

Secondary relaxation in the glass-transition regime of *ortho*-terphenyl observed by incoherent neutron scattering

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We report on incoherent-neutron-scattering measurements in the supercooled regime of the van der Waals liquid *ortho*-terphenyl. A secondary localized relaxational process on the picosecond time scale is found. In accordance with mode-coupling theories of the glass transition, the relaxational dynamics around a critical temperature T_c decomposes into two time regimes.

I. INTRODUCTION

Mode-coupling theory of simple classical fluids¹⁻³ predicts the existence of a dynamical instability at some temperature T_c above the calorimetric glass transition temperature T_g . This contribution to the understanding of the nature of the glass transition added a new perspective to an old puzzle: is there a "real" transition phenomenon (i.e., a phase transition) behind the conventional glass-forming process around T_g ?⁴ In the past there have been several attempts to describe an idealized glass transition as a structural phase transition in the limit of infinitely slow cooling rates.^{5,6} The corresponding transition temperature would thus be located below the calorimetric T_g . These theories can only describe macroscopic and integral properties as the shear viscosity. Mode-coupling theory offers a fully dynamical picture of the supercooled liquid state. On microscopic dimensions this theory locates the temperature where the molecular dynamics changes from liquidlike to glasslike behavior in the supercooled liquid regime, well above T_g . The phenomena around T_g are explained as simple freezing of the structural relaxation on the experimental time scale. In a simplified version, the theory predicts a strict ergodic to nonergodic transition at T_c . This behavior has not been found in real systems and is caused by an overestimation of the trapping of molecules in cages formed by neighboring molecules, the well-known cage effect of liquid dynamics. A more realistic extension of the theory cuts off this sharp transition, but introduces a change in the transport mechanism near T_c from liquidlike behavior above T_c to a solidlike hopping mechanism below T_c .⁷ Remnants of the sharp transition may strongly influence the molecular dynamics near T_c . Thus, the predicted anomaly may be of relevance for real laboratory glass-forming systems.

Several classes of glass formers have been investigated by neutron-scattering techniques, as neutron scattering is

ideally suited to resolve molecular-density fluctuations on those microscopic length scales and mesoscopic time scales which are dealt with by theory. Strong evidence for a dynamical anomaly above T_g was found in the following systems: the ionic glass $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$,⁸ the polymer glass polybutadiene,⁹ and the organic van der Waals system tri- α -naphthylbenzene.^{10,11} A similar dynamic behavior was found in the globular protein myoglobin.¹² In all cases, as predicted by theory, two dynamical processes were observed above the characteristic temperature T_c in addition to the elementary phononlike microscopic excitations: a fast local relaxational process, called the β process, which is associated with the mentioned cage effect, and a slower, strongly temperature-dependent process, called α relaxation, which is identified as the structural relaxation.

In this paper we present an analysis of the fast β relaxation in a van der Waals glass-forming system where it is attempted to separate vibrational and relaxational excitations accurately. van der Waals glasses are of special interest since, in our opinion, they represent the best experimental approximation to the hard-sphere and Lennard-Jones systems treated theoretically. In recent work we investigated the van der Waals liquid *ortho*-terphenyl (OTP) using high-resolution quasielastic neutron scattering.^{13,14} The main emphasis was on the study of the slow α relaxation. Several predictions of the mode-coupling theory could be verified. An anomaly in the Debye Waller factor (DWF) at $T_c = 290 \pm 5$ K could be established and the α relaxation was found to follow the time-temperature shift principle. The faster β relaxation was monitored only indirectly via a static property, the anomaly of the DWF. Here we report on incoherent-neutron-scattering measurements which directly monitor the dynamics of the β relaxation.

The remainder of the paper is organized as follows: After mentioning some experimental details (Sec. II), we present a detailed analysis and discussion of the results

(Sec. III). Emphasis is put on (i) the problem of factorizing of the Q and ω dependences of the dynamic structure factor, (ii) the combination of our present time-of-flight (TOF) data with earlier measured high-resolution data in the time domain, and (iii) dynamic susceptibilities as obtained from the measured data and their discussion in terms of mode-coupling theory. The paper concludes (Sec. IV) with some critical remarks on the difficulties to obtain quantitative results when testing mode-coupling theory.

