Wavenumber dependence of structural $\alpha$ relaxation in a molecular liquid

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Abstract. – Structural $\alpha$ relaxation in liquid orthoterphenyl is studied by means of coherent neutron time-of-flight and backscattering spectroscopy over a large temperature range. Not only amplitude and relaxation time but also the spectral line shape show a significant variation with wavenumber. As expected from mode coupling theory, these variations are correlated with the static structure factor. Even far above the melting point, $\alpha$ relaxation remains non-exponential.

The most outstanding features of structural $\alpha$ relaxation in glass-forming liquids are a strong temperature dependence of the relaxation time and the stretching phenomenon of the response function [1]. Very often, the correlation function $\Phi_X(t)$ of some observable $X$ obeys time temperature superposition (TTS): by a shift of the characteristic relaxation time $\tau_X(T)$ the response functions at different temperatures can be superimposed $\Phi_X(t; T) = \tilde{\Phi}_X(t)$, with $\tilde{t} = t/\tau_X(T)$. While the master function $\tilde{\Phi}_X(t)$ varies weakly with temperature, the scale $\tau_X(T)$ increases rapidly upon cooling. The other remarkable feature is the stretching phenomenon: the decay of $\Phi_X$ extends over a wider time range than expected for exponential relaxation; empirically, it is generally well described by the Kohlrausch function (KWW)

$$\Phi_X(t) = A_X \exp[-(t/\tau_X)^{\beta_X}], \quad \beta_X < 1. \quad (1)$$

Different observables $X$ may have not only different relaxation times $\tau_X$ but also different stretching exponents $\beta_X$. In light scattering, for instance, $\beta$ can be changed by just switching between polarized and depolarized geometry. Uncountable experiments have confirmed both observations for times varying from nanoseconds to hours, days, or longer.

A microscopic explanation of stretched relaxation has been given by mode coupling theory (MCT) [2]. Within MCT, time correlations decay in a two-step process which becomes
critically slow upon cooling due to a nonlinear feed–back mechanism in the microscopic dynamics of the particles. A fractal time dependence in the late intermediate time regime (β relaxation) \( Φ_X(t) = f_X - h_X c(T) t^{-b} \), \( b > 0 \) leads to the final decay of correlations and is the key to stretching \( [3] \). However, it does not necessarily match the short-time expansion of eq. 1; therefore, stretching exponents \( β_X \) must not equal \( b \) \( [4] \). As the feed–back effect is expressed by a memory function which depends on the static structure factor \( S(Q) \) the parameters for the density correlator become wavenumber \( (Q) \) dependent. Numerical solutions of MCT equations for hard spheres \( [2] \) and a binary mixture of soft spheres \( [1] \) show pronounced oscillations of the parameters \( A_Q, τQ \) and \( βQ \) (eq. 1) in phase with \( S(Q) \).

Experiments on molecular, ionic and even polymeric liquids have confirmed the predicted trend of \( A_Q \) and \( τQ \) to oscillate in phase with the static structure \( S(Q) \) \( [3] \). The wavenumber dependence of α line shapes has been studied far less. For intensity reasons, high-resolution neutron scattering experiments have most often been restricted to the structure factor maximum \( [5] \). Only in polybutadiene, a spin-echo measurement has been performed in the valley between the two maxima of \( S(Q) \) where the α relaxation was found to be more stretched than at the first maximum \( [6] \). However, the oscillations of \( τQ \) get lost and \( βQ \) becomes \( Q \)-independent when intra-chain motions are considered \( [7] \). Therefore, experimental evidence of the predicted oscillations of \( βQ \) is again missing. For supercooled water, molecular dynamics indicates weak oscillations of the stretching exponent \( βQ \) in phase with \( S(Q) \) \( [10] \).

In this Letter we present a neutron scattering study of the α scale and the stretching in a molecular liquid for different observables which are the closest related: density fluctuations for different wave vectors \( Q \). Particular emphasis is given on the wavenumber dependence. Neutron scattering is a particularly unique tool since it couples directly to density fluctuations and covers the microscopic time range as well as the length scale of the intermolecular correlations. While incoherent scattering from a protonated sample measures the tagged particle motion, collective motion is probed through the dynamic structure factor \( S(Q, ω) \) in coherent scattering from a deuterated sample. Any wavenumber dependence of the coherent dynamic structure factor may help to discriminate between different theories of α relaxation.

