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Dynamics in the supercooled liquid $Na_{0.5}Li_{0.5}PO_3$: A schematic mode coupling model analysis

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Abstract. – The temperature and wave number dependences of the dynamical structure factor obtained in a nonfragile glass-forming liquid by Brillouin scattering and coherent neutron scattering experiments are for the first time described by the solutions of a schematic mode coupling theory model over a wide frequency range. In intermediate regime, the crossover between vibrational excitations and fast relaxational processes observed above the susceptibility minimum in neutron spectra is well reproduced by the theoretical model. At lower Q-values, the temperature dependence of the Brillouin lineshape is also accurately described. Besides, the dynamical transition is shown to occur between 601 K and 637 K ($T_g = 515$ K, $T_m = 749$ K) in this supercooled liquid.

It is well known that in supercooled liquids, transport coefficients increase by more than ten orders of magnitude between the melting temperature T_m and the glass transition temperature T_g. Two dynamical regimes separated by a narrow crossover temperature range are usually distinguished: a low-viscosity regime at high temperatures where diffusive motions take place described by a cage model and a high-viscosity regime at lower temperatures where activated processes dominate the dynamics down to T_g. This crossover temperature region is actually the subject of many theoretical and experimental investigations [1] in connection with the recent development of the mode coupling theory for the liquid glass transition (MCT) [2]. In this approach, the dynamics of simple supercooled liquids is derived from a closed set of equations of motion for the normalized time-dependent correlation functions of the density fluctuations, $\phi_q(t) = \left\langle \delta\rho_q^*(t)\delta\rho_q(0)\right\rangle / S_q$, where S_q is the static structure factor. With the initial conditions, $\phi_q(0) = 1$, $\dot{\phi}_q(0) = 0$, the coupled kinetic equations of the MCT read as

$$\ddot{\phi}_q(t) + \Omega_q^2\phi_q(t) + \int_0^t M_q(t-t')\dot{\phi}_q(t')\mathrm{d}t' = 0\,, \tag{1}$$

where $\Omega_q = \sqrt{k_b T q^2/(mS_q)}$ characterizes the microscopic dynamics of the liquid. The memory kernel $M_q(t)$ in eq. (1) is usually split into a bare friction term $\nu_q\delta(t)$ and a mode coupling

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memory function $m_q(t)$ thus separating the dynamics into a fast and a slow part, $M_q(t) = \nu_q\delta(t) + \Omega_q^2 m_q(t)$. The nontrivial part of the MCT is the evaluation of the memory function $m_q(t)$ in order to describe the cage effect in the supercooled liquid [2]. $m_q(t)$ is developed as a polynomial $\mathcal{F}_q$ of products of the correlation functions $\phi_k(t)$ themselves, where the positive coefficients of the polynomial ($\mathbf{V}$) are completely determined by the static structure factor, $m_q(t) = \mathcal{F}_q[\mathbf{V}, \phi_{\mathbf{k}}(\mathbf{t})]$. For critical values of the vertices $\mathbf{V}_\mathrm{c}$, a sharp ergodic-nonergodic transition, that can be interpreted as an ideal glass transition, occurs in the weak supercooled liquid regime revealing specific features for all variables that couple to density fluctuations. Above a critical temperature T_c, a two-step decay of the correlation functions is then observed leading to the identification of a short-time dynamics in the picoseconds (β-process) and a long-time temperature-sensitive dynamics (α-process) that freezes below T_c.

First-order asymptotic expansions of the solutions of the mode coupling equations around the singularity provide us with handy formulas that can be experimentally checked. In particular, a scaling law fitting the susceptibility minimum between the two relaxational processes has been widely used to test the validity of MCT. Recent experimental data obtained mostly on fragile glass-forming liquids in Angell's classification [3] strongly support the MCT at least concerning the temperature range above T_c [4-6]. For more complicated systems, where the specific structure seems to play a crucial part, it has recently been demonstrated that the validity range of the asymptotic laws could be strongly reduced leading in particular to an overestimation of the correct crossover temperature T_c [7]. It is also unclear to what extent low-frequency vibrational excitations that form the so-called boson peak contribute to the dynamics in the β regime in these systems [8-10]. Then, in order to test the relevance of the MCT in such complex systems, we have to resolve the mode coupling equations within the frame of a schematic model that takes into account the specific dynamics of the system [7,11].

