Experimental evidence of mosaic structure in strongly supercooled molecular liquids

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When a liquid is cooled to produce a glass its dynamics, dominated by the structural relaxation, become very slow, and at the glass-transition temperature $T_g$ its characteristic relaxation time is about 100 s. At slightly elevated temperatures (~1.2 $T_g$) however, a second process known as the Johari-Goldstein relaxation, $\beta_{JG}$, decouples from the structural one and remains much faster than it down to $T_g$. While it is known that the $\beta_{JG}$-process is strongly coupled to the structural relaxation, its dedicated role in the glass-transition remains under debate. Here we use an experimental technique that permits us to investigate the spatial and temporal properties of the $\beta_{JG}$ relaxation, and give evidence that the molecules participating in it are highly mobile and spatially connected in a system-spanning, percolating cluster. This correlation of structural and dynamical properties provides strong experimental support for a picture, drawn from theoretical studies, of an intermittent mosaic structure in the deeply supercooled liquid phase.
The timescale, $\tau_{\alpha}$, of structural rearrangements in a typical liquid is in the ps range. If the liquid is supercooled below the melting temperature, $T_m$, it gets longer the lower is the temperature, until the dynamics become so slow that we speak of a solid rather than of a liquid: a glass has been obtained. Conventionally, the glass transition temperature, $T_g$, is defined as the temperature where this characteristic time is 100 s. However, this is not the only characteristic timescale for the molecular dynamics of a strongly supercooled liquid. At temperatures somewhat higher than $T_g$, a second characteristic timescale associated with a secondary relaxation process appears. This secondary process, known as Johari-Goldstein or $\beta_{IG}^1$, can be considered a precursor of the glass-transition in two ways: time and temperature. In time: it anticipates the structural (or $\alpha$) relaxation that freezes in at $T_g$ by many decades, being typically in the ms-µs time range at $T_\tau$ and remaining active also in the glass$^2$. 

In temperature: it decouples from the process in the supercooled liquid phase at temperatures lower than $T_{\alpha\beta} \approx 1.2 T_g$, thus anticipating the glass-transition by a stretch. On the role of the $\beta_{IG}$-relaxation in the glass-transition at least three generations of scientists have been debating since its discovery in the early seventies$^1$. While its phenomenology has been largely explored, the concomitant effects of (i) the lack of a firm microscopic theory of the glass-transition and (ii) the difficulty of experimental and numerical techniques to probe the spatial and the temporal properties of this process in the relevant time-range and temperature-range, make this debate still unsettled.

From the glass-transition perspective, it is becoming more and more clear that the vitrification kinetics is not only driven by the structural relaxation, as traditionally believed, but other, faster processes must play a role to reduce the effectiveness of the structural relaxation to lock the atomic dynamics$^3$. This is consistent with recent theoretical and numerical work pointing out that the free energy landscape relevant for the glassy state is much rougher than classically thought, with intra-state barriers associated with secondary relaxations$^4$. In the context of these findings, it is clear that direct investigations of the $\beta_{IG}$-relaxation are of crucial importance for a better understanding of the liquid-to-glass transition.

Many basic properties of the $\beta_{IG}$ process are known, mostly thanks to a large body of dielectric spectroscopy (DS)$^{5,6}$ and nuclear magnetic resonance$^7$ data. It is e.g. nowadays understood that the $\beta_{IG}$-relaxation is strongly connected to the $\alpha$-process$^{5,6,7}$, and thus is sensitive to the glass-transition. This conclusion is in apparent contrast with the restricted re-orientational dynamics of the process$^7$ and with its mild Arrhenius $T$-dependence, usually interpreted as the signature of a hindered, simply activated process$^2$. The few available neutron and X-ray scattering experiments also describe it, above $T_g$, as an essentially restricted if not localized molecular motion occurring mainly within the transient cages formed by the nearest-neighbors$^8-12$. Sub-$T_g$ experiments$^{13}$ and atomistic simulations$^{14,15}$ support instead of the idea that the $\beta_{IG}$-relaxation is rather cooperative and characterized by string-like excitations occurring via hopping between adjacent atomic sites.

