Dynamics in viscous orthoterphenyl: Results from coherent neutron scattering

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We have measured coherent neutron scattering from deuterated orthoterphenyl on a spin echo and a backscattering spectrometer. In agreement with mode coupling theory, pair correlations decay in two steps and follow the same scaling laws as those found previously for self-correlations. The temperature evolution of the intermediate plateau is compatible with the previously established $T_c = 290$ K. The spatial resolution has not been sufficient to fully resolve oscillations of parameters as functions of Q, which are predicted by mode coupling theory. Within this limitation, we find that the double peak structure of $S(Q)$ is not expressed in the nonergodicity parameter f_Q^c and that the de Gennes narrowing is missing.

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I. INTRODUCTION

The van der Waals liquid orthoterphenyl (OTP) is one of the best studied fragile glass formers where many thermodynamic and transport properties have been measured in the supercooled state [1–8]. The advent of a new theoretical approach, the mode coupling theory (MCT) of the glass transition [9–11], has drawn the attention of the experimentalists to the study of density correlation functions for collective motion $\Phi(Q,t)$ and for single-particle motion $\Phi^s(Q,t)$, which should exhibit a particular scaling behavior and other anomalies in the vicinity of a temperature T_c above the caloric glass transition temperature T_g. We have considered OTP to be a good model system for experimental tests of the MCT because it consists of relatively small, weakly interacting molecules that could be shown [12] to be rigid on the time scale of dynamic neutron scattering. In a series of experiments [13–18] we have measured the single-particle correlator $\Phi^s(Q,t)$ by incoherent neutron scattering of OTP using different spectrometers in order to obtain information over the widest possible Q and t ranges.

Our main results [13–16] can be summarized as follows. In the supercooled liquid regime ($T < T_m = 329$ K) the single-particle correlator develops a two-step decay [15,16]. The plateau value $f_Q^s(T)$ (often addressed also as the Mössbauer-Lamb factor) separating the β relaxation at mesoscopic times from the α relaxation at long times was determined by elastic scattering [$S(Q,\omega=0)$] at temperatures where the long time decay was not resolved [13,14]. $f_Q^s(T)$ shows an anomalous decrease at $T \gtrsim T_g = 243$ K, consistent with the onset of a fast localized motion, identified as the β process of MCT and attributed to rattling motion of particles trapped in transient cages. Assuming a scaling law for the slow α relaxation, $f_Q^s(T)$ could be fitted by a $\sqrt{T_c - T}$ law and leads to identification of a cusp at a crossover temperature $T_c \approx 290$ K. Whereas the static structure factor $S(Q)$ changes only smoothly when crossing $T_c = 290$ K [17], $\Phi^s(Q,t)$ shows a critical slowing down of the dynamics when approaching T_c from above. In the α-relaxation regime the time-temperature superposition principle holds, the corresponding master curves being well described by a Kohlrausch function [14]. In the β-relaxation regime $\Phi^s(Q,t)$ was found to factorize into a Q-dependent amplitude and a Q-independent master function [15,16], as predicted by theory. Using this master function, the relaxation dynamics in the mesoscopic time window could be described well over several decades [16]. The time and amplitude scales were found to follow power laws indicating a $T_c = 290$ K, in agreement with the value obtained from the Mössbauer-Lamb factor measurements [16]. Reviews of our OTP neutron scattering results have been recently published in Refs. [18] and [19].

Meanwhile, some of our findings have been reproduced in a simulation of a model system mimicking OTP [20]. Strong additional support for a change in microscopic dynamics near T_c comes from a study of self-diffusion, which is found to decouple from viscosity: below 290 K, the Stokes-Einstein relation is no longer valid [21]. In a dynamic light scattering study of OTP covering a broad frequency range, it was demonstrated that an analysis with the idealized MCT is consistent with a $T_c = 290$ K, although other processes dominate the dynamics at high frequencies and below T_c [22].

In the present paper, we report on results from coherent neutron scattering experiments initiated in order to study the density correlation function for collective motion $\Phi(Q,t)$ near the glass transition. MCT predicts that the density correlation function in the β-relaxation regime between the time scales of microscopic excitations t_0 and structural relaxations τ_α can be formulated as

$$\Phi(Q,t) = f_Q^c + H_Q(T) g(t/t_\varepsilon), \quad t_0 \ll t \ll \tau_\alpha, \quad T > T_c \tag{1a}$$

$$H_Q(T) = h_Q c_0 \left| \left| \frac{T_c - T}{T_c} \right| \right|^{1/2}, \tag{1b}$$

