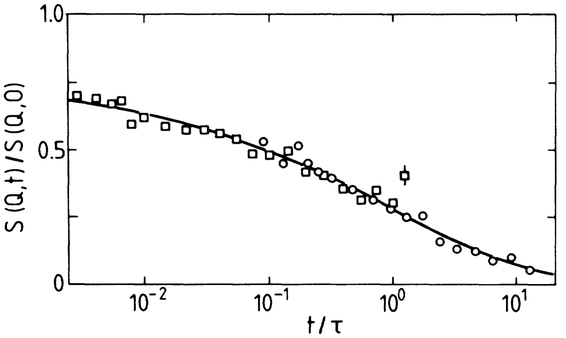

FIG. 1. Scaling representation of the intermediate scattering function from deuterated PB obtained at $Q = 1.88$ Å^{-1} for two different temperatures (□: $T = 240$ K; ○: $T = 280$ K). The scale τ is taken from the viscosity measurements of Ref. 14. The solid line is the result of a fit with a stretched exponential $S(Q,t)/S(Q,0) = f^0(Q)\exp\{-[t/\tau(T)]^\beta\}$ (Ref. 15).

Figure 1 displays results for the relaxation function at 240 and 280 K. Following the time-temperature superposition principle, the data are rescaled with the time scale $\tau(T) = \tau_0(Q)\zeta(T)/T$,[8] obtained from a viscosity measurement. Thereby, applying the Rouse model,[12] the monomeric friction coefficient $\zeta(T)$ is derived from the zero-shear viscosity $\eta(T)$. Unlike in Ref. 8, where we used the Vogel-Fulcher representation of $\zeta(T)$ as given by Berry and Fox,[13] here, in order to be consistent with mode coupling, we fitted the experimental data of Ref. 14 by a power law $\zeta(T) = A(T - T_c)^\gamma$, yielding $\gamma = -3.2$ and $T_c = 214 \pm 3$ K. The right-hand side of Fig. 2 compares the two theoretical representations with the experimental data. Obviously, the power law gives a good description of the viscosity data.

As already demonstrated at the structure-factor peak[8] the microscopic relaxation is well described by a Kohlrausch law and follows the viscosity temperature scale. Table I compares the Kohlrausch parameters obtained at the structure-factor peak and in the valley. For this purpose the data of Ref. 8 were refitted with the power-law description of $\tau(T)$. Compared to the relaxation behavior at $S(Q)_{\max}$, $f^0(Q)$ is considerably reduced, while the Kohlrausch law is more stretched. Furthermore, the time scale of relaxation has increased by more than a factor of 6. In order to obtain independent values for $f^0(Q)$ at the different temperatures, the spectra were

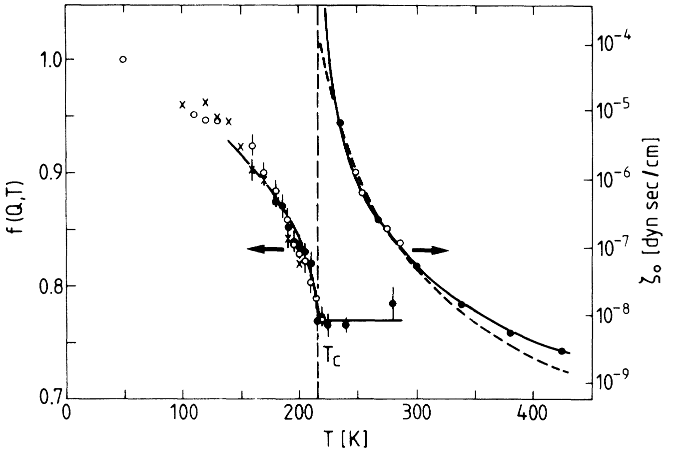

FIG. 2. Right-hand side: Monomeric friction coefficients derived from the viscosity measurements on PB (Ref. 14). The open and solid symbols denote results obtained from different molecular weights. Solid line: result of a power-law fit. Dashed line: Vogel-Fulcher parametrization following Ref. 14. Left-hand side: Temperature dependence of the nonergodicity parameter. The three symbols display results from three different independent experimental runs. Solid line: result of a fit with Eq. (2).

