"de Gennes" narrowing in supercooled molecular liquids: Evidence for center–of–mass dominated slow dynamics

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The density correlation function \( \Phi(q,t) \) of the two similar substituted aromatic liquids, Toluene and m–Toluidine, is studied by coherent neutron spin-echo and time-of-flight scattering for wave vectors \( q \) around the maximum \( q_{\text{max}} \) of the total static structure factor \( S(q) \) in the supercooled region. The wave-vector dependence of the mean structural \( \alpha \)-relaxation time \( \langle \tau_q \rangle \) shows in both liquids a very pronounced de Gennes-like narrowing centered around \( q_0 < q_{\text{max}} \), where \( q_0 \) corresponds to the first maximum in the center–of–mass static structure factor \( S_{\text{COM}}(q) \). We find that the narrowing can be described quantitatively by using \( S_{\text{COM}}(q)/q^2 \) instead of \( S_m(q)/q^2 \) indicating that at the corresponding molecular length scales the relaxation of \( \Phi(q,t) \) is dominated by purely translational motion.

It is well known that the half width of the experimentally observed dynamic structure factor \( S(q,\omega) \) (wave vector \( q \) and frequency \( \omega \)) of classical dense monoatomic fluids in equilibrium shows a pronounced minimum at wave vectors \( q \sim q_{\text{max}} \approx 2\pi/\sigma \) (\( \sigma \) being the atomic diameter) where the static structure factor \( S(q) \) has its first maximum. This effect, called “de Gennes narrowing” [1], was suggested by de Gennes in 1959 on the basis of sum-rule arguments. It implies that plane-wave density fluctuations with \( q \) in the vicinity of \( q_{\text{max}} \) decay slower in time due to the strong spatial correlations that exist at these wave vectors. Experimentally, this effect has been observed by coherent quasielastic neutron scattering on simple atomic fluids like noble gases [2] and also on liquid metals [3]. It has been confirmed by computer simulations on simple fluid models [4].

The extension of this simple concept to molecular liquids in the supercooled, i.e., high-density state, is difficult and far less investigated [5–7]. Experimentally, only a few studies of the wave vector dependence of the \( \alpha \)-relaxation in supercooled liquids [5–7] indicate that a narrowing is present. The effect, however, was small and the analysis remained only qualitative. Moreover, in glass forming polymers no evidence for any clear modulation was reported in an extended analysis where all relaxation processes were taken into account [5]. The difficulties mainly arise from the following reasons: (i) in the supercooled regime, the presence of memory effects leads to a structural \( \alpha \)-relaxation with a marked stretching of the correlation function; (ii) for molecular liquids the intermolecular structure factor \( S_m(q) \) is a linear combination of many partial atom-atom structure factors; (iii) the dynamical observables depend in general upon both translational and rotational degrees of freedom.

In this letter we present the first quantitative coherent neutron scattering study of two very similar substituted aromatic liquids Toluene and m–Toluidine. A large \( q \)-range was covered including the main peak of the static structure factor \( S_m(q) \) whose maximum is at \( q_{\text{max}} = 1.8 \text{ Å}^{-1} \).

In both liquids we find an extremely pronounced “de Gennes narrowing”, not yet reported for the \( \alpha \)-relaxation of any glass forming liquid. It is centered around a wave vector \( q_0 < q_{\text{max}} \), where \( q_0 \) is equal to the first maximum of the center–of–mass static structure factor \( S_{\text{COM}}(q) \). Moreover, the wave-vector dependence of the mean structural relaxation time \( \langle \tau_q \rangle \) can be quantitatively described by \( \langle \tau_q \rangle \propto S_{\text{COM}}(q)/q^2 \). This indicates that around these wave-vectors the translational motion dominates the relaxation of \( \Phi(q,t) \).

Fully deuterated Toluene (C\(_7\)D\(_8\), \( T_g=117 \text{ K}, T_m=178 \text{ K} \)) was obtained from Euriso-top and sealed into quartz capillaries (Fa. Hilgenberg, Malzfeld). Optical inspection showed no signs of crystallization when cooling down to \( T_g \). Fully deuterated m–Toluidine (C\(_7\)D\(_8\)ND\(_2\), \( T_g=183.5 \text{ K}, T_m=243.9 \text{ K} \)) was filled into a thin hollow aluminium cylinder. Note that for temperatures around the calorimetric glass transition the time scale of the methyl group rotation around their \( C_3 \)-axis is several orders of magnitude faster than the relevant \( \alpha \)-relaxation [8]. Moreover, the quasielastic contribution of the rotational motion is negligible [8]. Both liquids are simple molecular glass formers and particularly interesting as they can be thus considered as rigid planar and small organic molecules. Their dynamic has already been studied by a large variety of experimental methods, e. g. viscosimetry, dielectric relaxation, nuclear magnetic resonance, light- and incoherent neutron scattering [10].

