Ergodicity breaking in strong and network-forming glassy system

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The temperature dependence of the non-ergodicity factor of vitreous GeO2, \(f_q(T)\), as deduced from elastic and quasi-elastic neutron scattering experiments, is analyzed. The data are collected in a wide range of temperatures from the glassy phase, up to the glass transition temperature, and well above into the undercooled liquid state. Notwithstanding the investigated system is classified as prototype of strong glass, it is found that the temperature- and the \(q\)-behavior of \(f_q(T)\) follow some of the predictions of Mode Coupling Theory. The experimental data support the hypothesis of the existence of an ergodic to non-ergodic transition occurring also in network forming glassy systems.

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On cooling a liquid below the melting point of its crystal, its viscosity increases and its molecular motion is slowed down. Below the glass transition temperature, \(T_g\), no more molecular rearrangements typical of a liquid occur: the system, becoming a glass, is completely arrested, at least on the observation time scale. The structural (\(\alpha\)-) relaxation process describes the dynamical arrest. Its characteristic time \(\tau_\alpha\) exhibits a strong temperature dependence, usually mirrored by that of the static transport coefficients, such as the shear viscosity, \(\tau_\alpha \propto \eta\). In the glassy state, only secondary relaxation processes, \(\beta\), remain activated. They are attributed to local reorientational motions.

From the theoretical side, several different microscopic pictures have been proposed to universally describe the dynamical arrest characterizing the glass transition. The existence of a trapping effect that molecules or groups of molecules suffer, due to the presence of their neighbors, was formulated both in the phenomenological approach of the free volume and in the more formal framework of the Mode Coupling Theory (MCT). The MCT is, up to now, the only approximation which provides a self consistent treatment of the particles dynamics. Thanks to the introduction of a non-linear microscopic equation of motion, it allows to calculate the time evolution of \(\Phi_q(t)\), the normalized density autocorrelation function at momentum transfer \(q\). The glass-transition problem is approached introducing the existence of a dynamic instability at some temperature, \(T_c\), above \(T_g\). The transition from ergodic (high temperature) to non-ergodic (low temperature) state takes place at this temperature. From the microscopic point of view, \(T_c\) corresponds to a critical density from which each particle is trapped in the cage made by its neighbors. In this picture, only the rattling motion of the particles blocked inside the cages is permitted: this motion is the microscopic origin of the \(\beta\) relaxation.

In recent years, a considerable amount of work has been done to extend and solve the MCT equations for systems much more complex than simple liquids with spherically symmetric interactions for which the theory was originally formulated. Some universal features, largely independent from the particular system one is analyzing, were foreseen. For instance, in a temperature region close to \(T_c\), a cusp-like behavior of the long time limit of the density correlator, \(\Phi_q(t)_{\to \infty} f_q(T)\) is predicted. In fact, in a liquid, \(f_q(T)\) is equal to zero, indicating that at long enough times a given particle can leave the transient cage made by its nearest neighbors. Crossing \(T_c\), no more molecular rearrangement occurs and \(f_q(T)\) changes discontinuously assuming a finite value. In this sense \(f_q(T)\) is usually considered as an indicator of the ergodic to non-ergodic transition.

The Inelastic Neutron Scattering (INS) and Inelastic X-Ray Scattering (IXS) experiments provide a good mean to study the temperature evolution of \(f_q(T)\) in a wide \(q\) range. From a experimental point of view, \(\Phi_q(t)\) and \(f_q(T)\) are accessible measuring the intermediate scattering function, \(F(q,t)\). In a supercooled liquid, \(\Phi_q(t)\) is expected to go to zero exhibiting a two-step decay related to the \(\beta\) and \(\alpha\) relaxations respectively. On cooling the sample, the structural rearrangements become slower and slower, and the decay of \(\Phi_q(t)\) related to the \(\alpha\) relaxation is shifted to longer and longer times. When the temperature is low enough and the \(\alpha\) relaxation is frozen, the characteristic time of its decay is no more measurable and, for long times, \(\Phi_q(t)\) assumes a finite value: \(f_q(T)\). Alternatively, the plateau value separating the \(\beta\) relaxation from the \(\alpha\) one, sited at longer times, can be determined in the frequency space by measuring the dynamic structure factor, \(S(q,\omega)\). When the characteristic time of the \(\alpha\) process is shifted to so long time that \(1/\tau_\alpha\) is inside the frequency interval defined by the instrumental resolution function, the evolution of the \(\alpha\) process can be directly monitored by measuring the elastic scattering intensity. Under this condition, \(f_q(T)\) is determined...
by the ratio of the elastic to the total scattered intensity, that is \( f_q(T) = \frac{S_{el}(q, \omega = 0)T}{S(q)T} \).

