

Wavenumber dependence of structural α relaxation in a molecular liquid

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Abstract. Structural α 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. These variations are correlated with the static structure factor, in qualitative accord with mode-coupling results for simple liquids. Even far above the melting point, α relaxation remains non-exponential.

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1 Scaling and stretching

The most outstanding features of structural α relaxation in glass-forming liquids are a strong and universal dependence on temperature, and the stretching in time [1, 2].

Very often, the correlation function $\Phi_X(t)$ of some observable X obeys a scaling principle known as time-temperature superposition: measurements at different temperatures can be superimposed

$$\Phi_X(t; T) = \hat{\Phi}_X(\hat{t}) \quad (1)$$

by rescaling the time axis to $\hat{t} = t/\tau_X(T)$. While the master function $\hat{\Phi}_X(\hat{t})$ varies only weakly with temperature, the relaxation times $\tau_X(T)$ increase rapidly upon cooling. For different observables X , the same temperature dependence is observed, though absolute values of $\tau_X(T)$ may differ.

The other remarkable feature is the stretching phenomenon: the decay of Φ_X extends over a wider time range than expected for exponential relaxation; experimental results are usually well described by the Kohlrausch stretched exponential

$$\Phi_X(t) = A_X \exp[-(t/\tau_X)^{\beta_X}] \quad (2)$$

with an exponent $\beta_X < 1$.

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Different observables X may have not only different relaxation times τ_X but also different spectral line shapes, expressible through different stretching exponents β_X . Such variation of β_X with X demonstrates that an understanding of structural relaxation will not be possible without accounting for the different ways in which experimental probes couple to the microscopic degrees of freedom; this consideration alone disqualifies certain oversimplified explanations of (2).

For a more systematic study of α relaxation, there is particular interest in comparing different degrees of freedom that can be measured under identical conditions in the same experimental set-up. Such a comparison has been reported for light scattering in a polymer where the stretching exponent varies from $\beta_{VV} = 0.34$ to $\beta_{VH} = 0.40$ upon selecting polarised or depolarised scattering geometry [3].

With quasielastic neutron scattering, one can even access a continuous set of observables by measuring at different wavenumbers Q .

2 Wavenumber dependent stretching

The wavenumber dependence of the tagged-particle correlator $\Phi_Q^s(t)$ can be studied by *incoherent* neutron scattering. Available data are generally not sufficient for the unambiguous detection of line shape variations. In glycerol at least, a significant Q dependence of the stretching exponent β_Q^s has been found: for small Q , $\Phi_Q^s(t)$ crosses over

from stretched relaxation to simple exponential diffusion [4].

In the present communication we shall concentrate on the wavenumber dependence of the collective dynamics described by the density correlator $\Phi_Q(t)$ and experimentally accessible by *coherent* neutron scattering.

So far, the wavenumber dependence of $\Phi_Q(t)$ has been investigated mostly in an intermediate time window referred to as fast β relaxation, where the trapping of particles in transient cages leads to a plateau in Φ_Q versus $\ln t$. This trapping is modelled within mode-coupling (MC) theory [5,6] by a nonlinear feed-back mechanism, and it brings up a universal scaling form for time correlations $\Phi_X(t)$. On leaving the plateau region, the asymptotic power law

$$\Phi_X(t) = f_X - h_X c(T)t^b, \text{ with } b > 0 \quad (3)$$

leads up to the final decay of correlations in the α process; its fractal time dependence is the key to stretching [7].

On input, the MC nonlinearity contains basically the static structure factor $S(Q)$. As consequence, when applied to $\Phi_Q(t)$ the amplitudes in (3) reflect the oscillatory character of $S(Q)$. In several glass-forming liquids, coherent neutron scattering confirmed a trend of f_Q and h_Q^{-1} to oscillate in phase with $S(Q)$ [8–14]. In a colloidal suspension where interparticle distances are comparable to the wavelength of visible light, similar oscillations were observed by photon correlation spectroscopy [15–17]; they were in excellent quantitative agreement with numeric solutions of a MC model [17].

Matching (3) to (2) makes it plausible that the α -relaxation time τ_Q follows the Q dependence of f_Q/h_Q ; such oscillations of τ_Q , in a more general context known as de Gennes narrowing, have been observed and discussed in the literature [8,10,12,16].