The main experiments were performed on the neutron spin echo spectrometer (NSE) IN11 of the Institut Laue
Langevin in Grenoble, France. IN11 was operated in a double spin echo configuration with the new multidetector covering 30°. Different incident wavelengths $\lambda_i$ and scattering angles $2\theta$ were chosen to cover the $q$ region around the first diffraction peak \cite{11,12}. The polarization was measured for several temperatures. Normalization was achieved by division by the resolution function measured on a quartz rod of similar shape and by the polarization at $t = 0$. We thus obtain the normalized density correlation function $\Phi(q,t) = S(q,t)/S(q,0)$. Additional experiments have been performed for Toluene on the time-of-flight spectrometer (TOF) Mibémol of the Laboratoire Léon Brillouin in Saclay, France. The dynamic time-of-flight spectrometer (TOF) Mibémol of the Laboratoire Léon Brillouin in Saclay, France. The dynamic

The individual correlation functions $\Phi(q,t;T)$ shown in Fig. 1 indicate already without any fitting that the relaxation is slowed down by about a factor of ten around $q \simeq 1.3$ Å⁻¹ when compared to other $q$. Due to the stretched character and the strong $q$-dependence of $\tau_q$ a much larger dynamic time window would be needed in order to cover all $q$-dependent $\Phi(q,t;T)$ at one given temperature. Although a time range of about 2.5 decades is covered our data do not really allow for reliable three parameter fits to the individual $\Phi(q,t;T)$.

However, quantitative information and consistent results with acceptable error bars can be extracted by combining measurements at different temperatures. Without altering the interpretation of the underlying physics we apply the well-known time-temperature superposition principle which means that the correlation functions $\Phi(q,t;T)$ can be superimposed simply by rescaling the time axis. Its operational validity at least in a narrow temperature range of about 30 K in the time range of neutron scattering was demonstrated for a large number of glass forming substances \cite{11,12,13,14}. We use a compilation of $\alpha$-relaxation times $\tau_\alpha$ obtained by other spectroscopic techniques \cite{14} to rescale the experimental times according to $t = t_\alpha(T_0)/\tau_\alpha(T)$, with an arbitrary normalization at $T_0 = 140$ K and $T_0 = 230$ K for Toluene and m–Toluidine, respectively. Indeed, for both liquids all $\Phi(q,t;T)$ collapse onto a temperature-independent master curve $\Phi(q,\tilde{t})$ without any adjustment of $f_\tilde{q}(T)$ as illustrated in Fig. 2. The successful scaling implies that the microscopic relaxation time measured by neutron scattering is proportional to the ”macroscopic” relaxation time and that the exponents $\beta_q$ and the amplitudes $f_\tilde{q}$ cannot depend strongly on temperature.