In this letter, we report for the first time a full consistent analysis of the dynamical structure factor of the glass-forming liquid $Na_{0.5}Li_{0.5}PO_3$ from small wave numbers probed in a Brillouin scattering experiment up to 2.0 Å^{-1} obtained by coherent neutron scattering measurements. All the spectra in the whole supercooled liquid range are accurately described by the solutions of a two-component schematic MCT model. Neutron scattering experiments have been carried out on the multichopper time-of-flight spectrometer MIBEMOL at the LLB([1]) in the temperature range 300–773 K. With an incident wavelength set to $\lambda_i = 6.2$ Å, a resolution of 87 μeV (Full Width at Half Maximum) has been achieved, whereas a second series of spectra has been obtained with a better resolution: 30 μeV at $\lambda_i = 8.5$ Å. Brillouin spectra have been obtained in the same temperature range in the backscattering geometry with a triple-pass tandem of Fabry-Pérot interferometers which is characterized by very high contrast and resolution.

$Na_{0.5}Li_{0.5}PO_3$ ($T_\mathrm{g} = 515$ K, $T_\mathrm{m} = 749$ K) is a mixed alkali phosphate glass-forming liquid that forms long twisted chains of covalent bonded PO_4 tetrahedra of about 100 units. Recently, it has been demonstrated that the dynamics in this nonfragile supercooled liquid presents some specific features that hinder simple mode coupling analysis of the data with asymptotic results [12]. Thus, to go beyond this first analysis, we have used a two-component schematic MCT model as a basic description of the structural dynamics in $Na_{0.5}Li_{0.5}PO_3$. The first component is the well-studied F_{12} model [2] dealing with only one correlator $\phi_0(t)$ characterized by some frequency Ω_0 and damping constant ν_0. It uses a linear and a quadratic term in the memory function with two coupling parameters V_1 and V_2, $m_0(t) = V_1\phi_0(t) + V_2\phi_0^2(t)$. $\phi_0(t)$ is meant to represent the correlation function which governs the glassy dynamics. It drives the critical behavior from the weak-coupling liquid state to the strong-coupling glass state across

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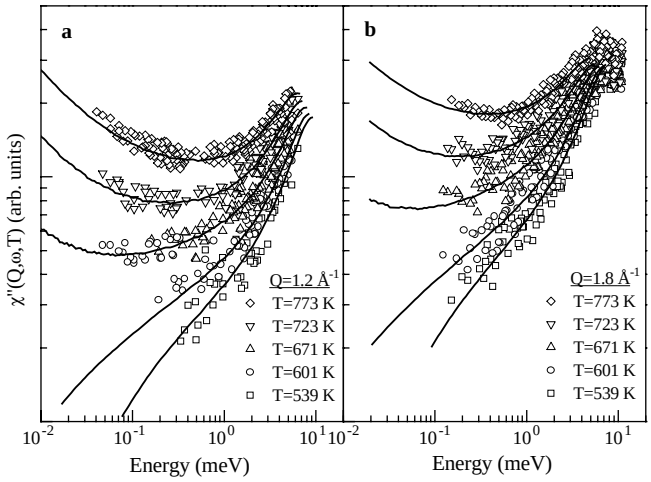

Fig. 1. – Dynamical susceptibility $\chi''(Q,\omega,T) = S(Q,\omega,T)/n(\omega,T)$ (symbols) from coherent neutron scattering in $Na_{0.5}Li_{0.5}PO_3$ for five selected temperatures between T_g and T_m at $Q = 1.2$ Å^{-1} (a) and $Q = 1.8$ Å^{-1} (b). The lines are the theoretical susceptibility spectra $\chi''_s(Q,\omega,T)$ discussed in the text.

the singularity. A second correlator $\phi_s(t)$ is then added to this model in order to describe the complex dynamical variable probed by the experiment. It obeys to the same dynamical equation of motion, characterized by a damping term ν_s and a microscopic frequency Ω_s but with only a quadratic term in the memory function specified by the single-coupling parameter V_s, $m_s(t) = V_s\phi_0(t)\phi_s(t)$. In this schematic model, the critical dynamics of the second correlator $\phi_s(t)$ is governed by the first one so that both correlators undergo the critical transition at the same time for a well-known set of coupling parameters (V_{1c}, V_{2c}).