II. EXPERIMENT

OTP, bought from Aldrich, was purified by vacuum distillation and recrystallization. The sample environment used has been described in detail in Ref. 13. The experiments were performed on the TOF spectrometer IN6 at the Institut Laue-Langevin in Grenoble, France. The wavelength of the incident neutrons was set to 5.1 \AA , resulting in an elastic energy resolution of $70 \text{ } \mu\text{eV}$ (FWHM). Thirty-eight scattering angles from 10.7° to 114.3° were recorded. Thus, the covered Q range for elastic scattering was $0.23\text{--}2.06 \text{ \AA}^{-1}$ with an average spacing ΔQ of 0.05 \AA^{-1} . We recorded TOF spectra at 2, 160, 200, 245, 290, 293, 298, 305, 312, 320, 327 K. All spectra have been corrected for absorption, self-shielding, and sample container scattering using standard ILL programs. Because of the high sample transmission of 0.87, multiple-scattering effects were neglected.

III. RESULTS AND DISCUSSION

Some resulting spectra are presented in Fig. 1 for temperatures well below T_g ($=243 \text{ K}$) up to temperatures near the melting point ($T_m = 329 \text{ K}$). At 200 K, only inelastic-scattering contributions due to vibrational excitations are visible as a structureless peak at 1.4 meV, merging with the elastic scattering. Around T_g , additional scattering intensity accumulates at low energies

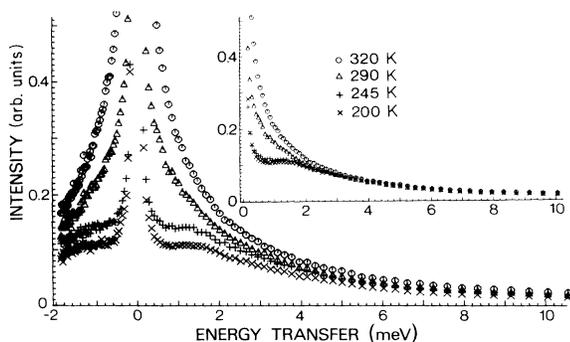


FIG. 1. Incoherent neutron spectra of protonated OTP as measured on the time-of-flight spectrometer IN6 for a momentum transfer of $Q_{\text{el}} = 1.4 \text{ \AA}^{-1}$ and various selected temperatures. Inset: Same spectra but Bose and Debye-Waller factors scaled to their values of 200 K. Note the coincidence of all scaled spectra for energy transfers $\geq 4 \text{ meV}$.

($E \leq 3 \text{ meV}$). This contribution grows in intensity as the temperature is increased. At the highest temperature only a broad quasielastic-scattering pattern is observable. To demonstrate this low-energy behavior more clearly, the effect of thermal occupation numbers and changes in the DWF are removed in the inset of Fig. 1. All spectra are scaled to a common temperature of 200 K with the proper ratio of Bose and Q -dependent Debye-Waller factors. The temperature dependence of the DWF was extrapolated from the elastic low-temperature DWF in Refs. 13 and 14 assuming a Debye behavior. The scaled spectra show the existence of a nonharmonic contribution for energies $\leq 3 \text{ meV}$ that increases with temperature. For larger energy transfers, the spectra coincide within experimental errors. This coincidence would be expected for harmonic lattice vibrations. Thus, the high-temperature spectra can be approximated by a nearly harmonic scattering background and additional nonharmonic contributions at low energies. The increased low-energy scattering occurs at the same temperature where an anomalous decrease of the DWF was observed.^{13,14} Thus, we can conclude that the lost elastic intensity reappears as inelastic scattering in the energy range $\leq 3 \text{ meV}$. This feature has been observed in several systems^{8–12} and has been attributed to the elementary β process described by mode-coupling theory.