However, theory does not claim that (3) should exactly match the short-time expansion of (2). In general, stretching exponents β_X will not equal b [18]; quite on the contrary, one expects that oscillations in f_Q and h_Q^{-1} lead also to oscillations in β_Q . This is fully confirmed by fits of (2) to numerical solutions of MC equations for the hard spheres system [19] and a soft spheres mixture [20]: all three parameters A_Q , τ_Q and β_Q show pronounced oscillations in phase with $S(Q)$.

The experimental determinations of small variations in the α relaxation shape is difficult.

Clear evidence for variation of β_Q with Q is available only from simulations: molecular dynamics indicates that β_Q of supercooled water oscillates weakly in phase with $S(Q)$ [21]. In dynamic light scattering from a colloid, the shape of α relaxation appeared to vary with Q but noise in the data precluded quantitative conclusions [17].

In structural glass formers, most scattering experiments on the single-detector spin-echo spectrometer have been restricted to the structure factor maximum. 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 [11]. Later, this effect was ascribed to intra-chain motion [22]. On multi-detector instruments, scattering under different wavenumbers can be observed simultaneously, but the data quality of routine measurements is generally too poor to exploit this advantage in a wavenumber dependent line shape analysis. Here we report on extended measurements on multi-detector time-of-flight and backscattering instruments that have been undertaken with the explicit aim of accurately determining β_Q .

3 Orthoterphenyl

The van der Waals liquid orthoterphenyl (OTP: $C_{18}H_{14}$, 1,2-diphenylbenzene, $T_m = 329$ K, $T_g = 243$ K) is a popular model in the study of glass transition dynamics; in particular, the scaling behaviour around the MC cross-over temperature $T_c = 290$ K has been investigated in much detail by inelastic neutron scattering [13,23] and depolarised light scattering [24,25].

As in other organic samples, one can easily select between coherent and incoherent neutron scattering by deuterating or not the sample; in our present study, we use perdeuterated $C_{18}D_{14}$ prepared by H. Zimmermann (Max-Planck-Institut für medizinische Forschung, Heidelberg); the deuteration reached about 99%.

Although OTP is a relatively simple molecule with an overall shape that comes close to the spherical particles preferred by theory, its structure factor (Fig. 4d) is rather complicated: it possesses a peak at 1.9 \AA^{-1} mainly built up by correlations within the phenyl rings, a maximum at $Q_p = 1.45 \text{ \AA}^{-1}$ associated with correlations between phenyl rings. A similar double-peak structure is found even in liquid benzene [26] and similarly simple phenyl systems [27]. The prepeak at $Q_0 = 0.9 \text{ \AA}^{-1}$ is presumably the most direct manifestation of intermolecular correlations [28,29].

Up to now we have employed coherent neutron scattering to study the critical dynamics near T_c [13]; α relaxation was partly covered but not particularly emphasized [12]. As in other liquids, A_Q or f_Q and h_Q^{-1} were found to oscillate in phase with $S(Q)$. Now we have remeasured α relaxation, over an extended temperature range from 288 up to 400 K.

4 Time-of-flight experiment

Quasielastic neutron scattering requires always a compromise between wavenumber coverage and energy resolution. In our time-of-flight experiment on the spectrometer IN 5 of the Institut Laue-Langevin, an incident wavelength of 6.5 \AA was chosen which leads to an energy resolution (fwhm) of $\sim 25 \mu\text{eV}$ while restricting the wavenumber range to $Q \leq 1.7 \text{ \AA}^{-1}$; the structure factor peak at 1.9 \AA^{-1} is not accessible.