In the past two decades, the existence of the specific theoretical predictions on the \( T \) and \( q \) behavior of \( f_q(T) \) motivated a large number of experiments and simulations aimed at testing the MCT in different systems \[10, 11, 12, 13, 14, 15\]. Recent studies tried also to relate the microscopic properties of the systems with the temperature dependence of their viscosity, when approaching the glass transition \[16, 17, 18, 19, 20\]. Up to now, the experimental studies performed by INS \[11, 12, 13\] and more recently also by IXS \[14, 15\] were carried out mainly on glass formers without directional bounds (Van der Waals or ionic systems) which show high fragility (high increase of viscosity upon cooling \[21\]). Recently, both theoretical and simulation studies \[4, 7\], and experimental data \[22, 23\], have suggested that the MCT can describe the behavior of \( f_q(T) \) also in systems with a spatial organization of the molecules.

The aim of the present work is to experimentally test which MCT predictions, if any, are valid also for strong and network forming glassy systems. For this purpose, we choose as prototype system the vitreous germania, \( \text{v-GeO}_2 \): it is one of the strongest glasses \( m_{\text{GeO}_2} = 20 \) \[25\] and it exhibits a rather low glass transition temperature easy accessible by the experiments (\( T_g \approx 800\,\text{K} \)). The samples were obtained by melt-quench process of the Germanium(IV) oxide crystalline powder purchase by Aldrich (purity greater than 99.998%). The system has been investigated by neutron scattering experiments.

Elastic and quasi-elastic measurements were performed on the thermal backscattering spectrometer IN13 at the Institut Laue-Langevin (ILL, Grenoble, France). The total elastic intensity, \( S_{el}(q, \omega = 0, T) \), was measured as a function of temperature from 20 K to 1100 K. Quasi-elastic spectra were collected at significant temperatures in the energy range \([-0.026\,\text{meV} \text{ to } +0.03\,\text{meV}] \) with an energy resolution \( \Delta \omega = 9\mu\text{eV} \).

The measurements of the static structure factor, \( S(q) \), were performed at the diffractometer 7C2 located on the hot source of the reactor Orphée of the Laboratoire Leon Brillouin (LLB, Saclay, France). The incident wavelength \( \lambda = 0.729\,\text{Å} \) was chosen to access a wide \( Q \) range between 0.4 and 15\,\text{Å}^{-1} \) and to minimize the inelasticity corrections. The \( S(q) \) was investigated in the temperature range from room temperature to the liquid phase.

The two sets of data were reduced using MonteCarlo simulation to estimate the multiple scattering, the cell contribution and the transmission coefficients \[24\].

In Fig. 1 where the quasi-elastic spectra are reported for selected temperatures, the decreasing intensity underlines the temperature effect of the atoms motion. In the inset of Fig. 1 we report the same spectra, normalized at the maximum intensity. No changes of the quasi-elastic line shape are observed in the whole explored temperature range, indicating that there are no detectable thermically activated processes, at least within the width of the experimental resolution. Therefore the \( \alpha \) relaxation process is always inside the elastic peak and the relation \( \Delta \omega \tau_a(T) >> 1 \) is always fulfilled. As mentioned before, under this condition the \( f_q(T) \) can be analyzed according to the previous description. In particular, considering that \( f_q(T \rightarrow 0) = 1 \), \( f_q(T) \) is obtained as \[13\]:

\[
\frac{S_{el}(q, \omega = 0)T}{S_{el}(q, \omega = 0)_{T=0}} = f_q(T) \cdot \frac{S(q)T}{S(q)_{T=0}}
\]

in this way each data set is normalized by its low temperature measurement, thus cancelling all instrumental normalization constants. Since our low temperature datum in the elastic scan is 20K, we linearly extrapolate the \( S(q, \omega = 0)_{T=20} \) to \( S(q, \omega = 0)_{T=0} \). Room temperature is the lowest temperature where the static structure factor was measured. Since the diffraction pattern does not show any significant change from room temperature up to 750K (as shown in the inset of Fig. 2), we safely approximate \( S(q)_{T=0} \) to \( S(q)_{T=350\,\text{K}} \). Smooth temperature evolution is found in the \( S(q) \) for temperatures greater than 750 K. In Fig. 2 \( S(q) \) is presented at two significant temperatures (\( T = 750\,\text{K} \) and \( T = 1000\,\text{K} \)) together with the ratio, \( r(q) \), between the two spectra. \( r(q) \) is almost constant in the whole range apart at very low \( q \), where slight differences are present.