Due to the simplicity of the model, it should be pointed out that the real nature of the correlators is not clear and not necessarily restricted to density correlators. In $Na_{0.5}Li_{0.5}PO_3$, one could assume that the first correlator $\phi_0(t,T)$ stands for the reorientations of the PO_4 complexes driving the glassy dynamics, whereas density fluctuations, probed in coherent neutron scattering and Brillouin scattering experiments, would be the probing variable described by the second correlator $\phi_s(Q,t,T)$. Accordingly, the parameters extracted from the fits do not have necessarily a precise microscopic meaning and should be considered as a minimal set of parameters allowing an accurate description of the structural dynamics of the system over a wide temperature range. In this framework, the four parameters $\Omega_0/2\pi = 13.15$ meV, $\nu_0/2\pi = 0$, $\Omega_s/2\pi = 2.30$ meV and $\nu_s/2\pi = 3.29$ meV have been kept constant for all the spectra. Consequently, the temperature and wave number dependences are contained in the parameters $V_1(T)$, $V_2(T)$ and $V_s(Q,T)$. The mode coupling equations have been numerically resolved in the time domain using an algorithm similar to the one described in [13]. A Fourier transform of $\phi_s(Q,t,T)$ is then performed to obtain the theoretical susceptibilities $\chi''_s(Q,\omega,T) = \omega\phi''_s(Q,\omega,T)S_{exp}(Q,T)$, where $S_{exp}(Q,T)$ is the experimental structure factor.

Figure 1 shows some of these calculated susceptibility spectra $\chi''_s(Q,\omega,T)$ compared to the experimental ones $\chi''(Q,\omega,T) = S(Q,\omega,T)/n(\omega,T)$, where $n(\omega,T)$ is the Bose factor for five selected temperatures at $Q = 1.2$ Å^{-1} (a) and $Q = 1.8$ Å^{-1} (b). Below $Q = 1.3$ Å^{-1}, data provided by both series of neutron experiments give wide frequency spectra down to 30 μeV, whereas above $Q = 1.3$ Å^{-1}, spectra are only shown between 100 μeV and 10 meV.

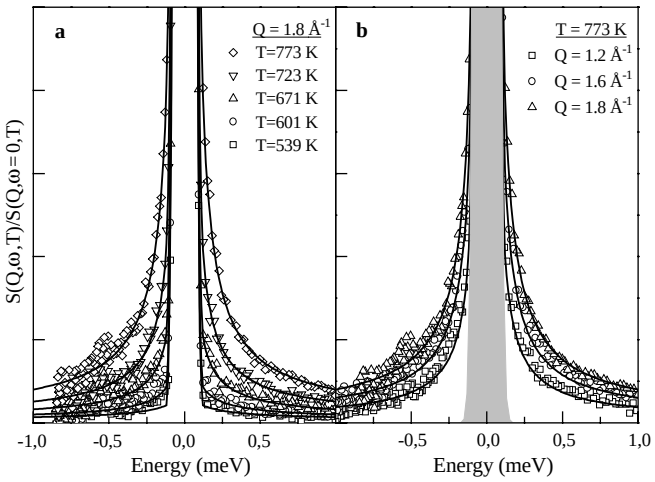

Fig. 2. – (a) Low-energy part of the dynamical structure factor from coherent neutron scattering in $Na_{0.5}Li_{0.5}PO_3$ (symbols) for five selected temperatures at $Q = 1.8$ Å^{-1} compared to the computed solutions of the MCT model convoluted with the resolution function of MIBEMOL (lines). (b) Q-dependence of the quasielastic spectral shape for three selected Q-values at $T = 773$ K. The three lines, fitting the data, have been obtained with the same set of parameters apart from V_s which is Q-dependent. The shaded area is the resolution function.