The theory predicts a decoupling property for this relaxational mode since the spectral contribution should factorize into a purely frequency-dependent and a purely Q -dependent term:³

$$S^\beta(Q, \omega) = h(Q)g(\omega). \quad (1)$$

According to Eq. (1), the Q dependence will be the same for different frequencies. Our data confirm this prediction as the inelastic intensities for different energy transfer can be scaled to a common Q -dependent curve (Fig. 2).

The usually applied procedure in analyzing neutron spectra line shapes, namely, the comparison of the spectra with theoretical curves convoluted with the experi-

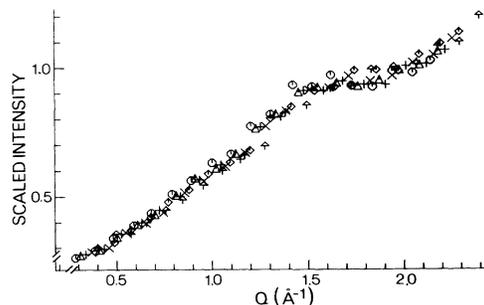


FIG. 2. Q dependence of the scaled inelastic intensities for 312 K: the inelastic intensities for different energy transfers are scaled to a common Q -dependent curve. For that purpose, the original TOF spectra have been interpolated into constant ω slices. Energy transfers: 0.59 (+), 0.845 (\times), 1.105 (Δ), 1.365 (\circ), 1.625 (\diamond), and 2.405 (\oplus) meV. The corresponding scaling factors are 0.261, 0.204, 0.174, 0.148, 0.127, and 0.079, respectively.

mental resolution function, is not applicable in the case of strongly undercooled liquids, especially when testing predictions of mode-coupling theory: Since three to four decades in frequency or time variation have to be covered to allow a detailed data analysis in terms of this theory, the dynamic window of just one instrument is too restricted to allow such an analysis^{3,8,13} with an acceptable significance. To cover the large dynamical range of relaxational processes in the glass-transition regime, we extended the dynamic window to lower energies by combining the present IN6 TOF data with former high-resolution measurements in the α regime.^{13,14} When combining data sets of different instruments, it is essential to remove instrumental resolution effects. These effects are highly instrument dependent and cause an incompatibility of data sets from different instruments. Therefore, the IN6 spectra were corrected for instrumental resolution effects by a standard fast-Fourier transform deconvolution, neglecting the time of flight as well as the time-focusing character of IN6. Due to these effects the instrumental resolution line shape depends on the energy transfer of the scattering process.¹⁵ Since we were mainly interested in the low-energy region, the time focusing was set on zero-energy transfer. With this setting the resolution profile in the spectral range of interest depends only weakly on the energy transfer. Thus, we assume that time focusing will not significantly distort the low-energy scattering pattern. The inelastic signal is not affected by resolution effects because it consists mainly of a broad unstructured peak with a width much larger than the instrumental resolution. The elastic scattering line shape of our sample at 2 K was chosen as resolution profile in this procedure. In the next step the spectra were interpolated to a constant Q scale. We restrict the discussion to the Q value of the first structure factor maximum [$Q_{\max} = 1.4 \text{ \AA}^{-1}$ (Ref. 16)] since we are interested in examining the dynamics on the length scale of nearest-neighbor distances.

One of the predictions of mode-coupling theory is the nonrelevance of the microscopic phonon excitations for the mesoscopic relaxations characterizing the glass-transition regime. Nevertheless, a problem of the theory is that the commonly used schematic models do not describe microscopic excitations realistically. As can be seen from the low-temperature spectra in Fig. 1, phonon-like excitations exist even at the lowest energies resolved in our experiment. An obvious way to compare our results of the β relaxations with theory is therefore to remove the phonon part in the experimental spectra in the following way. The inset of Fig. 1 shows that the β relaxation and vibrational scattering are nearly uncoupled dynamical processes. Therefore, we can assume the statistical independence of the two processes and write the intermediate-scattering function as a product

$$I(Q, t) = I^\beta(Q, t) I^{\text{phon}}(Q, t). \quad (2)$$

This simple scattering function suggests a data analysis in the time domain. Such an analysis will also simplify the combination of the presented data with previous high-resolution measurements which have already been analyzed in the time domain.¹⁴ After Fourier transforming

