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Cusp-like temperature behavior of the nonergodicity factor in polybutadiene revealed by a joint light and x-ray Brillouin scattering investigation

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The dynamic structure factor of supercooled and glassy polybutadiene has been studied by Brillouin light and inelastic x-ray scattering in the momentum (q) region between 0.04 and 4 nm^{-1}. The joint analysis of the spectra allows one to access a very large frequency range ($\approx 0.2-2000$ GHz), and poses severe constraints on the value of the parameters, thus overcoming the arbitrariness encountered in modeling a single-q spectrum. The nonergodicity factor—derived from the amplitude of the α relaxation—shows the square-root cusp predicted by the mode-coupling theory.

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I. INTRODUCTION

The study of density fluctuations in supercooled systems is of primary importance for the understanding of the dynamic anomalies related to the glass transition phenomenon. In recent years considerable advances have been made in the comprehension of the early stage of the supercooling of liquids, thanks to the development of mode coupling theory (MCT),[1] whose predictions have been favorably tested in a number of real and simulated systems . MCT describes the slowing down of the structural dynamics of a liquid in terms of a nonlinear coupling between density fluctuations which, eventually, causes a structural arrest at a critical temperature T_c. A number of peculiar behaviors are predicted by MCT in its idealized version, such as a power-law divergence of the structural relaxation time and the square-root singularity in the normalized amplitude of this relaxation. Though the MCT has been developed to model the behavior of simple liquids, these singularities are robust enough also to be detectable in complex systems, such as polymers, showing the *universal* character of the MCT.[1]

Polybutadiene (PB) is one of the first polymers for which a positive test of MCT was performed by neutron scattering in the high-q limit.[2–4] Neutron spin echo also allowed the study of the merging of structural and secondary relaxations of PB.[5] On the other hand, in the low-q region characteristic of Brillouin light scattering (BLS), only indirect indications were found of the MCT critical temperature. In particular, no signature could be revealed of the square-root singularity in the temperature behavior of the nonergodicity factor.[6,7]

A possible reason for the discrepancy between the results of these high-q and low-q investigations could be found in the existence of intramolecular relaxation channels, that could be strongly coupled to the low-q density fluctuations. Previous analyses of the BLS spectra of PB, similarly to many other glass formers, were performed using a single relaxation function. This approximation is obviously too crude in case of coexistence of structural and thermally activated secondary relaxations, and it can profoundly affect the results of the analysis. It must be noted that the presence of a secondary relaxation of intramolecular nature is quite common in molecular glass-forming systems, even in low molecular weight ones, like o-terphenyl (oTP).[8] On the other hand, the introduction of a second relaxation in the analysis of BLS spectra considerably increases the number of free parameters in fitting procedure, and the meaning of the fit itself quickly fades out.

In this work—taking advantage of the recently developed inelastic x-ray scattering (IXS) technique—we overcome the previous difficulties in the description of the rich pattern of relaxation processes of PB. Indeed, the joint analysis of the IXS and BLS spectra considerably enlarge the accessible frequency window, and gives the opportunity of using more realistic models for the dynamic structure factor. In the present work we use a simple two-step memory function for the density fluctuation variable, and show that it adequately represents the dynamics of supercooled PB in the whole exchanged momentum (q) region 0.04 $\text{nm}^{-1} < q < 4$ nm^{-1} covered by BLS and IXS. As a result of this analysis we verify the existence of a cusplike behavior in the temperature dependence of the nonergodicity factor f_q in the $q \rightarrow 0$ limit. This result complements the similar results obtained at high q,[2–4] thus supporting the universality of the MCT.

II. EXPERIMENTAL RESULTS

The utilized sample was deuterated 1,4-polybutadiene (PB) $(CD_2\text{-}CD{=}CD\text{-}CD_2\text{-})_n$, characterized by a molecular weight 25.000, prepared by anionic polymerization. It is the same sample used for a previous x-ray[9] and neutron-scattering investigation.[10]

The Brillouin spectra were collected in the temperature range 30–328 K, that is from the liquid down to the glassy phase ($T_g = 178$ K) using a Sandercock type $(3+3)$-pass