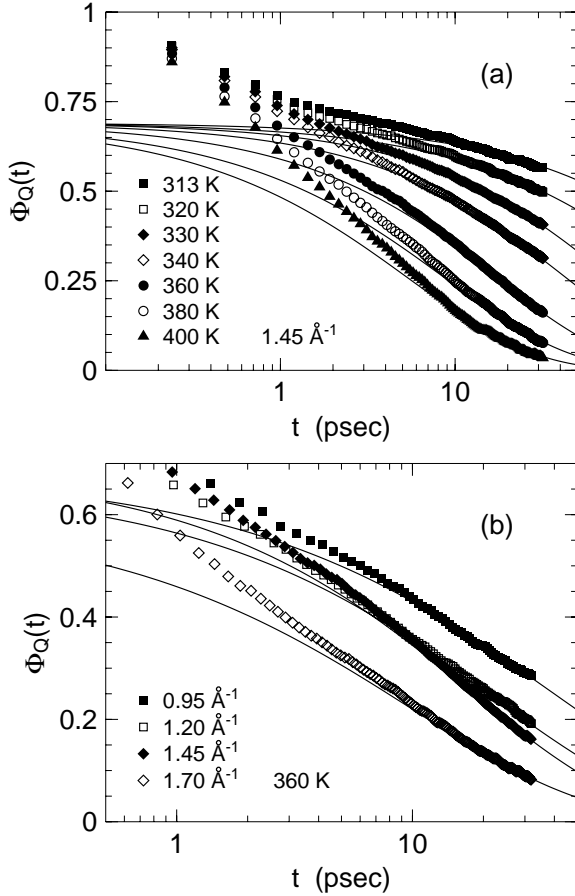


Fig. 1. Density correlation function, obtained by Fourier deconvolution of coherent neutron scattering spectra measured on the time-of-flight spectrometer IN5, (a) for different temperatures at the structure factor maximum $Q = Q_p = 1.45 \text{ \AA}^{-1}$, and (b) on an enlarged scale for 360 K at different wavenumbers. Solid lines are Kohlrausch stretched exponentials as determined from a master curve analysis (Fig. 2). Without any fitting one recognizes that correlations decay steeper at Q_p than at other wavenumbers.

For the Al sample holder, hollow cylinder geometry was chosen in order to keep self absorption and parasitic scattering as isotropic as possible; sample transmission was about 90%. Detectors were calibrated by a vanadium standard that yielded also the resolution functions. Data were interpolated to constant Q with steps $\Delta Q = 0.05 \text{ \AA}^{-1}$. After detailed-balance symmetrization, Fourier deconvolution with the measured resolution function, and division by the static structure factor $S(Q)$ we obtain $\Phi_Q(t) = S(Q, t)/S(Q)$.

Some of the data are shown in Figure 1. Up to high temperatures, far above the melting point, correlations decay in two steps. As expected for α relaxation, the second decay step is stretched and strongly temperature dependent.

In Figure 1b, α relaxation is plotted on an enlarged scale for different wavenumbers at the same temperature. Not only the mean relaxation time, but also the line shape exhibits a pronounced Q dependence. At $Q_p = 1.45 \text{ \AA}^{-1}$

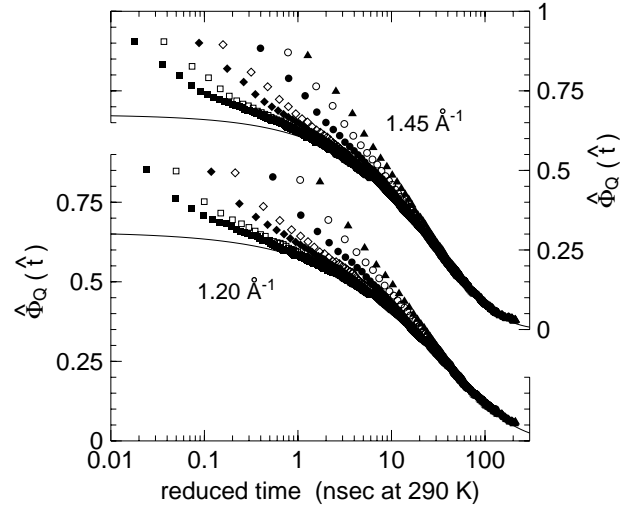


Fig. 2. Master curves $\hat{\Phi}_Q(\hat{t})$ are obtained by rescaling times to $\hat{t} = t[\eta(T_0)/T_0]/[\eta(T)/T]$. The viscosity η is taken from the literature [32,33]; the normalisation to $T_0 = 290 \text{ K}$ is arbitrary. Temperatures and symbols are the same as in Figure 1a. For long times, the data converge towards a common α relaxation asymptote. Such convergence has often been observed at the structure factor maximum: here we see that very much the same behaviour is observed at another wavenumber $Q \neq Q_p$. For $\hat{t} > 2 \text{ ns}$ the master curves are fitted by a Kohlrausch function (Eq. (2), solid lines).

the correlations decay steeper, that is, with *less* stretching, than at any other wave numbers.