the data into the time domain, the harmonic background was removed by deconvolution. For this purpose we measured a TOF spectrum at 160 K, where the existence of any relaxational modes can be safely excluded, and deconvoluted it for the instrumental resolution. It was then scaled to the interesting temperature by the proper ratio of Bose occupation numbers and DWF as explained in connection with Fig. 1. The corresponding time signal obtained from Fourier transformation of the so scaled low-temperature spectrum was considered to yield the phononic part of the high-temperature intermediate-scattering function. The phonon-corrected high-temperature time signal was evaluated by dividing the high-temperature time signal by the scaled low-temperature time signal. The resulting intermediate-scattering functions, shown as symbols in Fig. 3, turned out to be almost unaffected by our phonon-correction procedure for time larger than 3 ps. Figure 3 clearly shows a relaxational decay on a time scale of roughly 1 ps for all temperatures. The time scale of this process is only weakly temperature dependent.

As a first attempt to interpret these time data in terms of the mode-coupling β process, we try to fit the TOF $S(Q, t)$ data with the predicted power law³

$$S(Q, t) = f_Q^c + h_Q t^{-a}, \quad (3)$$

which should be valid for temperatures close to T_c , e.g., at 290 and 298 K. Here, the main problem is the uncertainty in the absolute amplitude f_Q^c . One tentative way to proceed is to fit f_Q^c, h_Q and the exponent a freely and look for consistency with data determined otherwise. To give an impression, we present in the inset of Fig. 3 curves which have been fitted by Eq. (3) using an exponent a obtained via the transcendental equation³

$$\Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b), \quad (4)$$

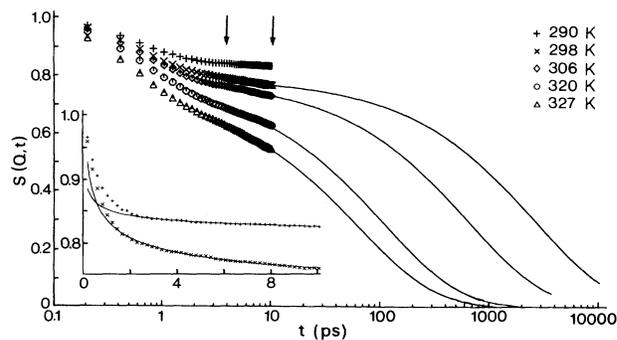


FIG. 3. Temperature dependence of the intermediate-scattering function $S(Q, t)$ for $Q_{\text{el}} = 1.4 \text{ \AA}^{-1}$. The solid curves are Kohlrausch fits to master functions obtained from high-resolution backscattering data, the symbols show the IN6 data. The two arrows indicate the range in time used to fix the Kohlrausch function amplitude in order to match the master functions and IN6 data. Inset: Fit of $S(Q, t)$ for two temperatures (+: 290 K; \times : 298 K) with the critical power law Eq. (3). The exponent a is fixed to the value 0.3 as obtained indirectly from the study of the α process (Ref. 14).

which relates the exponent a of the fast β relaxation to the critical exponent b dominating the slower α relaxation. With $b = 0.525$ as deduced in Ref. 14, Eq. (4) yields $a = 0.3$. It should be made clear that such fits can only state that a parametrization of the experimental data in terms of Eq. (3) is indeed possible, which is consistent with theory. The actual value of the exponent a depends most sensitively on f_Q^c . For instance, fitting the 290-K data with f_Q^c fixed yields $a(f_Q^c = 0.791) = 0.25$, $a(f_Q^c = 0.804) = 0.32$, $a(f_Q^c = 0.816) = 0.6$, where $f_Q^c = 0.804$ corresponds to the best value obtained by unrestricted fits. As Fig. 3 shows, there are deviations below 2 ps which might be attributed to low accuracy in accounting for the phononlike behavior in the deconvolution procedure [Eq. (2)] or to the limit of the validity range of Eq. (3). We also cannot exclude line-shape distortions because of the time-focusing character of the TOF instrument IN6. This discussion demonstrates that the dynamic range of less than one decade is certainly not sufficient to allow one to determine a critical behavior unambiguously.