Several phenomenological models of the $\beta_{IG}$ process are also available, based on an intuition of the main physical mechanism giving rise to it. For instance, according to the coupling model, the $\beta_{IG}$-relaxation consists of a distribution of elementary processes evolving with time by increasing the number of participating molecular units and culminating in the cooperative $\alpha$-relaxation: the $\alpha$-relaxation and $\beta_{IG}$-relaxation thus share many relevant properties$^2$. In another model based on the hypothesis of strong dynamical heterogeneity of the supercooled liquid, the $\beta_{IG}$-relaxation originates from the population exchange between regions of tightly confined molecules and of loosely confined ones$^{11}$. The random first-order transition theory identifies instead the $\beta_{IG}$-relaxation with cooperative rearrangements of string-like shaped regions of molecules which become more prominent with increasing temperature$^{16}$. While these ideas are not necessarily alternative to each other, unambiguous experimental input is required as a guide among these rather different views. Combining new X-ray scattering data on 1-propanol with data available in the literature$^{8-10,12}$ and here re-analyzed, evidence shall now be provided of two striking features related to the molecules participating in the $\beta_{IG}$-relaxation: (i) their mean-squared displacement satisfies the Lindemann criterion for structural instability and (ii) their number matches the threshold for site instability.

**Fig. 1 Temperature and scattering vector dependence of time-domain interferograms.** Time-domain interferometry data as a function of time (squares with ±1 SD errorbars) at different temperatures and at a fixed exchanged wave-vector ($q = 15$ nm$^{-1}$, roughly corresponding to the inter-molecular distance) and at the same temperature $T = 122.5$ K in the supercooled liquid state and at different $q$ values. The raw data have been averaged over a time range $\pm 0.7$ and $\pm 0.9$ ns, respectively, depending on the collected statistics, in order to improve the figure readability. The black solid lines are the model curves obtained from the fitting procedure. The blue solid lines are the calculated contrast functions, $\phi'$, along with the 68% confidence interval (gray area). $\phi'$ is proportional to the density correlation function.
percolation. They, therefore, form a mobile percolating, infinite cluster pervading the whole sample. This cluster evolves on the timescale of the $\beta_{\text{JG}}$-process, and careful experimental design is required to study it.

**Results**

Nuclear $\gamma$-resonance time-domain-interferometry (TDI) is one of the few techniques able to probe directly microscopic density fluctuations at the timescale where the $\beta_{\text{JG}}$-process decouples from the structural one. TDI is based on an interferometric analysis of the X-rays scattered by the sample and, as such, provides information that is both time and space resolved ($q$ being the momentum exchanged in the scattering process)\(^{12}\). TDI has been here employed to study 1-propanol, a model glass-former with a genuine $\beta_{\text{JG}}$-process\(^{17}\) rather coupled to the $\alpha$-relaxation. Some examples of the measured TDI beating patterns are reported in Fig. 1 (red squares) along with the fitting curves obtained using a model that accounts for one relaxation process (black lines, see “Methods” section). The beating pattern contrast function $\phi(q, t)$ (blue solid line in Fig. 1) is proportional to the density correlation function and allows extracting its main relaxation parameters, in particular the relaxation time, $\tau$, at different $q$ values. TDI is sensitive to the fastest relaxation process active in the explored time window: given its dynamical range of fewer than two decades in time, it was not possible to detect more than one relaxation process per experimental curve even when both the $\alpha$ and the $\beta_{\text{JG}}$ process were expected to be active.

Of particular interest is the $T$-dependence of $\tau$, which was investigated at two $q$-values, 15 and 25 nm\(^{-1}\), corresponding to the inter-molecular and to an intra-molecular length-scale, respectively. The measured $\tau$ values are shown in Fig. 2 along with the ones obtained by DS and relative to the reorientational dynamics (see “Methods” section and Supplementary Note 1).

The DS data provide a precise estimation of the $T$-dependence of the $\alpha$-process and $\beta_{\text{JG}}$-process characteristic times (gray and green dash-dotted lines in Fig. 2). These $T$-dependencies were then scaled onto the TDI data. This procedure, along with the study of the $q$-dependence of the relaxation time (see below), allowed us to unambiguously associate the process appearing in the density fluctuations to the $\alpha$-relaxation or $\beta_{\text{JG}}$-relaxation, see also Supplementary Note 2 for additional support to this interpretation.