\[ \frac{\tau_q(T)}{\tau_q(T_0)} \approx 3\beta_q \] From a fit with $\Phi(q,\tilde{t})$ to the master curves $\Phi(q,\tilde{t})$ we obtain the relaxation time $\langle \tau_q(T_0) \rangle$ which are displayed in Fig. 3 normalized to its maximum value at $q_0$. For both liquids, the relaxation time $\langle \tau_q \rangle$ has an overall variation with $q$ (far from the hydrodynamic regime on the low-$q$ side and from the free-particle behavior on the high-$q$ side) of a factor of ten. It passes through a maximum as $q$ is varied from 0.8 to 2.0 Å⁻¹. To our knowledge this variation is much stronger than that in any other liquid studied so far. More strikingly, the strength of the variation of $\langle \tau_q \rangle$ with $q$ and the position of its maximum can quantitatively be described by $\langle \tau_q \rangle \propto S_{\text{COM}}(q)/q^2$ where the center-of-mass static structure factor $S_{\text{COM}}(q)$ was obtained by Monte-Carlo simulations \cite{11,12,13}. It was not expected that de Gennes’s very general concept \cite{11,12,13} would strictly apply to molecular liquids like Toluene or m–Toluidine. It is far from being trivial because the correlation functions are stretched and the relaxation times are long compared to those of atomic fluids. In fact, our findings indicate that in the $q$-range corresponding to molecular length scales (van der Waals radius) and in the $\alpha$-relaxation regime, neutron scattering mainly probes the motion of the centers of mass, i.e. mainly probes the translational motion of the molecules. This result is of fundamental importance for the interpretation of neutron scattering spectra in general. What we actually measure are, of course, atom-atom correlations involving the H,D and C nuclei. In addition to a translational component, these correlations also contain contributions involving the rotational motions. Our joint use of Monte-Carlo simulations and neutron scattering experiments indicates that at the $q$ values considered and for the $\alpha$-relaxation, these latter contributions are small compared to the translational one. This finding is also of particular interest for microscopic glass transition theories like the mode–coupling (MC) theory, either in its idealized form \cite{12} or in the molecular version \cite{11,12}. Indeed in MC theory the static structure factor is the only major input that determines the slowing down of the $\alpha$–relaxation. The MC theory gives at least a qualitative description of the $q$-dependence of $\langle \tau_q \rangle$ around the static structure factor maximum \cite{17} and the importance of the center–of-mass slow dynamics in this framework is illustrated by the so-called semi schematic model \cite{18}.

To underline the robustness of our NSE results $\langle \tau_q \rangle$ has been independently obtained for Toluene from Mibémol experiments by fitting $\Phi(q,\tilde{t})$ the $S(q,\omega)$ at 200 K in frequency space convoluted with the measured resolution function (see Fig. 3). The stretching $\beta_q$ was kept fixed to 0.5 close to the average value 0.48 obtained from our spin–echo experiment (see below). As can be judged from
Fig. 3, excellent agreement within a few percent between NSE and TOF is found for the $q$–dependence of the relaxation time over a large $q$ range. To emphasis this good agreement even further we included in Fig. 2 $Φ(q, t)$ obtained from Mibémol spectra $S(q, ω)$ by Fourier deconvolution with the measured resolution function. Thus, an identical wave–vector dependence of $⟨τ_γ⟩$ is observed from the stable liquid state, where the typical relaxation times are of the order of picoseconds, to the supercooled state, with relaxation times of the order of nanoseconds. Such a behavior was also observed in ortho-terphenyl (OTP) [1].

Another important output of our study is the $q$–dependence of the amplitude $f_q$ of the $α$–relaxation. In Fig. 4, $f_q$ shows a maximum at $q = 1.4$ Å$^{-1}$ which is very close to the maximum of the center–of–mass static structure factor $S_{\text{COM}}(q)$, in agreement with the numerical solutions of mode–coupling equations [16]. However, contrary to this latter, it does not oscillate in phase with $S_{\text{COM}}(q)$ (nor $S_m(q)$), and only a very smoothly decreasing behavior is observed at higher $q$ due to additional rotational contributions [19]. We could not detect any systematic $q$–dependence of the stretching parameter $β_q$ which is at variance to theoretical predictions [21] and to the results in OTP [1]. Note however, that in OTP no variation of $β_q$ with $q$ was detected at wave numbers corresponding to the center–of–mass correlations but at larger $q$ values. From NSE we find an average $⟨β_q⟩_q ≃ 0.48 ± 0.02$ for Toluene and $⟨β_q⟩_q ≃ 0.58 ± 0.02$ for m–Toluidine. The conjecture of $q$ dependent oscillations of $β_q$ and $⟨τ_q⟩$ indicates a systematic error source in NSE experiments: since we have used a wave vector band $Δq/q = Δλ/λ ≃ 10\%$ which is nearly as broad as the diffraction peak itself [11][2] we have actually measured averages $⟨Φ(q,t;T)⟩_q$ of correlation functions with possibly different parameters $β_q$ and $⟨τ_q⟩$. In practice, a sum of different stretched exponentials can again be fitted by a Kohlrausch with a smaller effective exponent $β_{\text{eff}}$ and a different $⟨τ_q⟩_{\text{eff}}$. From numerical examples using $⟨τ_q⟩ ∝ q^{-2}S_{\text{COM}}$ and $0.4 ≤ β_q ≤ 0.5$ as input we conclude that the difference between $⟨τ_q⟩_{\text{eff}}$ and $⟨τ_q⟩$ is always less than 10% and the difference in the line-shape is anything between 0.01 and 0.05 which is far less than our experimental accuracy i.e. our conclusion remain valid.