5 Master curve analysis

The main result of the present communication, the significant Q dependence of the α -relaxation shape, is obvious to the unguided eye in Figure 1b. Nevertheless, we shall attempt a more quantitative analysis. Since the dynamic window of available spectrometers is not sufficient for fitting three free parameters of (2) to individual spectra, we employ time-temperature superposition to obtain master curves.

In our earlier work on OTP we found that the α -relaxation time scales with viscosity $\tau_Q \propto \eta(T)/T$, and that the line shape is temperature independent [12,30,31]. Fits to the long-time limit of our new data indicate that this form of time-temperature superposition holds for all Q and over the whole temperature range. Using published viscosities [32,33] we construct master curves $\hat{\Phi}_Q(\hat{t})$ by simply rescaling experimental times to

$$\hat{t} = t[\eta(T_0)/T_0]/[\eta(T)/T] \quad (4)$$

with an arbitrary normalization at $T_0 = 290 \text{ K}$.

Without any further adjustment, the data converge towards a temperature-independent long-time asymptote (Fig. 2). This behaviour is in accord with recent light scattering results which showed a constant α -relaxation amplitude over the same temperature range [25].

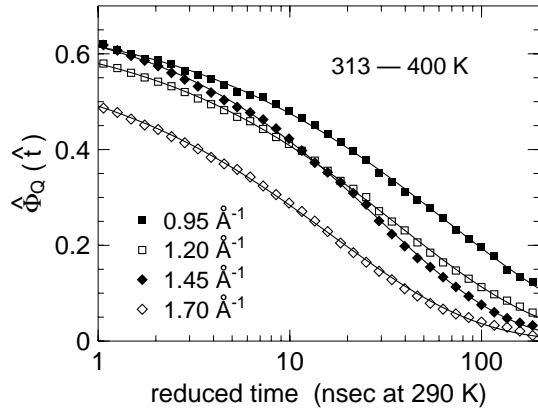


Fig. 3. Same data as in Figure 2, now for four different wavenumbers, and retaining only those points that fall onto the temperature-independent long-time asymptote. These master curves show even clearer than the raw data in Figure 1 that the decay of $\hat{\Phi}_Q(t)$ is less stretched at Q_p than at other wavenumbers. Fits are the same as in Figure 2.

In Figure 3, master curves at different wavenumbers are shown together. As in Figure 1b, one recognises immediately the variations in shape.

All master curves are well fitted by the Kohlrausch function (2). Resulting A_Q , β_Q and $\tau_Q(T_0)$ are shown in Figure 4 and compared to the static structure factor. All three parameters show more or less pronounced oscillations in phase with $S(Q)$. The amplitude A_Q is in qualitative agreement with the Debye-Waller factor f_Q previously obtained from the β relaxation plateau [13]. The relaxation time τ_Q shows two plateaus around Q_0 and Q_p and an overall decrease which could be a Q^{-2} dependence. Most important, the stretching exponent shows a systematic variation by more than 0.1 – which is quite significant for a quantity which different experimental methods in different molecular liquids always found to fall between 0.45 and 0.75 [34].

Some reservation is necessary for the smallest wavenumbers ($Q \lesssim 0.6 \text{ \AA}^{-1}$) where A_Q tends towards 1: in this region, one expects significant background from incoherent scattering which contributes about 15% of the total cross section and from multiple scattering. A separation of coherent and incoherent scattering by the use of polarized neutrons would be helpful.

No reservation is necessary with respect to a possible temperature dependence of β_Q : such dependence cannot be excluded, but it will not affect our conclusions. The fitted τ_Q and β_Q depend essentially on rescaled data from a rather narrow temperature range 340-380 K. Furthermore, the results of Figure 4 have been cross-checked by individual Kohlrausch fits at temperatures from 313 to 400 K. As shown in Figure 5, A_Q and β_Q are essentially temperature independent; while the relaxation time scale varies by nearly two decades, the Q dependence of τ_Q remains unchanged.