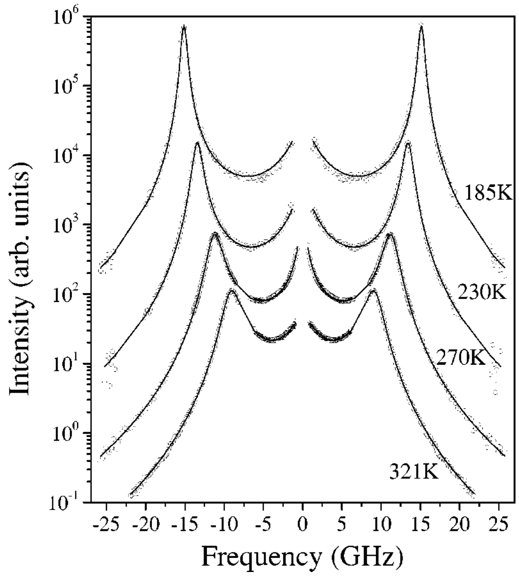

FIG. 1. Isotropic Brillouin light spectra of supercooled deuterated polybutadiene obtained at the indicated temperatures. The frequency region around the elastic peak and around the ghosts of the Fabry-Perot response function have been blanked, and were not used in the fitting procedure.

tandem Fabry-Perot interferometer. Polarized $I_{\parallel}$ spectra and depolarized $I_{\perp}$ spectra were recorded in the backscattering ($q\approx 0.04\ \mathrm{nm}^{-1}$) geometry and the isotropic spectra, proportional to the dynamic structure factor $S(q,\omega)$, were obtained as $I_{\rho\rho}=I_{\parallel}-r^{-1}I_{\perp}$. The depolarization ratio r has been determined using the procedure reported in Ref. 11. Selected $I_{\rho\rho}$ spectra obtained at different temperatures are reported in Fig. 1. The overall instrumental resolution was ≈ 100 MHz. The use of a narrow band filter and the negligible dark counts of the detector allows us to obtain a reliable signal up to twice the frequency of the Brillouin peak resonance as well as in the more important Mountain peak region, situated below the Brillouin peak.

The inelastic x-ray experiment was carried out at the very high energy resolution IXS beamline (ID16)[12] at the European Synchrotron Radiation Facility using the Si(11 11 11) reflection for the monocromator and for the analyzers. In this configuration the energy resolution is ≈ 1.5 meV. In IXS experiments the collected spectra are directly proportional to the atomic number density fluctuation $S(q,\omega)$. The IXS spectra $I_{\rho\rho}$ have been collected in the 50–335-K temperature range and, for each temperature, the q values spanned a range between 1 and 12 nm^{-1}. The total q resolution was set to 0.2 (0.4) nm^{-1} for $q \leqslant (>) 2\ \mathrm{nm}^{-1}$. The collected data were normalized to the intensity of the incident beam and the empty cell contribution as well as the electronic background were subtracted from the spectra. As an example, IXS spectra obtained at $T=249$ K are shown in Fig. 2 at the indicated q values together with the BLS spectrum at the same temperature.

III. DATA ANALYSIS

On a qualitative ground all the BLS spectra show a linewidth (Γ_{app}) of the Brillouin peaks (located at ω_{app}) larger