$$g(t \lesssim t^*) = t^{-a} + A_1 t^a + A_2 t^{3a} + \cdots , \quad (1c)$$

$$g(t \gtrsim t^*) = B_0 t^b + (B_1/B_0) t^{-b} + \cdots , \quad (1d)$$

where $f_Q^c = f_Q(T_c)$ is the plateau value (also called the Debye-Waller factor) at T_c and $g(t)$ is a T- and Q-independent scaling function. The two exponents a and b, the coefficients A_i and B_i, and the crossover time t^* are tabulated [11] as functions of the exponent parameter λ. The expansions (1c) and (1d) match at $t = t^*$ within 1% if they are evaluated up to t^{5a} and t^{-b}, respectively. Thus the temperature dependence is introduced only by the amplitude factor $H_Q(T)$ and the time scale t_ε. $g(t)$ is universal in the sense that for a given substance it is predicted to be the same for any correlator that couples to density fluctuations, in particular $\Phi^s(Q,t) = f_Q^{c,s} + H_Q^s(T) g(t/t_\varepsilon)$ for the single-particle correlator, which is determined by incoherent neutron scattering. MCT predicts an important difference in the Q dependence of $\Phi(Q,t)$ and $\Phi^s(Q,t)$ for a hard-sphere system: Whereas $f_Q^{s,c}$ and H_Q^s [via h_Q^s; cf. (1b)] depend on Q rather smoothly, f_Q^c and H_Q (via h_Q) are found to oscillate in phase and out of phase with the static structure factor $S(Q)$, respectively. This Q dependence has been verified recently with high accuracy by coherent light scattering from a colloidal suspension of hard spheres [23]. It is therefore interesting to see whether similar effects can also be observed on a molecular level.

II. NEUTRON SCATTERING

The quantity central to our work is the density autocorrelation function $\Phi(Q,t)$, i.e., the intermediate scattering function $S(Q,t)$ normalized to its initial value, the static structure factor $S(Q)$ [38],

$$\Phi(Q,t) = \frac{S(Q,t)}{S(Q,t=0)} = \frac{1}{S(Q)} \frac{1}{N} \sum_{i,j}^{N} \langle b_i b_j e^{i\mathbf{Q}\cdot\mathbf{r}_i(0)} e^{-i\mathbf{Q}\cdot\mathbf{r}_j(t)} \rangle , \quad (2)$$

as it completely specifies the dynamics of an N-particle system by correlating the positions of particles $\mathbf{r}_i(0)$ with scattering power b_i at some initial time $t = 0$ with the positions of particles $\mathbf{r}_j(t)$ with scattering power b_j at some later time t. The density autocorrelation function $\Phi(Q,t)$ can be obtained by neutron scattering experiments either directly on neutron spin echo instruments or via the corresponding spectra $S(Q,\omega)$, i.e., the Fourier transform of the intermediate scattering function,

$$S(Q,\omega) = (1/2\pi\hbar) \int S(Q,t) e^{-i\omega t} dt = S(Q)(1/2\pi\hbar) \int \Phi(Q,t) e^{-i\omega t} dt , \quad (3)$$

using, e.g., backscattering or time of flight spectrometers. As the scattering lengths b_i vary from one nucleus to another owing to nuclear spin and/or the presence of isotopes the experimental neutron cross section $(d\sigma/d\Omega dE)$, i.e., the number of neutrons having a final energy between E and dE and scattered into the solid angle $d\Omega$, is generally composed of a coherent and an incoherent contribution

$$\left[\frac{d\sigma}{d\Omega dE}\right] \sim (\bar{b})^2 S(Q,\omega) + \{\overline{b^2} - (\bar{b})^2\} S_{\text{inc}}(Q,\omega) , \quad (4)$$

where the overbar denotes averaging over the distribution of nuclear spins and isotopes. The incoherent spectrum S_{inc} is related to the density autocorrelation function for single-particle motion $\Phi^s(Q,t)$ in the same way that $S(Q,\omega)$ is related to $\Phi(Q,t)$ for collective motion [the summation in Eq. (2) performed under the condition $i = j$ and $S(Q)$ replaced by unity]. This feature of neutron scattering allows us to predominantly study either collective motion via coherent scattering or single-particle motion via incoherent scattering depending on the isotopic composition of the sample (e.g., protonated samples for incoherent scattering and deuterated species for coherent scattering; cf. sample preparation in Sec. III). When $\Phi(Q,t)$ does not decay to zero at long times, the long-time limit,

$$\Phi(Q, t \to \infty) = f_Q(T) , \quad (5)$$

is called a Debye-Waller factor [in the case of incoherent scattering it is called a Mössbauer-Lamb factor $f_Q^s(T)$]. Since the plateau value of MCT separating α and β relaxation appears as a Debye-Waller factor in neutron scattering experiments where the α relaxation is not resolved, both notations for $f_Q(T)$ are synonymous in the following.

III. EXPERIMENT

A. Sample preparation

Deuterated orthoterphenyl OTP-D_{14} was prepared and purified as described previously [12]. The purity of the sample was 99% as determined by mass spectrometry and gas chromatography [24]. With a deuteration ratio of 98%, the coherent scattering contributes about 84.5% to the total cross section. To avoid crystallization problems, OTP was sealed in soda lime glass capillary tubes with an inner diameter of 1 mm and a wall thickness of 0.04 mm. On the single-detector instrument IN11, the tubes were arranged in three parallel rows (59 tubes); on the multidetector instrument IN13, a hollow cylinder was approximated by placing tubes in three concentric rings (outer diameter 30 mm, 105 tubes). In both cases, the transmission was about 85%. These samples, however, could not be cooled much below 200 K because mechanical tensions lead to cracking of an increasing number of capillaries. To cover lower temperatures we used an aluminum hollow cylinder with an outer diameter of 30 mm and a sample layer of 1 mm.