A clear change in the $T$-dependence of $\tau$ measured by TDI occurs around $T_{\text{ab}} \approx 131$ K at $q = 25$ nm\(^{-1}\). At $q = 15$ nm\(^{-1}\) the crossover from the $\alpha$ to the $\beta_{\text{JG}}$-process is instead too weak to be appreciated. Interestingly, at $q = 15$ nm\(^{-1}\) the $T$-dependence of $\tau$ can also be described accounting only for that of the $\beta_{\text{JG}}$-relaxation (blue dashed line in Fig. 2): a similar match cannot be obtained instead considering only the $\alpha$-process. It is then evident that, at least for $T \leq 131.4$ K, TDI is sensitive to the $\beta_{\text{JG}}$-process both at the inter and intra-molecular lengthscales. This provides broader validity to similar observations for another monoalcohol\(^{12}\).

Further insights can be gained from the $q$-dependence of the relaxation parameters which were investigated at two temperatures: 131.4 and 122.5 K (see Fig. 3a). At the former one, slightly higher than the decoupling temperature $T_{\text{ab}}$, the $\alpha$-relaxation is expected to be dominant, whereas at the latter one Fig. 2 shows that TDI is sensitive only to the $\beta_{\text{JG}}$-process. In order to facilitate the comparison to the DS results, the TDI characteristic times have been converted to those, $\tau_p$, corresponding to the peak of the susceptibility function (see “Methods” section). The obtained $\tau_p$ values are plotted in Fig. 3b along with the curves obtained from fitting them to a power-law $\tau_p \propto q^{-n}$. The power-law exponents, $n$, obtained from the fits, namely $n = 2.0(7)$ at $T = 131.4$ K and $n = 3.9(9)$ at $T = 122.5$ K (see Fig. 3c), strongly support that for $T > T_{\text{ab}}$ the $\alpha$-relaxation, with a quadratic $q$-dependence of the characteristic time, dominates the microscopic dynamics, whereas below $T_{\text{ab}}$ the characteristic super-quadratic $q$-dependence of $\tau_p$ confirms that the $\beta_{\text{JG}}$-relaxation is rather observed.

**Discussion**

The $\alpha$-process in 1-propanol is still diffusive around $T_{\text{ab}}$ while the microscopic dynamics associated with the $\beta_{\text{JG}}$-process is clearly restricted ($n > 2$) already at a relatively high $T$ (122.5 K $\approx 1.25 T_p$), giving broader significance to similar observations reported for the other two glass-formers studied using TDI: 5M2H\(^{12}\) and OTP\(^{3,9}\).

There are then some interesting common features for the three glass-formers investigated by TDI: (i) density fluctuations are coupled to the $\beta_{\text{JG}}$ relaxation at/close to both the inter and intra-molecular length-scale; (ii) the characteristic times of the $\beta_{\text{JG}}$ relaxation appearing in the density fluctuations show a strong $q$-dependence, indicative of a reduced dynamics, and (iii) cross the
dielectric \( \tau_{\beta G} \) at a \( q \)-value, \( q_{DS} \), somewhat larger than \( q_{\text{max}} \). The length \( L_{q_{DS}} \) identifies the characteristic scale for the center-of-mass motion within the \( \beta_G \)-relaxation. More in detail, it is possible to relate \( q_{DS} \) to the molecular root-mean-squared displacement within an anomalous diffusion model (see discussion in the Supplementary Note 3) as:

\[
\Delta r_{\beta G} = \sqrt{\langle r^2(\tau_{\beta G}) \rangle} = \sqrt{6} q_{DS}.
\]

Here \( \Delta r_{\beta G} \) has to be regarded as the most probable displacement of the molecules participating in the \( \beta_G \)-relaxation at \( \tau_{\beta G} \).