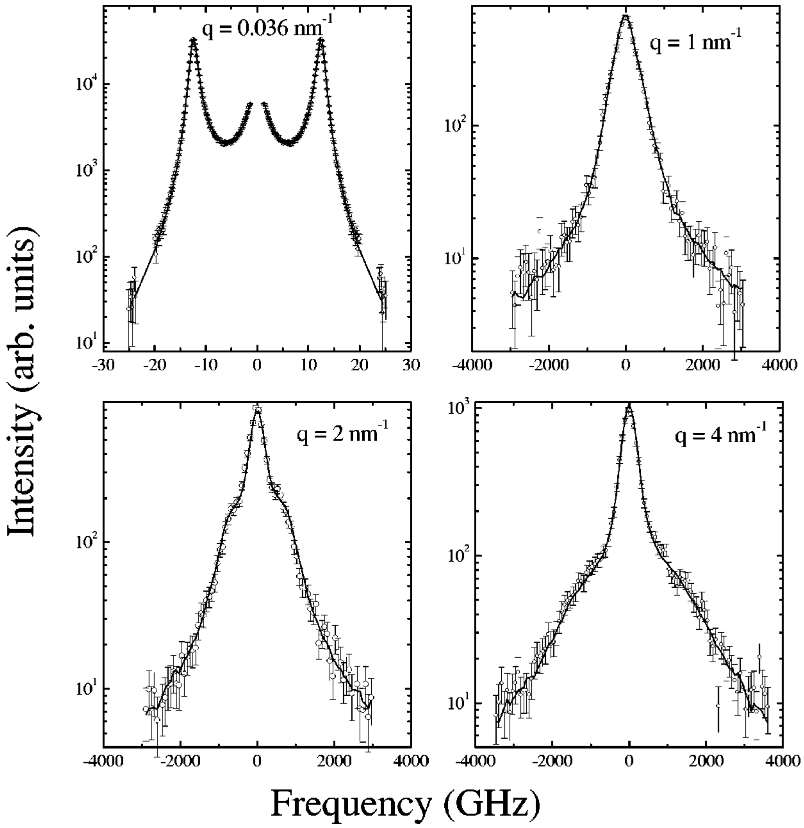

FIG. 2. Density fluctuation spectra of supercooled deuterated polybutadiene obtained by light ($q=0.036\ \mathrm{nm}^{-1}$) and x-ray ($q=1$, 2, and 4 nm^{-1}) scattering at $T=249$ K.

than the instrumental function and a non-negligible quasielastic (Mountain) contribution (see Fig. 1), a clear indication of the presence of a relaxation process. This feature is present also around and below T_g, where the α process characteristic time τ_α obeys $\tau_\alpha \omega_{app} \gg 1$ and cannot affect neither the Brillouin linewidth nor the Mountain region; we thus conclude that some secondary relaxation process is active in the system.

In order to extract quantitative information from the BLS and IXS spectra, we model the shape of the dynamic structure factor according to the *generalized hydrodynamics* formalism:[13,14]

$$I_{\rho\rho}(q,\omega)=\frac{M_T I_0}{\pi\omega}\,\frac{M''(\omega)}{[\omega^2\rho_M/q^2-M'(\omega)]^2+[M''(\omega)]^2}. \tag{1}$$

Here ρ_M is the mass density, I_0 is a proportionality factor, M_T is the isothermal modulus, and $M(\omega)=M'(\omega)-iM''(\omega)$ is the generalized longitudinal acoustic modulus. To model the latter quantity we follow the same guess recently proposed by some of us to represent the generalized longitudinal modulus in both epoxy systems and oTP, which are examples of molecular glass formers where a secondary relaxation process was also clearly revealed.[8,11] The function $M(\omega)$ is written as[15]

$$M(\omega)=M_\infty+\frac{\Delta_f}{(1+i\omega\tau_f)^{\beta_f}}+\frac{\Delta_\alpha}{(1+i\omega\tau_\alpha)^{\beta_\alpha}}+i\omega\eta_\infty, \tag{2}$$

where τ_α, β_α, and τ_f, β_f are the relaxation times and stretching parameters of the structural and secondary relaxations, respectively, $\Delta_f=(M_{\infty\alpha}-M_\infty)$, $\Delta_\alpha=(M_0-M_{\infty\alpha})$, $M_\infty=\rho_M c_\infty^2$, $M_{\infty\alpha}=\rho_M c_{\infty\alpha}^2$, and $M_0=\rho_M c_0^2$ are the high-, intermediate-, and low-frequency values of the longitudinal modulus, respectively, corresponding to the high- (c_∞), intermediate- ($c_{\infty\alpha}$) and low- (c_0) frequency values of the longitudinal acoustic velocity. The relaxation processes characterized by a time so short to be out of the experimental frequency window are considered as *instantaneous* and their effects are described by the unrelaxed viscosity η_∞.