In order to circumvent these problems, we choose a data analysis which does not require f_Q^c as input and which allows the extension of the dynamic range. For this purpose the TOF data were extended to longer times by a Kohlrausch fit to master functions obtained with IN13 backscattering data,¹⁴ shown as drawn curves in Fig. 3. To assure a smooth overlap, the absolute intensities of the Kohlrausch fits have been adjusted to the intensities of the TOF spectra. This combination can be justified in the temperature range $298 \leq T \leq 327$ K, where the measured IN13 data could be well described by a Kohlrausch law and scaled to a common master curve. For $T \leq 293$ K, the α process could no longer be resolved by IN13. Therefore, we are not allowed to extend the combination below 298 K.

The combined TOF and backscattering data show a two-step decay for all temperatures: a fast relaxational process (β process), which was found to be localized,^{10,13,14} and a slower strongly temperature-dependent process (α process), which was identified as structural relaxation.^{13,14} Approaching higher temperatures, the two processes merge.

This decomposition of the relaxational dynamics into two time regimes can be even better visualized in the dynamic susceptibility $\chi_Q''(\omega) \sim (\omega/k_B T) S(Q, \omega)$. Converting the time signals (Fig. 3) into rescaled susceptibilities $\hat{\chi}'' = \chi''/\chi''_{\min}$, we find that the resulting curves coincide around the minimum separating two dynamical regimes (Fig. 4). These findings, the clear scaling property at the minimum, and the decomposition into two frequency regimes close above T_c are a qualitative confirmation of basic predictions of mode-coupling theory of the glass transition

Furthermore, mode-coupling theory predicts, for temperatures closely above T_c , the following critical power law for the T dependence of the locations E_{\min} of the susceptibility minima:³

$$E_{\min} \sim (T - T_c)^{1/(2a)}, \quad a < 0.5, \quad (5)$$

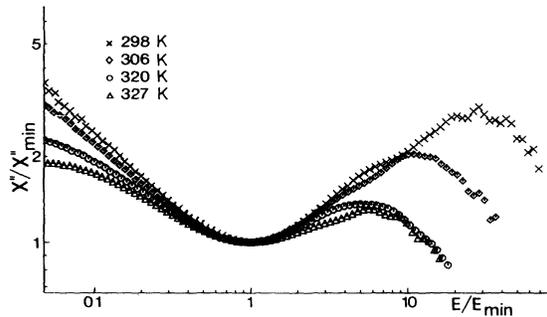


FIG. 4. Temperature dependence of the rescaled dynamic susceptibilities vs the rescaled frequencies at $Q = 1.4 \text{ \AA}^{-1}$. The susceptibilities show a scaling property in the minimum region.

where the exponent a is related to b via Eq. (4). Figure 5 shows a linearized plot of the minimum positions E_{\min}^{2a} vs T for two choices of a . Inspection of the data shows that the linearity seems to be well fulfilled except for the highest temperature point. Since the theoretical predictions hold only in a narrow range around T_c , we neglect this possibly too high temperature in the further discussion. It turns out that the previously derived value $a = 0.3$ obtained from Eq. (4) and $b = 0.525$ (Ref. 14) yields a T_c of 281 K, a value not compatible with our previous finding of $T_c = 290 \pm 5$ K.¹⁴ On the other hand, fixing T_c at 290 K results in $a = 0.45$, a value not compatible with our previous finding $b = 0.525$ (Ref. 14) in connection with Eq. (4). Whereas Fig. 5 alone suggests compatibility with theory, it also demonstrates that the data show no sensibility on the choice of the exponent a . Together with our previous results [$T_c = 290 \pm 5$ K; $a = 0.3$ (Ref. 14)], inconsistencies occur. Figure 5 demonstrates the problems encountered when trying to extract critical parameters from susceptibility data. We have made sure that the problems are not produced by our phonon correction since uncorrected data sets produce similar results. In view of the small set of usable temperatures, the