B. Instrumental details and data treatment

The experiments were performed on the spectrometers IN11 and IN13 at the Institut Laue-Langevin (ILL) in Grenoble, France. On IN13 we monitored the elastic scattering intensity $S(Q,\omega \approx 0)(T)$ while cooling down from 340 K to a final temperature of 180 K with a cooling rate of 0.125 K min^{-1} using the hollow cylinder geometry with capillary tubes. In addition, full spectra

$S(Q,\omega)$ were recorded at 293, 305, 320, and 334 K. The temperature stability was ± 1 K and the spectra were collected in runs of 57 up to 71-h duration. The sample treatment during and in between different experiments was as reported for protonated OTP [13,14]. In order to extend the $S(Q,\omega\approx 0)(T)$ data to temperatures lower than 180 K a fixed window run was performed using the aluminum hollow cylinder. As the sample crystallized when cooling down slowly, the sample was shock frozen down to liquid helium temperatures and the elastic intensity was recorded on heating with the same rate as in the cooling experiment with the capillary tubes. $S(Q,\omega\approx 0)$ was thus obtained for temperatures ranging from 2 to 270 K. At higher temperatures crystallization started and the data were thus discarded. The instrumental setting was the same as that used previously [14], except for a slightly enlarged dynamic range: energy resolution $\delta(\hbar\omega)=8$ μeV, dynamic range $\Delta(\hbar\omega)=-110$–240 μeV, and Q range $\Delta Q=1.2$–5.5 Å$^{-1}\pm(0.1$–$0.2)$ Å^{-1} (32 detectors). The data were corrected for container scattering and absorption using standard ILL programs with the hollow cylinder option. Due to the complicated sample geometry, no multiple scattering corrections have been applied. With a sample transmission factor of 0.87, however, multiple scattering effects are expected to be small in the Q range analyzed in this paper. The corrected fixed window runs were found to coincide in the overlap region (180–270 K) within experimental accuracy and were combined. Thus a temperature range of 2–340 K was covered.

On the spin echo spectrometer IN11 the normalized intermediate scattering function $S(Q,t)/S(Q,t=0)$ was recorded at 12 temperatures between 200 and 339 K using the slab sample. The dynamic range amounted to 1×10^{-12} s up to 2.2×10^{-9} s. The Q value of 1.9 ± 0.15 Å^{-1} monitored corresponds to the second maximum of the main peak of the static structure factor $S(Q)$ [17]. With a sample transmission of 0.85, an absorption correction had to be performed together with a correction for container scattering. Multiple scattering was again neglected and data were resolution corrected by dividing the corrected time domain data by the normalized intermediate scattering function obtained on a slab of silica chosen to represent the sample geometry as closely as possible. Up to 284 K the resulting curves were constant within some experimental scatter and were time averaged.

In order to compare quantities such as the Debye-Waller factor $f_Q(T)$ or the amplitude factor H_Q extracted from different experiments (IN11 vs IN13) with each other and with theoretical results for the hard-sphere system the spectra and intermediate scattering functions must be known on an absolute scale. Data obtained on the backscattering instrument IN13 are usually normalized with respect to a vanadium standard having the same scattering geometry as the sample. Due to the very special sample geometry used in our case, this procedure is not feasible. The alternative is to normalize the data by dividing them by sample runs taken at 2 K, where $\Phi_Q(t)=1$ is expected to hold, thereby canceling systematic errors and normalization constants. In terms of the intermediate scattering function this yields

$$\frac{S(Q,t)(T)}{S(Q,t)(2\text{ K})}=\frac{\Phi(Q,t)(T)S(Q)(T)}{\Phi(Q,t)(2\text{ K})S(Q)(2\text{ K})}=\Phi(Q,t)(T)\left[\frac{S(Q)(T)}{S(Q)(2\text{ K})}\right]. \quad (6)$$

In a similar fashion, the Debye-Waller factor $f_Q(T)$ is obtained from the elastic scattering intensity $S(Q,\omega\approx 0)$ at temperatures where the α relaxation is not resolved:

$$\frac{S(Q,\omega\approx 0)(T)}{S(Q,\omega\approx 0)(2\text{ K})}=\frac{S(Q,t\rightarrow\text{“}\infty\text{”})(T)}{S(Q,t\rightarrow\text{“}\infty\text{”})(2\text{ K})}=\frac{\Phi(Q,t\rightarrow\text{“}\infty\text{”})(T)S(Q)(T)}{\Phi(Q,t\rightarrow\text{“}\infty\text{”})(2\text{ K})S(Q)(2\text{ K})}=f_Q(T)\left[\frac{S(Q)(T)}{S(Q)(2\text{ K})}\right]. \quad (7)$$

The quotation marks indicate that no true long time limit is meant, but rather the time where the β relaxation has decayed to $f_Q(T)$. From (6) and (7) it becomes clear that in addition to the normalization to the 2 K data, which in (6) takes care of the resolution as well, knowledge of the temperature dependence of $S(Q)$ is necessary to obtain absolute values. Due to the reactor shutdown at the ILL, the 2 K spectra could not be measured with the aluminum container [25]. Thus the IN13 spectra were only resolution corrected using a vanadium standard and could not be obtained on an absolute scale so far, in contrast to the "elastic scan" data.