In accord with recent light scattering results [25], and in contrast to an often held belief, the stretching exponents do not increase with temperature towards a diffusion limit

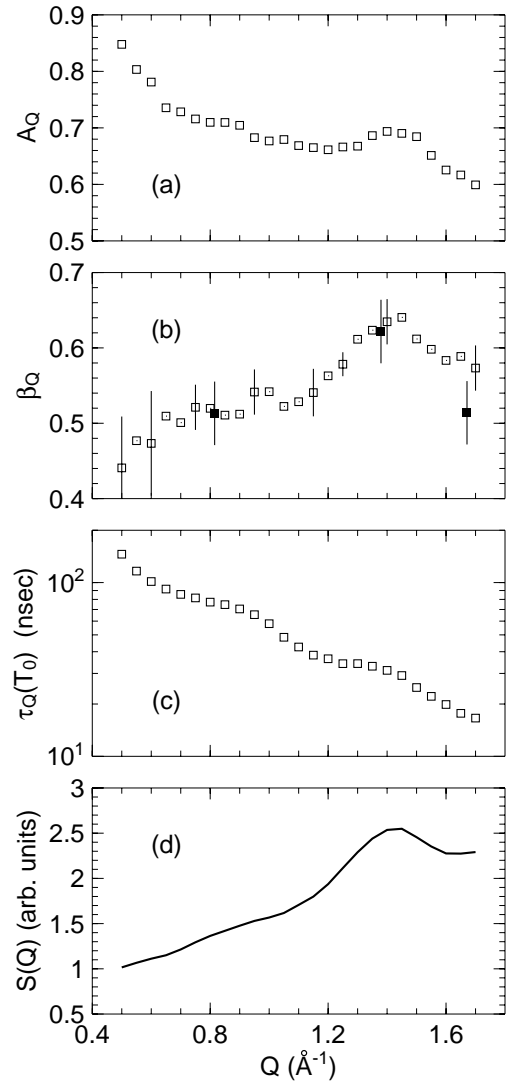


Fig. 4. (a–c) Parameters A_Q , β_Q , and τ_Q obtained from Kohlrausch fits to the master curves (open symbols: time-of-flight, closed symbols: backscattering). Note the presence of oscillations in all three parameters. Error bars for A_Q and τ_Q are of the size of the symbol; the error in β_Q results mostly from temperature uncertainty. (d) Static structure factor $S(Q)$ of OTP at 380 K, obtained by integration over the kinematically accessible region of IN5.

$\beta = 1$ in the normal liquid phase. Even 70 K above the melting temperature, $\hat{\Phi}_Q(t)$ remains stretched.

6 Backscattering experiment

Our earlier backscattering experiment [12] on the thermal neutron spectrometer IN 13 had not allowed to discern the Q dependence of α relaxation. We now retried on the new cold neutron backscattering instrument IN 16. Using the Si₁₁₁ reflection for 6.27 Å neutrons, the energy resolution was 1 μeV; the Q resolution was improved by covering part of the analyser surface with large cadmium shields [35].