The experiments were performed on the time–of–flight spectrometer (TOF) IN5 and on the backscattering spectrometer (BS) IN16 of the Institute Laue Langevin in Grenoble, France. The incident wavelengths were set to 6.5 Å\(^{-1}\) and 6.27 Å\(^{-1}\) leading to resolutions (fwhm) of \( ∼25 \mu\text{eV} \) and \( ∼1 \mu\text{eV} \), respectively, which allows us to detect relaxation processes from the ps/c (TOF) to nsec (BS) time range. In the BS experiment part of the analyser surface was covered with large Cadmium shields in order to increase the \( Q \) resolution. Vanadium was used to calibrate the detectors and yielded the resolution functions. Our system is the widely studied molecular liquid orthoterphenyl \( (\text{OTP}: \text{C}_{18}\text{H}_{14}, \ T_m = 329 \text{K}, \ T_g = 243 \text{K}) \). A thin walled hollow aluminum cylinder filled with 99% deuterated OTP \( [11] \) was used to keep self absorption and parasite scattering as isotropic as possible. The TOF–data were interpolated to constant \( Q \) with step \( ΔQ = 0.05 \text{Å}^{-1} \). After Fourier deconvolution with the measured resolution function and division by the static structure factor \( S(Q) \) we obtain the density correlator \( Φ_Q(t) = S(Q, t)/S(Q) \).

Fig. 1a presents the density correlators (IN5) at the structure factor maximum \( Q_p = 1.45 \text{Å}^{-1} \) for temperatures between 313 and 400 K. In agreement with MCT all correlators show a two–step decay. The second decay (α relaxation) becomes slower and more separated with decreasing temperature and exhibits a pronounced stretching. Fig. 1b shows the correlator at 360 K for four \( Q \) values. We recognize that the α relaxation time scale on which the correlator decays to zero as well as its shape exhibit a rather non trivial \( Q \) dependence. The relaxation time \( τQ \) does not follow a simple power law \( Q^{-2} \) expected for diffusion like motion. At \( Q_p = 1.45 \text{Å}^{-1} \) the correlations decay steeper i. e. with less stretching than for other wave
numbers. This observation is also valid for the other temperatures where the α relaxation falls into the accessible time window.

The spectral range of one instrument hardly allows to determine the line shape of a complex relaxation from a single measurement. However, consistent results with acceptable error bars can be obtained by combination of measurements from different temperatures.

In our earlier work on OTP we found for selected Q that the relaxation time scales with viscosity \( \tau_Q \propto \eta(T)/T \) and that the line shape is temperature independent [12]. Here, preliminary fits to the long time tail of the correlators indicate that this viscosity scaling holds equally for all Q over the whole temperature range. Using published viscosity data [13] we construct master curves \( \Phi_Q(\hat{t}) \) via \( \hat{t} = t[\eta(T_0)/T_0]/[\eta(T)/T] \) with an arbitrary normalization \( T_0 = 290 \text{ K} \). From a KWW fit to \( \Phi_Q(\hat{t}) \) a first approximation of \( A_Q, \beta_Q \) and \( \tau_Q(T_0) \) is obtained. Fixing \( \beta_Q \) and \( \tau_Q(T) \) in fits to the individual \( \Phi_Q(t) \) results in a set of amplitudes \( A_Q(T) \) which are then used to calculate reduced correlators \( \Phi_Q(\hat{t})/A_Q \). This procedure is repeated and converges after 1 (3) iteration(s) for the TOF (BS) data. The amplitudes \( A_Q \) turn our to be temperature independent (as can be seen directly from the successful first rescaling, cf. fig. 2) in agreement with a recent light scattering result in OTP in the same temperature range [14].

From fig. 2 and 3 we recognize that the TTS works quite well. (Note, from the TOF data we disregard the fraction of the correlators which do not scale e. g. the microscopic dynamics and the β process; in the BS experiment we observe only α relaxation.) Both data sets show that the density correlations around \( Q_p \) decay with less stretching and the relaxation time is slightly slowed down compared to a \( Q^{-2} \) dependence. In order to quantify these effects eq. 1 is fitted to the long time tail of the master curves.

In fig. 4 the fit results are compared to the static structure factor \( S(Q) \) at 380 K obtained by integration over the kinematically accessible region of IN5. We note the presence of oscillations in all parameters highly correlated with the oscillations in \( S(Q) \) at the first diffraction peak [1] around \( Q_0 \approx 0.9 \text{ Å}^{-1} \) and first structure factor maximum at \( Q_p \approx 1.45 \text{ Å}^{-1} \). \( A_Q \) is in qualitative agreement with the Debye–Waller factor \( f_Q \) obtained from the analysis of the fast β relaxation [1]. Both, the BS and the TOF experiment yield independently a
Fig. 2. – Master curves $\Phi_Q(\hat{t})$ constructed via viscosity scaling from TOF–data for $Q=1.2$ Å$^{-1}$ (a) and $Q=1.45$ Å$^{-1}$ (b). Results from the first rescaling the times are shown without any adjustment of the amplitudes. Full lines are fits with eq. 1 for reduced times $\hat{t}$ longer than 2 nsec.