In the case of the neutron spin echo instrument IN11, normalization to an absolute scale is achieved by dividing the data by the signal measured with the spin echo scan switched off, i.e., the static structure factor $S(Q)$. However, due to the limited transmission band feature of the detector system, contributions to the static structure factor $S(Q)=S(Q,t=0)=\int S(Q,\omega)d\omega$ from energies higher than 3 meV (corresponding to excitations faster than 1.4 ps) are cut off completely. Consequently, most of the phononlike contributions are suppressed, except for a remnant of a few percent [26]. As the shortest time resolved in our experiments is 1.6 ps, the net effect of this instrumental feature corresponds to a normalization error. This fact has to be kept in mind when comparing spin echo data with results obtained on other instruments where the microscopic excitations are not filtered out.

In order to compare values of $f_Q(T)$ and H_Q obtained on the two different instruments, we assume that they can be decomposed into a vibrational and a relaxational part according to $x_Q=x_Q^{\text{vib}}x_Q^{\text{rel}}$ ($x=f_Q(T),H_Q$). When dealing with spin echo data $x_Q^{\text{vib}}(T)$ can be replaced by 1 (introducing an error of a few percent [26]). In the case of backscattering data $x_Q^{\text{vib}}(T)$ will be approximated by extrapolating the low-temperature behavior [where $x_Q^{\text{rel}}(T)=1$] to higher temperatures and eliminating it from $x_Q(T)$ by division. In addition, this treatment [even though approximate, as it implies $\Phi_Q(t)=\Phi_Q^{\text{vib}}(t)\Phi_Q^{\text{rel}}(t)$] will also alleviate the comparison with mode coupling results on absolute scale, as contributions from processes

not contained in the theory (e.g., the boson peak [22,27]) will be largely removed. This has already been demonstrated in the case of our incoherent data [14].

IV. RESULTS AND DISCUSSION

A. Spectra and time decay of density fluctuations

In Fig. 1, $S(Q,\omega)$ and $S^s(Q,\omega)$ (from [14]) are compared directly for selected Q at temperatures $T \gtrsim T_c$ where the α relaxation causes quasielastic broadening. Within experimental uncertainty the spectral line shapes coincide. This is a rather surprising result, within MCT as well as in a wider context. Under very general assumptions, comparing the moments $\langle\omega^2\rangle$ and $\langle\omega^4\rangle$ of $S(Q,\omega)$, de Gennes [28] showed that quasielastic broadening should be small around peaks of $S(Q)$. Such behavior has subsequently been observed in simple liquids such as argon [29] as well as in glass formers such as $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ [30] or deuterated polybutadiene [31]. A MCT calculation of α relaxation for hard spheres [32] equally reproduced de Gennes narrowing and is in excellent agreement with light scattering from a colloidal system [23]. It is therefore quite astonishing that the spectral shape of α relaxation in OTP-D_{14} shows no oscillation with Q.

For a more quantitative analysis, we consider the normalized intermediate scattering function $\Phi(Q,t) = S(Q,t)/S(Q,t=0)$ (Fig. 2). As from incoherent scattering, one finds that correlations decay in two steps. Most of the first step, however, is completed in less than 1 ps. Our measurements essentially cover the intermediate plateau and the bending over to the long time regime.

A comparison of the time scales of the β relaxation t_ε obtained by evaluation of the incoherent data [33], with the time range covered by the neutron spin echo experiments, led to the conclusion that for several temperatures the density autocorrelation functions $\Phi_Q(t)$ cannot be interpreted merely in terms of the α relaxation as has been done previously [14], this being correct only for times $t > t_\varepsilon$ [34]. Moreover, as the crossover region from β to α relaxation, the so-called von Schweidler regime, is not only obtained as the short time limit of the α relaxation but describes at the same time the long time part of the β relaxation above T_c [11], a large part of the spin echo data should also be interpretable via (1) in terms of the β