In summary, our phenomenological model includes the *instantaneous* process, one fast secondary relaxation, the structural relaxation, and the thermal diffusion mode. All these processes are, in principle, characterized by q-dependent parameters. Although Brillouin light spectra are taken in a q region well inside the hydrodynamic regime, IXS spectra are just at the border where the q dependence starts to play a role. Our choice of considering this q dependence as negligible is motivated by two main reasons, i.e., that the IXS spectra included in the analysis are characterized by a linear dispersion of the frequency of LA peaks (q independence of the velocity of sound) and that, where a direct comparison was possible, the values of η_∞ were also shown to be q independent within the experimental error. Also in this favorable condition, the number of parameters needed for describing the spectrum is considerably high. As a whole, we have nine relevant parameters, i.e., M_∞, $M_{\infty\alpha}$, M_0, M_T, τ_α, τ_f, β_α, β_f, and η_∞, which is too much for a single Brillouin spectrum. This is the main reason which has discouraged, up to now, an analysis of BLS spectra with more than a single stretched relaxation. Here, to overcome this difficulty, we simultaneously fit, at each temperature, BLS and IXS spectra up to exchanged q values of 4 nm^{-1}. In this way, we extend the experimental frequency window to the range 0.2–2000 GHz, large enough to discriminate the different relaxation processes. Moreover, to reduce the number of free parameters, we adopt the following procedure: (i) The full spectrum analysis is performed at temperatures higher than T_g only, i.e., in the equilibrium phase of the system. At lower temperatures the possible presence of residual elastic stress in the sample, and the lack of thermodynamic data presently discourage such a detailed analysis. (ii) The values of c_0 have been fixed to those estimated by ultrasonic measurements in the hydrogenated sample, rescaled by the constant factor 0.96, which corresponds to the scaling factor obtained from the values of sound velocity measured by BLS in the deuterated and hydrogenated samples.[16] We thus used $c_0=[1525-3.09T(°\mathrm{C})]\mathrm{m/s}$. (iii) The values of the isothermal sound velocity c_T are obtained by the adiabatic ones c_0 through the usual relationship $c_0^2/c_T^2=\gamma$, where the value of γ has been taken from the correspondent state relationship between γ and T/T_g for amorphous polymers.[18] In this way for γ we obtain a value of 1.3 at $T=321$ K, which decreases with decreasing temperature and reaches a value of 1.06 at the glass transition of PB. (iv) The values of the stretching parameters β_α and β_f are fixed to the average value $\beta=0.3$ that is the mean value of these parameters obtained after a first round of full spectrum fits and consistent with the value obtained by an independent analysis of the temperature dependence of frequency position and linewidth of Brillouin peaks reported in Ref. 16 (v) The value of τ_α has been considered as a free parameter for $T \geqslant 249$ K only. At lower temperatures the contribution of the structural relaxation to the spectrum has been considered as a δ function centered at zero frequency with amplitude $I_0(1-M_0/M_{\infty\alpha})$. We note that, even in this unfavorable condition, the spectra provide enough information to give uncorrelated values for the whole set of fitting parameters, apart from τ_α. In fact, M_∞ is mainly determined by the position of Brillouin peaks in IXS spectra, η_∞, from their linewidth τ_f, and β from the shape of Brillouin light spectra, M_0, from ultrasonic measurements and $M_{\infty\alpha}$ (i.e., $1-M_0/M_{\infty\alpha}$) from the elastic to inelastic integrated intensity ratio of IXS spectra together with the shape of the BLS spectrum.

The full lines in Figs. 1 and 2 show the results of the joint fit of Eq. (1) on BLS and IXS spectra at $T=249$ K, and on BLS spectra at different temperatures. The corresponding parameters are reported in Table I. The quality of the fits is very high, and gives further confidence to the generalized hydrodynamic model here adopted.

TABLE I. Parameters of the *joint* line shape fitting analysis of the BLS and IXS spectra of polybutadiene.

T (K)	$c_{\infty\alpha}$ (km/s)	c_∞ (km/s)	τ_α (10^{-9} s)	τ_f (10^{-9} s)	η_∞/ρ (10^{-3} cm^2 s^{-1})
187	2.47	2.67	–	0.24	6.9
200	2.35	2.35	–	0.16	6.5
217	2.23	2.56	–	0.14	6.3
230	2.11	2.47	–	0.12	6.8
249	2.00	2.41	8.3	0.088	6.7
270	1.95	2.27	0.47	0.035	6.5
297	1.84	2.19	0.20	0.026	6.9
308	1.80	2.17	0.24	0.019	5.1
321	1.73	2.11	0.10	0.018	5.6

IV. DISCUSSION

Here we concentrate on the main result of the present analysis, i.e., the temperature dependence of the nonergodicity parameter $f(q)$ (see Fig. 3). The nonergodicity parameter in the low-q limit has been evaluated from relaxed and unrelaxed values of the longitudinal modulus *relative to the structural relaxation* $f(0)=1-M_0/M_{\infty\alpha}$. In Fig. 3 it is evident the presence of a discontinuous behavior not far from the critical temperature $T_c=216$ K estimated by previous neutron scattering investigations of PB.[2–4] Mode-coupling theory predicts that the low-temperature part $T<T_c$ is described by the square-root behavior $f(q,T)=f(q)+h(q)\sqrt{(1-T/T_c)}$, and the high-temperature region to be temperature independent $f(q,T)=f(q)$. The fit of this theoretical expectation to the data of Fig. 3 gives $T_c=224\pm5$ K, $f(0)=0.37\pm0.01$, and $h(0)=0.23\pm0.03$. This cusplike behavior was previously observed in PB by neutron scattering but never before by light scattering to our knowledge. In fact, the temperature dependence of $f(0)$, obtained in previous works on hydrogenated samples,[6,7] shows a flat behavior with no signature of square-root singularities. We can now attribute those results to the poor choice of the relaxation function, based on a single relaxation ansatz. PB, similar to other *real* glass-forming systems, is affected by a strong secondary relaxation process of intramolecular nature, which is not included in MCT. Indeed, we have recently given evidence of the existence of a fast secondary relaxation in PB by a careful analysis of frequency position and linewidth of Brillouin light spectra at temperatures lower than T_g.[16] The value of the activation energy we found, $E_a=7.2\pm0.6$ kJ/mol, is not far from 8 kJ/mol reported by Gee and Boyd[17] for the rotation around both $-\mathrm{CH_2}-\mathrm{CH}=$ bonds (α bonds) of PB backbone. It is now clear that trying to fit the spectra by a single relaxation function above T_g, where both α and fast processes coexist, one obtains somewhat average parameters which are not able to put into evidence the peculiarities of the structural relaxation alone. The presence of two relaxations in Eq. (2), although still a crude approximation of the spectral components at high frequencies, is good enough to grasp the main peculiarities of the structural dynamics of the system. In fact, the rather small difference of 3–8 K in the value of T_c with respect to that obtained by neutron scattering could be attributed to the approximation introduced by the phenomenological model of Eq. (2).