TABLE I. Parameters defining the Kohlschrausch law (stretched exponential) for the structural relaxation in PB at two different Q values.

Q (Å^{-1})	$f^0(Q)$	$\beta(Q)$	τ ($T=240$ K) (ns)
1.48	0.917 ± 0.006	0.45 ± 0.01	8.57 ± 0.5
1.88	0.77 ± 0.017	0.37 ± 0.025	1.29 ± 0.15

fitted separately fixing $\tau(T)$ and β to the values from the joint fit. Having shown that the stretched exponential serves well as a master curve at different temperatures, we consider this extrapolation to $t \rightarrow 0$ as a valid procedure leading to accurate results. As already realized in earlier NSE experiments[5,16] in the regime of the primary relaxation, $f(Q,T)$ always extrapolates to a temperature-independent constant value.

The left-hand side of Fig. 2 compiles the results for the elastic spectral contribution or the nonergodicity parameter over the full temperature range. In order to test for reproducibility, three different experimental runs were performed, the results of which are characterized by the different symbols. Between 100 and 220 K the elastic intensities or the plateau values of $S(Q,t)/S(Q,0)$ decrease critically following the predicted $(T_c - T)^{1/2}$ relation. The solid line represents a fit with Eq. (2) yielding $T_c = 216 \pm 1$ K in close agreement to the critical temperature obtained from the fit of the viscosity data above T_c ($T_c = 214 \pm 3$ K) and in good coincidence with 220 K, estimated earlier on the basis of an incoherent-neutron-scattering study on PB.[7] If we also allow for a variation of the temperature exponent, we find $(T_c - T)^a$ with $a = 0.58 \pm 0.03$. From the $t \rightarrow 0$ extrapolation of the stretched exponential, we conclude that above critical temperature $f(Q,T)$ does not decay further. Therefore, at 216 K, $f(Q,T)$ exhibits a cusplike behavior. Thus, the experimentally determined temperature dependence of the nonergodicity parameter agrees with the prediction of Eq. (2). Thereby, it confirms one of the fundamental results of the mode-coupling theory with respect to the topological nature of the glass-transition singularity.[9]

In order to dwell further on this crucial result, covering a similar temperature range, we have performed a neutron TOF experiment on the same deuterated PB sample using the spectrometer IN6 at the ILL. In order to compare with the NSE results we have integrated the energy-converted time-of-flight data $S(\vartheta,\omega)$ (2ϑ is the scattering angle) over an energy window corresponding to the dynamic range of the NSE spectrometer (±200 μeV). Then we have normalized this "elastic" intensity to an integral of $S(\vartheta,\omega)$ (-1.5, 4 meV) corresponding to the bandpass of the NSE machine. Figure 3 presents the thus obtained elastic fraction $f^{\mathrm{TOF}}(Q,T)$ for an elastic Q of $Q = 1.76$ Å^{-1}. The temperature dependence at low T agrees very well with that of the spin-echo data. But near $T_c \approx 216$ K the elastic intensities continue to decrease and no plateau is found. However, from the relaxation spectra in Fig. 1 we know that a considerable part of the decay at higher temperatures occurs outside the ± 200-μeV window. In Fig. 2 this effect was taken into account by the extrapolation procedure of $S(Q,t)$ towares $t \rightarrow 0$. If we Fourier transform the relaxation function obtained by NSE and integrate it over the full dynamic range, we can correct the $f^{\mathrm{TOF}}(Q,T)$ values for the missing intensity outside the 200-μeV window. This leads to the corrected $f^{\mathrm{TOF}}(Q,T)$ points in Fig. 3. They level off around 220 K and form a plateau at $f^{\mathrm{TOF}}(Q,T) \approx 0.77$. Thus, in spite of the intrinsic difficulties in comparing the integrated $S(Q,\omega)$ data with the NSE $S(Q,t)$ data, we arrive at consistent results, supporting thereby the correctness of the applied extrapolation scheme.