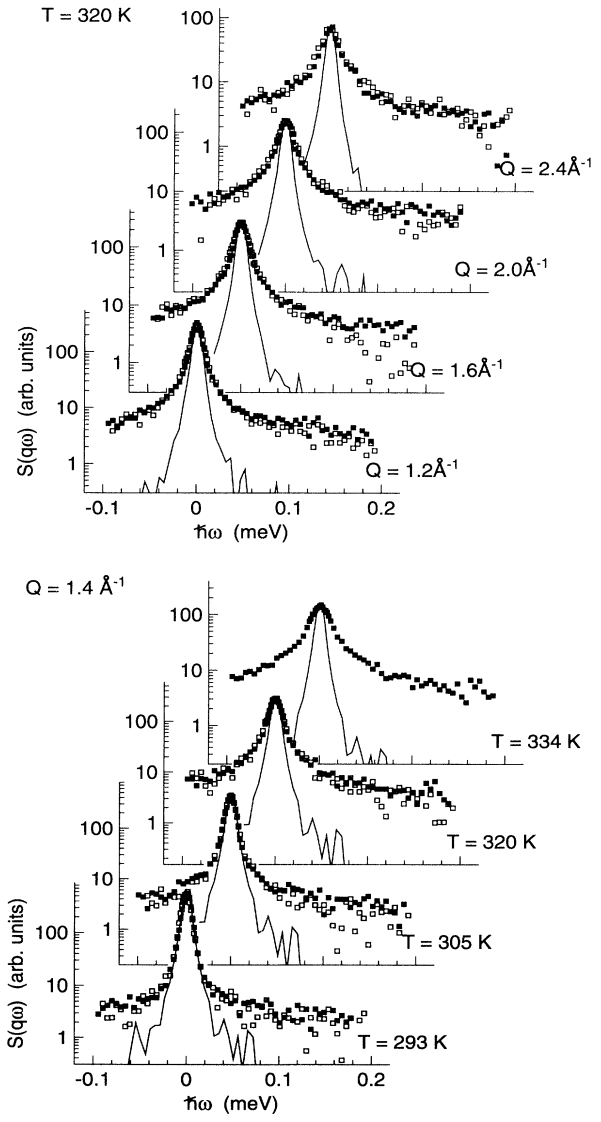

FIG. 1. Quasielastic spectra $S(Q,\omega)$ of OTP-D_{14} (■) and OTP-D_0 (□) at selected T and Q. The solid line shows the instrumental resolution of IN13 as measured on vanadium. The intensity scale is arbitrary but the same for all OTP-D_{14} spectra; the other data are matched at $\omega=0$.

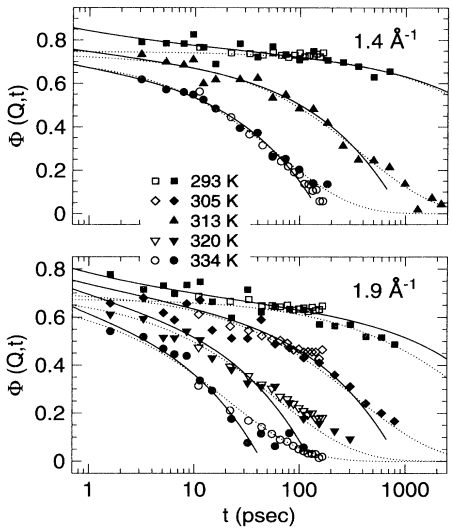

FIG. 2. Spin echo data $\Phi(Q,t)$ from IN11 for some representative temperatures (full symbols). The Fourier transforms of IN13 spectra are rescaled in height (open symbols) and 1.9-Å^{-1} data are averaged from 1.8- and 2.0-Å^{-1} detectors. Solid lines are fits with the MCT scaling law (1) using $\lambda=0.76$ (corresponding to $a=0.3$ and $b=0.54$) and dotted lines are stretched exponentials (8), obtained by converting back to natural time scale the master curves presented in Fig. 4.

relaxation as long as the condition $t < \tau_\alpha$ is obeyed.

This situation is demonstrated in Fig. 2. The full lines are fits with (1), the β relaxation of MCT, whereas the dotted lines are stretched exponentials

$$\Phi(Q,t)=a_Q(T)\exp\{-[t/\tau_Q(T)]^{\beta_Q}\}$$

$$\tau_Q(T)=\tau_Q\tau_\alpha(T)\ , \quad (8)$$

which approximate the α relaxation within MCT. Here the Q-dependent quantities $a_Q(T)$ and β_Q denote the strength of the α relaxation and the stretching parameter (specifying the deviation from exponential decay), respectively. The scale factor τ_Q connects the α-relaxation time for density fluctuations $\tau_Q(T)$ to the universal time scale $\tau_\alpha(T)$ of α relaxation [11]. Note that the α-scaling prediction of MCT, $\Phi[Q,t/\tau_\alpha(T)]=F_Q(t)$, implies a temperature-independent β_Q.

It is apparent from Fig. 2 that the experimental data are described by the full and the dotted lines in the short and the long time regions, respectively. In Fig. 3, master curves $\Phi[Q,t/\tau_\alpha(t)]$ for α relaxation are shown, obtained by rescaling the time axis by the α-relaxation time $\tau_\alpha(T)\sim\eta(T)/T$. The scaling prediction of MCT is confirmed within experimental accuracy. As has been discussed previously [18,19], this result is not simply a consequence of the particular choice of $\tau_\alpha(T)$. Free fits of the individual $\Phi(Q,t)$ with (8) demonstrated the temperature independence of β_Q—implying scaling—within experimental error.

The fit curves in Figs. 2 and 3 were calculated as follows. As stated above, if MCT is applicable to OTP, the scaling function $g(t)$ as well as the time scale t_ε of β relaxation in (1) should be the same for $\Phi(Q,t)$ and $\Phi^s(Q,t)$ and were taken over from the analysis of the incoherent data [33] yielding constant $\lambda=0.76$, $a=0.3$, and $b=0.54$ [connected via the transcendental equation $\Gamma^2(1+b)/\Gamma(1+2b)=\lambda=\Gamma^2(1-a)/\Gamma(1-2a)$; Γ denotes the Gamma function]. In principle, f_Q^c can be fixed independently as well, via the condition $\Phi_Q(t=t_\varepsilon)=f_Q^3$ [11]. In practice, however, this was not feasible, given the considerably experimental noise in the measured spin echo curves.

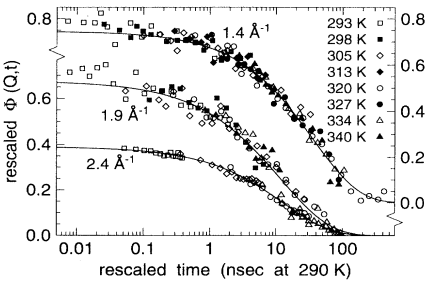

FIG. 3. Scaling analysis of α relaxation: master curve $\Phi\{Q,t/[\tau_Q\tau_\alpha(T)]\}/a_Q(T)$, where $a_Q(T)$ and τ_Q are obtained from iterative fits with (8) (solid lines). The temperature dependence $\tau_\alpha(T)\sim\eta/T$ was used to rescale the abscissa according to $t/\tau_\alpha(T)$. The upper two curves are from IN11 and the bottom curve from IN13.