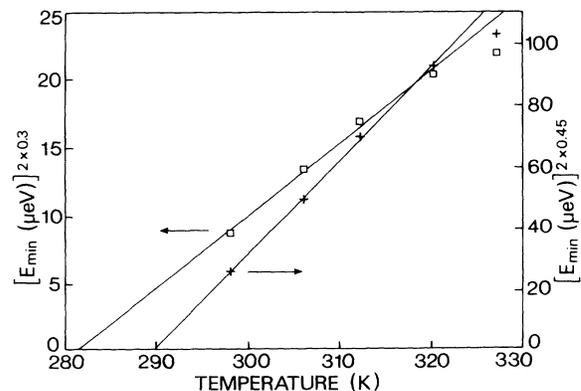


FIG. 5. Fits of the temperature dependence of the susceptibility minimum energy [Eq. (5)] plotted in a linearized way E_{\min}^{2a} vs T . Left scale: $a = 0.3$ (\square); right scale: $a = 0.45$ ($+$). For a detailed discussion see text.

limited statistical accuracy, and the unknown validity range of theory, there is not enough evidence to state a clear contradiction with theory.

We do not attempt to fit the susceptibility spectra since, in addition to the above-mentioned problems, there are even more possible sources for line-shape distortions: Since another Fourier transformation from time back into frequency domain is needed, an eventual mismatching of the two spectrometers will produce wiggles in the frequency domain. Furthermore, calculation of $\omega S(Q, \omega)$ will blow up errors at high frequencies. However, even without a quantitative analysis of $\chi''_Q(\omega)$, the qualitative features presented here, the two-step decay of $S(Q, t)$ and the minimum of the susceptibilities with a scaling property, are well enough established and will pass further scrutiny.

IV. CONCLUSIONS

In the glass-transition regime, the low-energy dynamics of OTP decomposes into a phononlike vibrational part with harmonic behavior and a strongly anharmonic part of the quasielastic line shape. The latter has been attributed to a fast relaxational process (β process). The experimental data were combined with results of a previously studied^{13,14} slower relaxation in the α regime. These combined data show a pronounced decomposition of the relaxational behavior into two dynamic regimes in the time as in the energy domain. The dynamical behavior of the β process was found to be Q independent. Its scaling property was exemplified by the minimum of the dynamic susceptibility.

The quantitative analysis of the TOF data is questionable. It has not been possible to use the susceptibility data for a line-shape analysis. For instance, a naive look at the high-frequency slope of the χ'' data at 298 K (see Fig. 4) suggests an exponent of $a \approx 0.4$. However, this actual value should not be taken too seriously because of the following points.

(1) An essential input of our data analysis is the assumption of a harmonic phonon background for which the data are corrected. It is not clear at all to which extent this assumption is justified. Anharmonicities might well distort the line shape in the supercooled liquid re-

gime. We believe that a possible way to account for the influence of phonons can be an appropriate inclusion of microscopic excitations by theory.

(2) It seems that in microscopic glass formers like OTP there is generally no sufficient significant time-scale separation between phonons and the β process.^{9,12}

(3) Another severe problem is the necessity to combine data taken at different spectrometers. The minima χ''_{\min} lie just in the energy range where TOF and backscattering overlap and none of the methods *alone* is able to establish the minimum. This range is most sensible to errors introduced by the necessary raw data corrections. There is no neutron-scattering spectrometer yet that meets the requirements of covering the necessary large dynamic range with a sufficient resolution and high flux. This shows that the required experiments are beyond what is presently feasible.

On the other hand, we have made sure that Fourier transformation, apart from some apparent high-frequency oscillations introduced by the already discussed mismatch between different instruments, is *not* the primary source of problems in the data treatment. The analysis of the temperature dependence of the susceptibility minima supports mode-coupling theory. It is not clear if discrepancies in the scaling exponents are caused by deviations from scaling in the system OTP or by the above-discussed problems in the data analysis. As we have pointed out, extraction of the critical exponents in the supercooled liquid regime is most delicate and requires further investigation. Our data support our previous interpretations in terms of a dynamical anomaly in the supercooled liquid regime where the β process plays the role of localized precursor fluctuations which desintegrate around T_c to long-range structural relaxations of the α process.

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