Fig. 3. – (a) Master curve $\Phi_Q(\hat{t})$ from TOF data for the same $Q$ values as in fig. 1b. (b) Normalized master curve $\Phi_Q(\hat{t})/A_Q$ form BS data for three values of $Q$ obtained after the rescaling procedure explained in the text for 288, 293, 298, 305, 313 and 320 K. Both experiments show: at $Q_p$ the relaxation is less stretched and the relaxation time is slowed down compared to a $Q^{-2}$ dependence.

maximum of the exponent parameter $\beta_Q$ at $Q_p$ whose value is compatible with the one obtained earlier in a spin–echo experiment [12]. No sign for a further oscillation in $\beta_Q$ is found. The reduced relaxation time $\tau_Q$ shows two plateaus around $Q_0$ and $Q_p$ modulating an overall $Q^{-2}$ dependence. We would like to point out that $\tau_Q$ and $\beta_Q$ depend on the rescaled data of a rather narrow temperature range i. e. 340 - 380 K for TOF and 298 - 313 K for BS. A possible slight temperature dependence of the parameters will not alter the results. The absolute values depend on the quality of scaling; their $Q$ dependence, however, is not affected. Notwithstanding, the variations of $\tau_Q$ and $\beta_Q$ with $Q$ are clearly present in the raw data (fig 1,2,3). At very low wave numbers ($Q \lesssim 0.6$ Å$^{-1}$), where $A_Q$ tends towards 1 the results may be spoiled by the remaining 15% incoherent scattering which contribute
Fig. 4. – Left side: Fitting parameters of the master curve according to the stretched exponential function eq. 1. Note the presence of oscillations in all three parameters. Errors of $A_Q$ and $\tau_Q$ are of the size of the symbol; error in $\beta_Q$ results from temperature uncertainty. Right side: Kohlrausch parameters as determined from fits to the individual correlators in which the other two parameters were kept fixed to the values obtained from the scaling analysis. Amplitude $A_Q$ and stretching $\beta_Q$ are roughly temperature independent. The relaxation times $\tau_Q$ are compared to $\eta(T)/T$ which is modulated by the generic $Q$ dependence and scaled properly. Symbols are the same as in fig. 1a. The arrows indicate results from depolarized light scattering ($Q \simeq 0$) \cite{14} for 320, 330, 340, 360, 380, 395 K.

particularly strong to the dynamic structure factor where $S(Q)$ itself is small. A separation of coherent and incoherent scattering by the use of polarized neutrons would be helpful.

In order to get the temperature dependence of the parameters we fit eq. 1 to the individual correlators fixing mutually the two others to the values obtained from the analysis of the master curve. Fig. 4 shows that the viscosity scaling is obeyed within experimental accuracy over several decades for all wavenumbers $Q$ (This corroborates the observation that the quality
of scaling is nearly identical for all $Q$, cf. fig. 2.). The curves corresponding to different temperatures are only shifted vertically due to the temperature dependence of the relaxation time just what is expected if $\alpha$–scale universality holds. The $Q$ dependence is given by a temperature independent function $C(Q)$. Note the appearance of the two plateaus for all temperatures. Results from depolarized light scattering ($Q \simeq 0$) are included for comparison. Finally, $A_Q$ and $\beta_Q$ are in a good approximation independent of temperature as observed earlier. For all temperatures qualitatively the same oscillations are found so they are clearly significant. No indications for an increase of $\beta_Q(T)$ with increasing temperature towards $\beta = 1$ is found as in ref. Even 70 K above the melting temperature where one would naively expect ordinary diffusion a reminder of a two step decay is still seen.

In conclusion, the $\alpha$ relaxation time for density fluctuations $\tau_Q(T)$ obeys $\alpha$–scale universality; amplitude $A_Q$ and stretching parameter $\beta_Q$ are in good approximation temperature independent. The $Q$ dependence of amplitude $A_Q$, relaxation time $\tau_Q$ and stretching parameter $\beta_Q$ are qualitatively similar to the one predicted by MCT all oscillating in phase with the static structure factor $S(Q)$. Correlations which are preferred by the system and build up the static structure factor maxima decay more slowly and with less stretching.

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