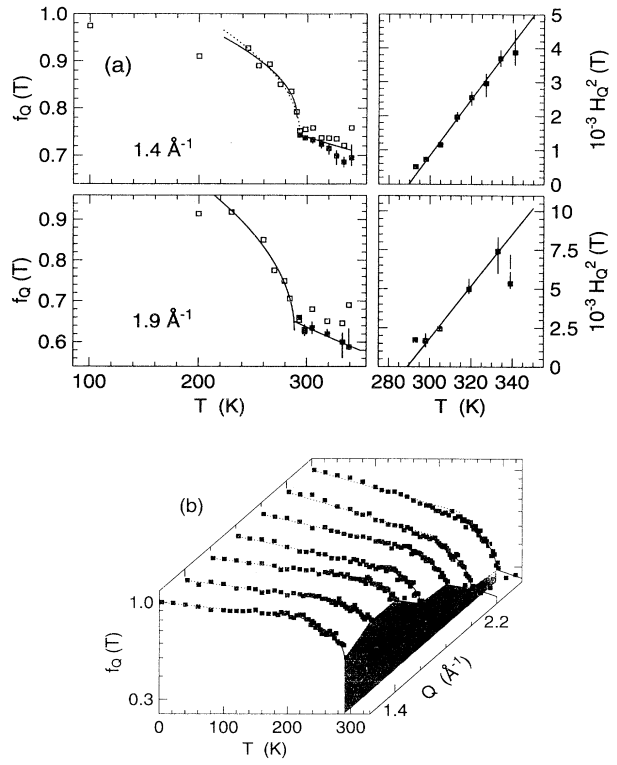

FIG. 4. Temperature dependence of various parameters. (a) Left-hand side: normalized Debye-Waller factor $f_Q(T)$ as measured on IN11 (□). For $T>290$ K, we show both $f_Q(T)$ from (1) (■) and $a_Q(T)$ from (8) (□). Fits with (9) are indicated by the curved lines. (a) Right-hand side: amplitude H_Q, from fit with (1) in Fig. 2, shown as H_Q^2. The straight lines indicate the power law (1b). (b) Normalized Debye-Waller factor as measured on IN13. Full symbols, values obtained from $S(Q,\omega\approx0)$; open symbols values obtained from α-scaling analysis (cf. Fig. 3). The latter data were not obtained on an absolute scale and are merely included to demonstrate the change of slope in $f_Q(T)$. For this purpose the data were rescaled such that an extrapolation to 290 K coincides with the value obtained from fits with (9) (curves lines); the dotted lines follow the low-temperature behavior $-\ln f_Q(T)\sim T$, which is compared to the weak temperature dependence of $f_Q(T)$ above 290 K in (a) and (b) (straight solid lines).

f_Q^c values extracted from the analysis of the Debye-Waller factor $f_Q(T)$ obtained on the backscattering instrument IN13 could not be used because of the different effect of vibrational contributions (see Sec. II). Thus f_Q^c was treated as a free fit parameter in addition to $H_Q(T)$ in order to obtain the solid lines in Fig. 2. The values resulting from the fits are presented in Fig. 4 and are discussed below.

In previous work [14] we have demonstrated that α relaxation above 290 K follows the time-temperature superposition principle for single-particle motion as well as for collective motion at the first maximum of the main peak in $S(Q)$ ($Q=1.4$ Å^{-1}). To analyze the coherent data

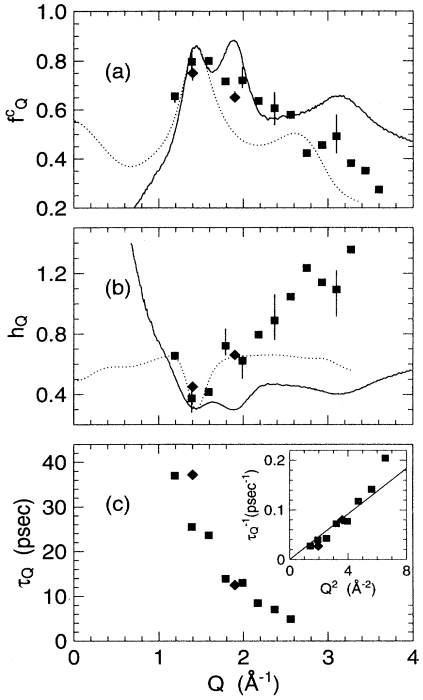

FIG. 5. Dependence on scattering vector Q. (a) Plateau value $f_Q(T_c)=f_Q^c$, from the fit with (9) in Figs. 4(a) and 4(b) (IN11, ◆; IN13, ■) compared to the static structure factor of OTP (solid line) and of a hard-sphere system with a hard-sphere diameter $\sigma=4.9$ Å^{-1} (dotted line). (b) Amplitude h_Q (symbols as above), for same fit setting $c_0=1$, compared to the theoretical hard-sphere values (dotted line) and to the inverse of the static structure factor of OTP (solid line). (c) Time constant τ_Q (symbols as above) of α relaxation. The inset compares τ_Q^{-1} to a Q^2 behavior (solid line). Error bars were obtained by repeating fits with (9) using $T_c=290\pm5$ K.