The main result of our communication concerns the wave vector dependence of the $α$ relaxation time $⟨τ_q⟩$. The maximum in $⟨τ_q⟩$ at $q_0 < q_{\text{max}}$ can be interpreted as a de Gennes narrowing for molecular glass forming liquids resulting from the strong spatial correlations between the centers–of–mass of the molecules. The relaxation time characteristic is quantitatively described by $τ_q ∝ S_{\text{COM}}(q)/q^2$. $S_{\text{COM}}(q)$ is the spatial Fourier transform of the orientationally averaged pair correlation function. On molecular scales and microscopic times, the time evolution of density fluctuations of the glassforming Toluene and m–Toluidine is dominated by translational dynamics, i.e. the center–of–mass relaxational dynamics. Such a strong de Gennes narrowing effect has not yet been reported for the $α$-relaxation of low molecular-weight glass-forming liquids. Whether $S_{\text{COM}}(q)$ is the right input for a sophisticated mode-coupling analysis in the supercooled high-density state can only be decided by further molecular dynamics simulations [19]. Some fortuitous compensation effects in the orientational fluctuations can play an important role.

Despite the structural similarity of both molecules there is an important difference that might play an interesting role in the structural relaxation dynamics: the formation of hydrogen bonds in a system like m–Toluidine induces clustering of a few molecules whose signature is a well defined prepeak around $q ≃ 0.5$ Å$^{-1}$ in the static structure factor [14]. Unfortunately, our experiments in this low $q$-range are of too low statistical quality — NSE experiments outside the diffraction maximum are extremely difficult to perform — to decide whether this static heterogeneity has a counterpart in the dynamics or not.

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Figure captions

Figure 1:
Density correlation functions $\Phi(q, t)$ at 160 K for Toluene at three different wave vectors $q$. Lines are fits with the Kohlrausch function (1). Note, at $q_0 = 1.3\text{ Å}^{-1}$, close to the first maximum of the center–of–mass static structure factor $S_{\text{COM}}(q)$, the correlations decay much slower than for other wave vectors.

Figure 2:
Master curves $\Phi(q, \hat{t})$ at several $q$ for Toluene (a) and m–Toluidine (b) as obtained by rescaling times to $\hat{t} = t\tau_\alpha(T_0)/\tau_\alpha(T)$. The data fall onto a temperature-independent master curve. The dense points at long times stem from Fourier deconvoluted Miémol TOF spectra $S(q, \omega)$. For Toluene $\Phi(q, \hat{t})$ at 200 K for $q = 0.9\text{ Å}^{-1}$ and $q = 1.3\text{ Å}^{-1}$ is included (a). For m–Toluidine $\Phi(q, \hat{t})$ for $q = 1.3\text{ Å}^{-1}$ from a fragmentary experiment on Miémol at 273 K is included in (b). Note the excellent agreement between NSE and TOF.

Figure 3:
(a) Wave vector dependence of the structural relaxation time $\langle \tau_q(T) \rangle/\langle \tau_{q_0}(T) \rangle$ for Toluene obtained from fits with (1) to the neutron spin–echo master curves (cf. Fig. 2) (open symbols). Results from fits with the Fourier transformation of (1) to the dynamic structure factor $S(q, \omega)$ from Miémol at 200 K are included (closed symbols). The solid line is $q^{-2}S_{\text{COM}}(q)$, obtained by Monte-Carlo simulations at 160 K. The dotted lines is the experimentally observed total $q^{-2}S_m(q)$ at 161 K [11,12]. (b) The same for m–Toluidine with $q^{-2}S_{\text{COM}}(q)$ at 260 K and $q^{-2}S_m(q)$ at 248 K.

Figure 4:
Wave vector dependences of the the prefactor $f_q$ obtained from fits of (1) to the master curves. Open squares: Toluene (NSE), open circles: m–Toluidine (NSE). The closed squares are plateau values from Miémol TOF data obtained by time averaging $\Phi(q, t)$ at 140 K in the range $3\text{ psec} \leq t \leq 8\text{ psec}$ and multiplied by 1.1 to match NSE data. Solid line: $S_{\text{COM}}(q)$, dotted line $S_m(q)$ for Toluene as in Fig. 3.
Toluene 160 K

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