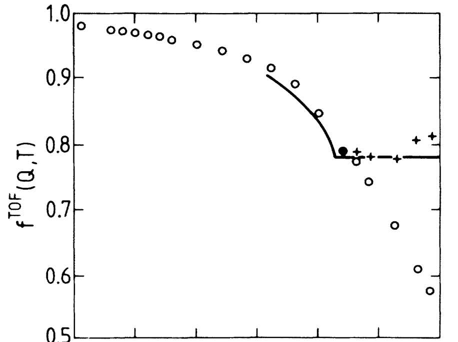

FIG. 3. Normalized elastic intensities from the neutron time-of-flight experiment (○). The corrected values for $f^{\mathrm{TOF}}(Q,T)$(+). The solid line represents the fit to the NSE data shown in Fig. 2.

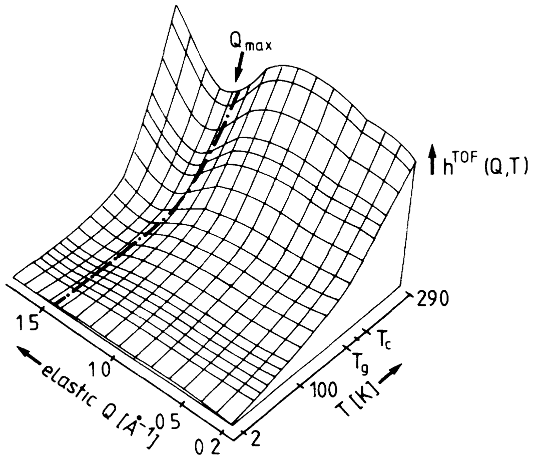

FIG. 4. Temperature and Q dependence of $h^{\mathrm{TOF}}(Q,T)$. The dot-dashed line indicates the position of $S(Q)_{\max}$ (Ref. 18).

Finally, Fig. 4 displays the Q and temperature dependence of the normalized "inelastic" intensity obtained in the time-of-flight experiment. By inelastic intensity we mean the scattered intensity within the energy window $0.2 < E < 4$ meV. This intensity is normalized to the total intensity within the $(-1.5, 4$ meV$)$ range. The thus obtained inelastic intensity $h^{\mathrm{TOF}}(Q,T)$ is a measure for the inelastic fraction $h(Q)$ of Eq. (2). At higher temperatures $h^{\mathrm{TOF}}(Q,T)$ oscillates in antiphase with $S(Q)$. It diplays a pronounced minimum where $S(Q)$ has its first maximum (indicated by $Q_{\max}$). Thus, the relative fraction of inelastic intensity is modulated in antiphase to $S(Q)$. We emphasize that this behavior is distinctly different from what is expected for sound-wave-like excitation, where this inelastic fraction would scale with $Q^2S(Q)/S(Q) \sim Q^2$.[17] It is, however, in good agreement with the out-of-phase oscillation of $h(Q)$ discussed in connection with Eq. (2). In closing, we note that above T_c the $h^{\mathrm{TOF}}(Q,t)$ values contain contributions from the structural relaxation. In order to obtain the truly inelastic scattering, a similar correction procedure would have to be applied as discussed in connection with $f^{\mathrm{TOF}}(Q,T)$.

Summarizing, our experiments verify the mode-coupling prediction of a critical decrease of the elastic spectral contribution approaching a critical temperature T_c. They are in very good agreement with a $(T_c - T)^{1/2}$ decrease of the nonergodicity parameter below T_c. Above T_c the spectral contribution of the structural relaxation depends only weakly on temperature. The resulting cusp in $f(Q,T)$ appears very close to the critical temperature obtained from a power-law fit of the temperature-dependent monomeric friction coefficient above T_c. With respect to the dependence on Q, the modulations of the normalized inelastic-scattering intensity occur in antiphase with the structure factor $S(Q)$. Theoretically, according to the mode-coupling theory, the $(T_c - T)^{1/2}$ law is directly connected to the bifurcation fold which underlies the glass transition. Therefore, our experimental observation of such a $(T - T_c)^{1/2}$ singularity strongly supports the applicability of the mode-coupling approach to the liquid-glass transition problem. The measured antiphase Q modulation agrees qualitatively with the expectation. A quantitative comparison would require a choice of coupling parameters describing the detailed molecular structure of the polymer—a task which is far beyond what can be done presently.

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