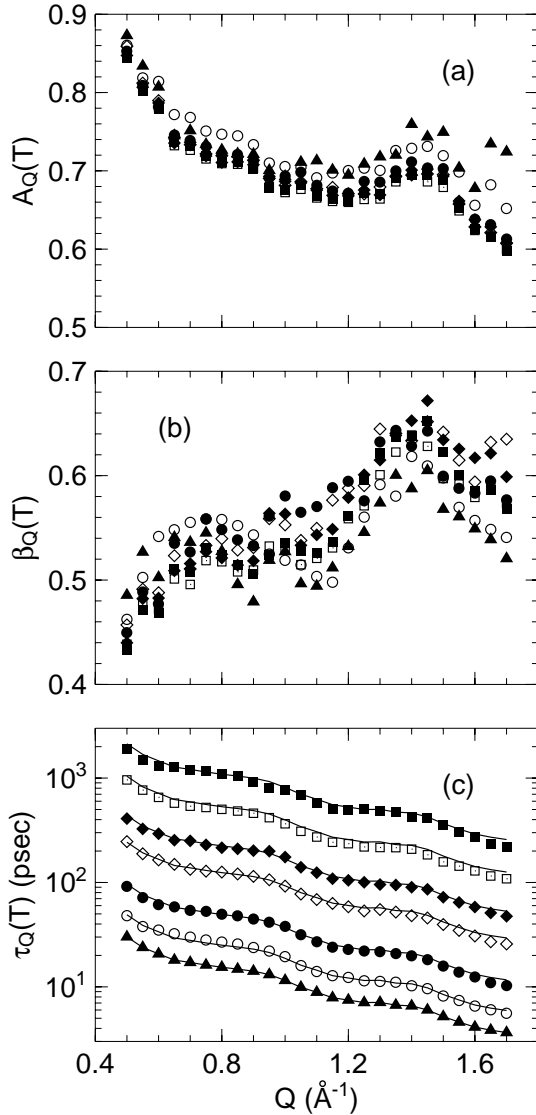


Fig. 5. Kohlrausch parameters of individual time-of flight spectra at seven different temperatures from 313 to 400 K (same symbols as in Fig. 1a). In each of these fits, one parameter was free while the two others were fixed at the values obtained from the master curve analysis. Amplitude A_Q and stretching exponent β_Q are roughly temperature independent which confirms the validity of the scaling approach.

Data were reduced as in Section 4. In contrast to the time-of-flight experiment, master curves could not be obtained by rescaling times alone; it was necessary to admit a temperature dependent amplitude. Assuming again an invariant line shape

$$\hat{\Phi}_Q(\hat{t}) = \Phi_Q(t; T)/A_Q(T), \quad (5)$$

$A_Q(T)$ and $\tau_Q(T)$ were determined in a rapidly converging iterative procedure [30]. The resulting $\hat{\Phi}_Q(\hat{t}; T)$, shown in Figure 6, fall moderately well onto each other; discrepancies, in particular at 1.7 \AA^{-1} , are more likely to be caused by experimental limitations than by any systematic failure of time-temperature superposition.

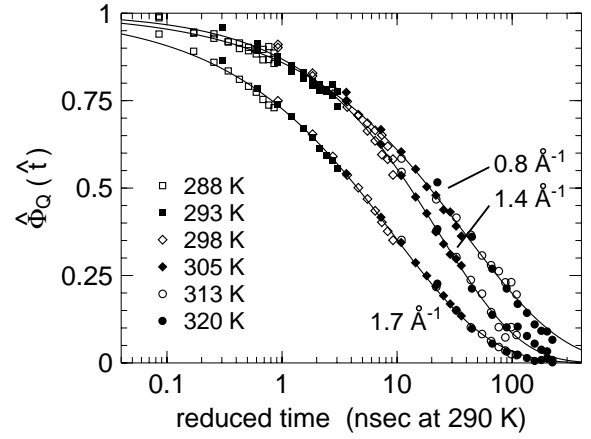


Fig. 6. Towards lower temperatures, the long-time asymptote has been measured on the backscattering spectrometer IN 16. The data are rescaled in time and amplitude by an iterative procedure as discussed in the text; solid lines are Kohlrausch fits. The wavenumber dependence of stretching is salient.

Anyhow, the variation of line shape with wavenumber is obvious. Quantitatively, the exponents β_Q are in excellent agreement with the time-of-flight results (Fig. 4b) as well as with an earlier determination of β_{Q_p} by spin-echo scattering [12,30,31].

7 Conclusions

The main importance of wavenumber dependent stretching is: it excludes any theory of structural relaxation which cannot account for such a dependence.

While it is less easy to give our results a positive interpretation, it appears that mode-coupling theory is at least on the right track: the wavenumber variation of α relaxation is clearly correlated to the static structure factor. Of course, theory cannot be applied literally to a complex system like OTP, nor can we equate the coherent neutron scattering law with an interparticle-correlation function: on the contrary, the pronounced peaks in $S(Q)$ stem mainly from intramolecular correlations. Insofar it may even surprise that these peaks have a counterpart in the slow dynamics, on a time scale where intramolecular vibrations play definitely no role – the explanation lies most probably in molecular rotations which only most recently came into the reach of mode-coupling theory [36,37].

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