presented here we followed the same iterative procedure as that described in [14] to allow for a weak temperature dependence of the amplitude $a_Q(T)=f_Q^c f_Q^{\mathrm{vib}}(T)$. Rescaling the time axis according to $\hat{t}=t/\tau_\alpha$ with $\tau_\alpha\sim\eta(T)/T$ [$\eta(T)$ being the shear viscosity], master curves could be constructed at the second maximum of the main peak in $S(Q)$ ($Q=1.9$ Å^{-1}) from the neutron spin echo data and for the Fourier transformed backscattering spectra in the Q range 1.2 Å$^{-1}\le Q\le 2.6$ Å^{-1}. During the iterative procedure only those data points where the limiting condition $t>t_\varepsilon$ was fulfilled were used. Parametrization of the resulting master curves according to (8) (shown as solid lines in Fig. 3 for $Q=1.4$ and 1.9 Å^{-1} on IN11 [35] and a representative Q on IN13) yielded the temperature-independent line shape parameters τ_Q and β_Q, which are discussed below in the context of the Q dependence. The temperature-dependent amplitudes $a_Q(T)$ are included in Fig. 4. Converting the parametrized master curves back to natural time scales via (8), the dotted lines in Fig. 2 are obtained.

B. Debye-Waller factor

In Fig. 4, we show the Debye-Waller factor $f_Q(T)$ as a function of T and Q. MCT predicts in leading order [$O(\ )$ denotes the order of]

$$f_Q(T)=\begin{cases} f_Q^c+h_Q c_0\sqrt{(T_c-T)/T_c}+O(T)\ , & T_c<T \\ f_Q^c+O(T)\ , & T_c\ge T\ . \end{cases} \tag{9}$$

A test with the neutron spin echo instrument IN11 should be most straightforward since the vibrational contribution to $f_Q(T)$ is largely suppressed and the weak temperature dependence of $S(Q)$ [17] is accounted for as $\Phi(Q,t)$ is directly observed (see Sec. III B). At $T\lesssim T_c$, where the scattering is still elastic, $f_Q(T)$ is measured directly [Fig. 4(a), open squares]. At higher temperatures it can be obtained by analyzing the time decay curves either in terms of the α-relaxation fit by the Kohlrausch-Williams-Watts (KWW) function (8), where $a_Q(T)$ is extracted in the same way as described previously for incoherent scattering [14] [open squares in Fig. 4(a)] or by β-relaxation fits via (1) [solid squares in Fig. 4(a)]. It is clearly seen in Fig. 4(a) that both procedures yield a cusp at $T_c\approx290$ K even without reference to any fits. The full lines in Fig. 4(a) are fits with the square root law (9) for $T<T_c$ yielding T_c, f_Q^c, and $h_Q c_0$ equal to 290.4 K, 0.78, and 0.35 ($Q=1.4$ Å^{-1}) and 288.7 K, 0.63, and 0.66 ($Q=1.9$ Å^{-1}), respectively. The dashed line at $Q=1.4$ Å^{-1} demonstrates the sensitivity of the results on the fit range chosen: including the point at 293 K leads to $T_c=293$ K, $f_Q^c=0.74$, and $h_Q c_0=0.45$ with a fit of comparable quality.

Figure 4(b) shows $f_Q(T)$ as obtained from the backscattering instrument IN13 after correction for the T dependence of $S(Q)$ according to (7). Here the vibrational contribution of $f_Q(T)$ is not negligible and can be described by an exponential T dependence at low temperatures characteristic of harmonic behavior as is apparent from the straight lines in Fig. 4(b). For $T\gtrsim220$ K, we have *assumed* that the vibrational contribution has the same temperature dependence as at low T and that the factorization described at the end of Sec. III B is a reasonable approximation: $f_Q(T)=f_Q^{\mathrm{vib}}(T)f_Q^{\mathrm{rel}}(T)$. The resulting square root law fits shown in Fig. 4(b) are in good agreement with the experimental data (the extracted f_Q^c and h_Q are presented in Fig. 5). Since the IN13 spectra could not be normalized at $T>T_c$ (see Sec. III B) we have arbitrarily shifted the data points obtained by the α-relaxation analysis such that their extrapolation to 290 K yields the same values as the fits of the fixed window scan data for $T\lesssim290$ K with (9). Even though no numerical value for T_c can thus be extracted, its existence can be surmised from the observed bending over to a weaker temperature dependence.

A further test of internal consistency is achieved by plotting $H_Q^2=(h_Q c_\varepsilon)^2$ versus T. According to MCT, this should yield straight lines intersecting the abscissa at T_c due to the square root dependence $c_\varepsilon=c_0[(T-T_c)/T_c]^{1/2}$ at $T\ge T_c$ [11]. The data shown in Fig. 4(a) (right-

hand side) are consistent with this prediction and yield $T_c \approx 290$ K as well.