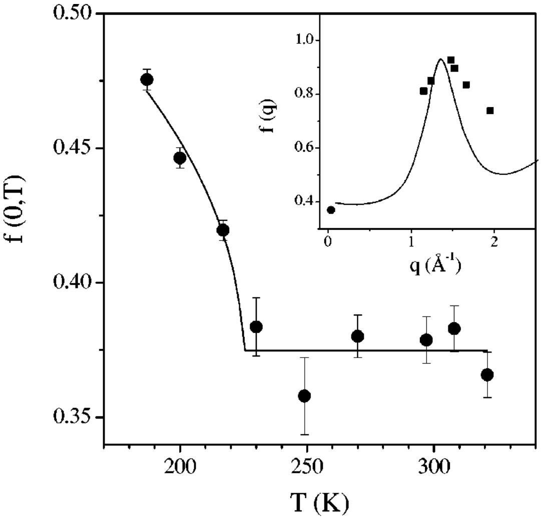

FIG. 3. Temperature dependence of the nonergodicity parameter of PB obtained by the joint analysis of BLS and IXS spectra. The inset shows the q behavior of $f(q)$ obtained in the hydrodynamic limit (circle) and by neutron spin echo measurements (Ref. 2) in the high-q region (squares). The full line is proportional to the static structure factor measured by neutron scattering at $T=270$ K (Ref. 19).

A further consistence with the predictions of MCT comes from the q dependence of the nonergodicity factor shown in the inset of Fig. 3. In fact, it can be seen that it oscillates in phase with the static structure factor, consistent with the MCT predictions for simple liquids. The fact that MCT succeeds in describing the center-of-mass dynamics of polymers and more generally of complicated molecular systems, as recently confirmed by simulations of liquid water,[20] strongly supports the existence of a universality underlying the dynamics of supercooled liquids.

V. CONCLUSIONS

In conclusion, we have here reported on a joint analysis of BLS and IXS spectra, allowing us to study the dynamics of density fluctuation of a supercooled system in the 10^8–10^{12}-Hz frequency range. Thanks to this very wide accessed frequency region, evidence is given of the existence of at least two relaxation processes responsible for acoustic loss: the usual α process and a secondary relaxation process whose characteristic time lies in the picosecond region. The structural relaxation shows the fingerprint of the mode-coupling dynamics and, in particular, the square-root singularity of the nonergodicity factor. The evidence of this square-root cusp from the spectrum of density fluctuations in the hydrodynamic regime indicates the universal behavior of supercooled systems, and supports their description in terms of the mode-coupling theory.

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[14] To account for the asymmetry between the Stokes and anti-Stokes sides of the IXS spectra, in the fitting procedure we empirically multiply the classical $I_{\rho\rho}$ by the factor $[n(\omega)+1]\hbar\omega/k_BT$, where $[n(\omega)+1]=[1-\exp(-\hbar\omega/k_BT)]^{-1}$.

[15] In the present work we use the same formalism as Ref. 11. Moreover, the generalized modulus $M(\omega)$ used here is related to the memory function $m_q(t)$ of Ref. 8 via $M(\omega)=i\rho/q^2\omega m_q(\omega)+M_o$, where M_o is the adiabatic low-frequency modulus. Finally, the thermal relaxation takes place at frequencies much smaller than those investigated here, and its contribution to the spectrum has been approximated by a δ function with area $I_0(1-M_T/M_0)$.

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