The obtained \( f_q(T) \) values are reported in Fig. 3 as a function of temperature, for three selected wave vector transfers, \( q \). The data follow the same trend, without any significant deviation, in the whole \( q \) range here investigated. In the low temperature region, the temperature dependence of \( f_q(T) \) is fairly well described by a linear behavior. Increasing the temperature a strong slope variation is clearly identified. It occurs at the same
temperature independently from the analyzed $q$ value. In the highest temperature range $f_q(T)$ becomes almost temperature independent at a value which strongly depends on $q$. Interestingly, a very similar temperature dependence is also found in v-SiO$_2$ reported in the inset of Fig. 3 These measurements were collected using the IN6 spectrometer installed at ILL, with $q \sim 2.6\,\text{Å}^{-1}$ $^{[26]}$. As previously described, in the MCT, $f_q(T)$ is expected to display a cusp behavior in the region close to the critical temperature, $T_c$, which should be located above $T_g$. The theory foresees that close to $T_c$ the following relationship holds:

$$f_q(T) = \begin{cases} f_q^c + h_q(T - T_c)^\beta & T < T_c \\ f_q^c & T > T_c \end{cases}$$

where $\beta = 0.5$ is expected and $f_q^c$ and $h_q$ are positive quantities depending only on $q$ $^{[3]}$. In order to apply this relation the static structure factor $S(q)$ must depend smoothly on the temperature: this guarantees that any change in the temperature behavior is not related to a structural rearrangement, but it has a dynamical origin. This condition is fulfilled by our data as shown in Fig. 3. As foreseen by MCT, the presented data suggest the existence of a break in the trend of $f_q(T)$ versus temperature. The strong slope variation in the temperature dependence of $f_q(T)$ is located near $T_g$. It is not straightforward to identify the temperature of the break as $T_c$ defined in Eq. 2 since in strong glasses it is expected to largely exceed $T_g$ $^{[27]}$. However it is evident that a transition occurs and the system starts to anomalously change its dynamics. It is quite interesting to observe that the same behaviour is observed also in v-SiO$_2$ where $T_c$ is expected to be much higher than the temperature where the break occurs, i.e. 1500 K. Concerning the temperature dependence of $f_q(T)$, in the cases of these two strong glasses the linear trend of the non-ergodicity factor is maintained up to temperatures close to $T_g$. We have to recall that Eq. (2) is valid when $T$ is close to $T_c$ (probably a few degrees), while the experimental data span a wide temperature range. Indeed, the data are perfectly compatible with a power law, with $\beta = 0.5$, at least within some 50 K above $T_g$. This behavior can be obtained taking into account that the measured $f_q(T)$ is the superposition of two contribution: the first related to the relaxational process described by Eq.(2), the second related to the pure vibrational contribution. The latter, calculated by the density of vibrational state measured at $T=300\,\text{K}$ $^{[28]}$, show an almost linear trend in the low temperature range. However, an accurate analysis in the region close to $T_c$ is probably beyond the present investigation capability in terms of energy resolution, $Q$ range, and statistics.

A further test to ensure that the constant value reached by $f_q(T)$ in the high temperature range is really $f_q^c$ of eq.2, is represented by its $q$ dependence. According to MCT calculations for simple liquids, $f_q^c$ has to follow in
phase the oscillations of the static structure factor, $S(q)$. This behavior has been experimentally observed in different glass-forming systems. The comparison between the $q$ behavior of $S(q)$ and $f_q$ obtained by our data is reported in Fig. 4. Again, also in the present case the ability of $f_q$ to oscillate in phase with the main feature of $S(q)$ is confirmed.

Our results confirm that, also in the analyzed system, the MCT is able to qualitatively describe some universal aspects of the glass transition. Even if the temperature, at which the ergodicity breaking occurs, is astonishing close $T_g$, its existence is observed in v-GeO$_2$ and seems to be visible also in v-SiO$_2$. The existence of the ergodicity breaking in network forming glassy systems has been previously formulated analyzing the results on B$_2$O$_3$ where the $f_q(T)$ was investigated by different experimental techniques. However, in this latter case, $f_q(T)$ does not show a well-defined discontinuity in its temperature dependence but only a gradual change in a temperature range about 200 K wide. Our findings suggest that MCT predictions could be extended to a wide class of materials, such as network forming glassy system. This result is somehow unexpected, in fact these systems are characterized by a local structure determined by covalent bounds and the significate of caging effect on these materials is far from being trivial.

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