C. Q dependence

Although no difference is seen between the coherent and incoherent spectra shown in Fig. 1, it is useful to have a closer look at the Q dependence of coherent f_Q^c, h_Q, τ_Q, and β_Q as obtained by the analysis via (1), (8), and (9). The results shown in Fig. 5 are compared with the static structure factor of OTP (full lines) [17] and of a hard-sphere system (dotted lines) adjusted such that the first maximum coincides with that of OTP. The latter has been included since it is by no means clear what would be the relevant structural quantity to which the Q-dependent dynamical quantities have to be compared. The "static structure factor" of molecular systems comprises intramolecular as well as intermolecular correlations, the clear-cut separation of both being only feasible in favorable cases [36]. Moreover, that quantity which can be expected to correspond most likely to the $S(Q)$ of atomic systems, the Fourier transform of the correlation function of molecular centers, is even more difficult to extract. Consequently, few comparisons between the Q dependence of dynamical and structural quantities have been made. For polybutadiene it has been demonstrated that the relaxation time τ_Q of the α relaxation and the nonergodicity parameter oscillate in phase with the experimental $S(Q)$ while h_Q oscillates out of phase [31,37].

The comparison with the Q dependence of the experimental $S(Q)$ of OTP shows that some of its major features are found in f_Q^c as well. There is a close similarity at the first maximum of the main peak of $S(Q)$ and the second peak at 3.2 Å^{-1} is indicated as well. However, one main feature of $S(Q)$ is almost completely missing in f_Q^c. The pronounced second maximum of the main peak of $S(Q)$ at about 1.9 Å^{-1} is not seen in f_Q^c except for a small shoulder. Whether this is just an effect of the low Q resolution of the neutron spectrometers or implies that this structural feature is not related to the glass transition dynamics is not clear at present. This question is, however, of much interest as this maximum in $S(Q)$ increases significantly with decreasing temperature as compared to other Q values [17] and the molecular nature of this phenomenon has up to now not been understood.

The same overall features are seen in Fig. 5(b) for the amplitude h_Q of the β relaxation. The resulting values are compared to the hard-sphere values and the inverse of $S(Q)$. Again we find some resemblance around the first maximum. However, at larger Q values there is a pronounced discrepancy, the theoretical amplitudes starting to fall off with increasing Q while the experimental values increase drastically. This again underlines the distinction between a hard-sphere system and the more complex OTP. Nevertheless one can state that the Q dependence of the amplitude h_Q of the additional process, which leads to the anomalous decay of the Debye-Waller factor in Fig. 4, clearly does not follow the $Q^2S(Q)$ dependence expected for vibrational motion [38]. The behavior of h_Q is qualitatively more similar to that predicted for relaxational motion in the framework of mode coupling theory, i.e., oscillations out of phase with the static structure factor of the system.

In contrast to the Q dependencies of f_Q^c and h_Q a serious discrepancy with expectations derived from mode coupling theory and results on other systems arises with respect to the Q dependence of the time constants of the α relaxation τ_Q, depicted in Fig. 5(c), since they do not follow at all the oscillations of the static structure factor as predicted by mode coupling theory or from a more general viewpoint by de Gennes [28]. Instead, they decrease monotonously with increasing Q. That this is not only a consequence of the limited data set available on IN13 and numerical artifacts is indicated by the values derived from the master curves obtained with the spin echo instrument IN11 that show the same tendency. Plotting the time constant as τ_Q^{-1} versus Q^2 one finds a straight line [see the inset of Fig. 5(c)] that compares well with the result obtained for the incoherent data (cf. Fig. 10 of [14]). We emphasize that speculations about the origin of this unexpected behavior should await better experimental data. However, we should bear in mind that coherent neutron scattering measures correlations of single atoms. In addition to a translational component, these correlations contain also contributions from rotational motion relative to the molecular center of mass. Whether this contribution is relevant can be decided only by joint use of different experimental techniques and molecular dynamics simulations on appropriate models.

Finally, we note that the stretching parameter β_Q obtained from the analysis of α relaxation via (8) is Q independent within experimental accuracy and agrees with that found for incoherent scattering [14]. Since for a hard-sphere system this quantity is predicted to oscillate in phase with $S(Q)$ as well [32], a more precise experimental determination of its Q dependence is required.

V. CONCLUSIONS

The results obtained on the collective dynamics of the molecular glass former orthoterphenyl are consistent with the behavior of the single-particle motion analyzed in previous work and are well understood in terms of the idealized mode coupling theory as concerns the universal dynamical features: the existence of $T_c \approx 290$ K, the α scaling, and the square root anomaly are well established. A significant time range of the spin echo data can be analyzed in terms of the β relaxation using the same master function as for the single-particle motion yielding power law behavior of the amplitude scale $h_Q c_\varepsilon$ and again $T_c \approx 290$ K. In contrast, the Q dependence is much less understood. Although it appears that the oscillations of $S(Q)$ are reflected in f_Q^c and h_Q, the limited Q resolution does not allow for a decisive statement. The present data suggest further that the double peak structure of $S(Q)$ is missing in f_Q^c and h_Q and that the Q dependence of the α-relaxation times is at variance with the de Gennes narrowing at the structure factor maximum; however, we also need data with improved Q resolution in order to substantiate this result. A decisive answer is of particular

interest since in atomic systems the slowing down of the dynamics on approaching T_c from above is triggered by the increase of the structure factor peak. It would indeed be very peculiar if the peak in $S(Q)$ that shows the largest T dependence in OTP is not reflected in the Q dependence of f_Q^c.

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