Figure 4a shows \( \Delta r_{\beta G} \) for 1-propanol (red symbol), 5M2H (blue symbols), and OTP (green symbols, see Supplementary Note 4) estimated from the \( q \)-dependencies reported in Fig. 3 and in refs. 8,9,12 and normalized to the corresponding average inter-molecular distance (center-of-mass to center-of-mass), \( \tau_p = \tau_{\text{rel}} \), where \( \tau_{\text{rel}} \) is the molecular volume. Figure 4b reports the corresponding relaxation times of the three samples probed by DS and depolarized dynamic light-scattering as a function of \( T/T_g \) and scaled by the value of \( \tau_{\beta G} \) at \( T_g \). Figure 4a shows that \( \Delta r_{\beta G} \) is larger for 1-propanol (28%) than for 5M2H and OTP (12%). This difference can be related to the higher normalized temperature at which the dynamics of 1-propanol were investigated, i.e., \( T/T_g \approx 1.25 \). In all cases, \( \Delta r_{\beta G} \) amounts to a non-negligible fraction of the average inter-molecular distance, a result evocative of the Lindemann criterion for the stability of crystalline solids. In fact, all the estimated values for \( \Delta r_{\beta G}/r_p \) fall inside the gray band in Fig. 4a which enlightens the range of typical values for the Lindemann criterion in crystals (see ref. 20 and references therein) expressed in terms of root-mean-squared displacement.
It is interesting to read this value in the light of the number of nearest neighbors ($z$) for the samples here considered. $z$ can be estimated from the radial pair distribution function, $g(r)$: for 1-propanol and OTP the room temperature values are $z \approx 12$ (D.T. Bowron, private communication) and $z \approx 15$\textsuperscript{31}, respectively (see Supplementary Note 5). No $g(r)$ data are instead available in the literature for 5M2H but we can expect its number of nearest neighbors to be similar to that of 1-propanol, given the similarity of their structure. The available values of $z$ are close to that for an fcc lattice, and remarkably lattices with such connectivity present a threshold for site percolation ($p_z^{cc} = 0.198$\textsuperscript{22}) which is comparable with $f_q^{(\alpha)}$. The molecules participating in the $\beta_G$-relaxation must then be spatially connected in a percolating (or close to percolation) cluster pervading the whole sample, see Fig. 5. Clearly, this spatial connection does not imply dynamical correlations among all the molecules participating in the $\beta_G$-process. In fact, though the $\beta_G$-relaxation might be cooperative to some extent, as our results for 5M2H\textsuperscript{12} and 1-propanol also suggest, its strong sub-diffusivity clearly evidences that it is of prevalent local nature.

The present results establish an interesting correlation between spatial and temporal properties of the molecules participating in the $\beta_G$ process: the most mobile molecules (on a time scale that precedes the $\alpha$-process) are spatially distributed as a percolating cluster. In other terms, the $\beta_G$ process marks the development of a mosaic state in the undercooled phase with patches of less mobile molecules separated by an intermittent and ever-changing network of more mobile ones. These results, obtained in the deeply supercooled liquid phase, give then a new perspective to concepts used to imagine the dynamical heterogeneities which develop on lowering the temperature towards $T_g$, while the size of the patches of the mosaic structure shows in the investigated cases a mild temperature dependence\textsuperscript{26,28–29}: the development of a percolating, infinite cluster at temperatures below $T_g = 1.2$ $T_g$ signaled by the $\beta_G$-process is a very suggestive result supporting the idea that a dynamical transition is taking place there. This point is in line with the basic idea underlying the random phase order transition theory\textsuperscript{6,29}.

**Methods**

**Nuclear resonance time-domain interferometry measurements.** The nuclear $\gamma$-resonance TDI experiments were performed at the nuclear resonance beamline ID18\textsuperscript{30} of the European Synchrotron Radiation Facility (ESRF) in Grenoble (F) employing an optimized implementation of what is originally described in ref. 31.

TDI experiments are designed to detect X-ray scattering using an interferometer that allows probing density fluctuations in the 10 ns–10 μs range\textsuperscript{8,12,32,33}. Two single-line $^{57}$Fe-containing absorbers were therefore installed upstream of the sample, on the incoming beam, and downstream of the sample, on the scattered beam, to provide the probe and reference beams of a time-domain interferometer. In order to obtain different excitation energies, the probe absorber was mounted on a velocity transducer and driven at the constant velocity $v \sim 10$ mm/s with a relative accuracy better than 0.1%. The resulting shift was of $\Delta \theta = 10^5 \mu rad$, where $\Delta \theta = 4.66$ meV is the natural linewidth of the first excited state of $^{57}$Fe. The incident X-ray radiation used to excite the nuclear resonance of the absorbers was characterized by a bandwidth of 2.5 meV at the energy of the first nuclear transition of $^{57}$Fe at 14.412 keV. The photons quasi-elastically scattered by the sample at two different scattering vectors $q = 2\pi \sin(\theta/2)$, where $\theta$ is the scattering angle and $k_0 = 73$ nm$^{-1}$ is the wave-vector of the nuclear fluorescence from the first excited state of $^{57}$Fe, were simultaneously collected by two avalanche photodiode (APD) detectors. The setup was designed to span the $q$-range $9–42$ nm$^{-1}$.

The TDI interferograms were analyzed as reported in the literature\textsuperscript{1,2,3–4}. More precisely, in TDI experiments with identical single-line nuclear absorbers the time evolution of the intensity emerging from the interferometer is described by\textsuperscript{12,32,33}:

$$I(q,t) = |R(q,t)|^2(1 + \cos(\Omega t)\phi(q,t)).$$

Here $R(q,t)$ is the time response of the nuclear absorbers\textsuperscript{12,32,33} and $\phi(q,t)$ (blue solid line with gray area in Fig. 1) is the contrast function\textsuperscript{12}, $\phi(q,t)$ is related to the density correlation function (also known as normalized intermediate scattering function), $\phi(q,t)$, via:

$$\phi(q,t) = \frac{\phi(q,t)}{\phi(0)}$$

where $f_{\alpha}^{(\alpha)}$ depends both on the experimental set-up and on sample properties\textsuperscript{32,34}. $\phi$ has been modeled using the KWW function\textsuperscript{2} in order to introduce a minimum bias in the fitting procedure\textsuperscript{32,33}:

$$\phi(q,t) = f_0 \exp\left(-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right).$$

Here $f_0$ is the initial beating pattern contrast (see Supplementary Note 6 for the obtained results), $\tau$ is the relaxation time of density fluctuations and $\beta_{KWW}$ is the stretching parameter. In the fitting procedure $\beta_{KWW}$ was fixed to an average value obtained from DS measurements ($\langle \beta_{KWW} \rangle = 0.66$) for $q > q_{max}$ similarly to what reported in refs. 8,10,11. Concerning the data collected at $q_{max}$, $\beta_{KWW}$ has been increased by 20% ($\langle \beta_{KWW} \rangle = 0.79$) in order to take into account its $q$-dependence, consistently to what discussed in ref. 12. $\phi$ has also been modeled using the Mittag–Leffler function\textsuperscript{35}, the Fourier transform of the Cole–Cole function well known to properly describe the $\beta_G$ relaxation in DS data\textsuperscript{3}. This approach is delicate given the fact that (i) the TDI signal covers less than two decades in time and (ii) the Fourier transform of the Cole–Cole function has a very stretched tail. In other terms, the measured TDI signal is in general not very sensitive to the parameters of the (Fourier transform of) the Cole–Cole function. However, for the data-sets where this happens to be the case, modeling the TDI signal within the $\beta_G$-relaxation using the Cole–Cole susceptibility provides results very close to those obtained using the KWW function for what concerns both the quality of the fit and the estimated parameters, which turn out to be in mutual agreement within one standard deviation.

**1-propanol.** The 1-propanol sample was purchased from Sigma Aldrich (anhydrous, 99.76% pure) and used as received. 1-propanol, differently from other glassformers investigated by TDI\textsuperscript{8,12}, is characterized, above $T_g = 97$ K, by rather coupled $\alpha$ and $\beta_G$ processes\textsuperscript{36}, thus offering the possibility to study the $\beta_G$-relaxation in a regime still unexplored by density fluctuations. The TDI experiment on 1-propanol has been carried out in the temperature interval from 1.44 $T_g$ down to...
Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request. The data used to produce Fig. 5 have been taken from http://www.physics.emory.edu/faculty/weeks/data/mono.html.

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Author contributions

The project was conceived by F.C. and G.M. The TDI experiments were performed by F.C., S.C., S.V., M.M., A.I.C., and G.M. The TDI data were analyzed by F.C. with inputs from A.I.C. and G.M. The DS experiment and the related data analysis were performed by S.C. and S.V. All the authors discussed the results. The paper was written by F.C. and G.M. with inputs from all the authors.

Competing interests

The authors declare no competing interests.

Additional information

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