Experimental data at lower energies are more and more influenced by the resolution function and thus have been removed from the plot but not from the analysis. Indeed, these data are needed to correctly define the width and intensity of the narrow quasielastic part of the spectra (α-process). As shown in fig. 1, the crossover region between fast processes and vibrational motions exhibited by the experimental data around 1–5 meV is completely reproduced by the solutions of this schematic model. The transition from a sublinear frequency dependence of the susceptibility at low energy towards a more steeply frequency dependence at higher energy revealing the boson peak is clearly demonstrated at low temperatures in the calculated spectra. The susceptibility minimum that appears above 671 K in the experimental data due to the incoming structural relaxation is also correctly reproduced at all the temperatures.

At lower energy, the complex shape of the ill-resolved structural relaxation and its temperature dependence are well described by the solutions of this schematic mode coupling model as more clearly seen in fig. 2(a). It shows that calculated spectra convoluted with the resolution funtion of the spectrometer perfectly match the quasielastic experimental spectra. Using Q-independent coupling parameters V_1 and V_2, this schematic model describes also the experimental data obtained at different wave numbers when the third coupling parameter V_s is modified as shown in fig. 2(b). In particular, the well-known narrowing of the quasielastic scattering due to the structural relaxation around the first maximum of the static structure factor, which occurs at $Q = 1.2$ Å^{-1} in this supercooled liquid, is very well reproduced as shown at $T = 773$ K.

An important output of the analysis is obviously the trajectory of (V_1,V_2) in the coupling parameters plane. As shown in fig. 3(a), the coupling parameters (V_1,V_2) used to describe the spectra cross the bifurcation line of the F_{12} model between 601 K and 637 K, *i.e.* around 1.2 T_g as in most fragile supercooled liquids. It is striking to notice that the trajectory seems to be very similar to what has been obtained recently with the same schematic model on depolarized light scattering data in glycerol, another nonfragile glass-former [7]. At the transition point, the

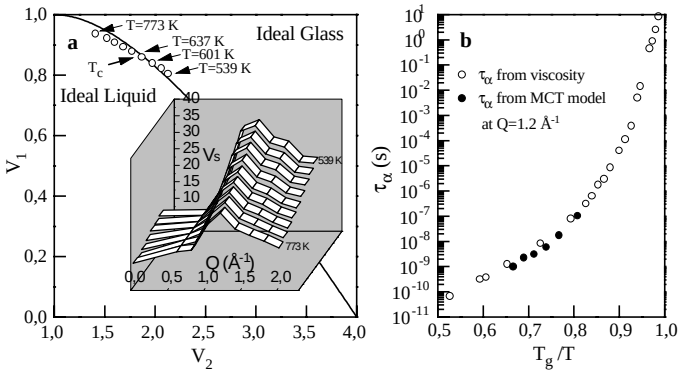

Fig. 3. – (a) Trajectory in the coupling parameters plane of the coupling parameters (V_1,V_2) used to fit the data. The critical line of the F_{12} model is crossed between 601 K and 637 K, *i.e.* at 1.2 T_g in this system. The inset shows the temperature and wave number dependences of the third coupling parameter V_s revealing a peak around the first maximum of the static structure factor at 1.2 Å^{-1}. The values found to describe the Brillouin lines are plotted at $Q = 0$. (b) Temperature dependence of the structural relaxation timescale in $Na_{0.5}Li_{0.5}PO_3$ from viscosity ($\tau_\alpha \propto \eta_s/T$) compared to the correlation times of the α-process that can be inferred from the computed spectra at the first maximum of the structure factor.

critical vertices are $V_{1c} = 0.847$ and $V_{2c} = 1.935$ leading to an exponent parameter $\lambda = 0.719$. The anomalous exponents are then $a = 0.319$ and $b = 0.609$, whereas the Debye-Waller factor for the α-peak of the correlator $\phi(t)$ is $f^c = 0.281$. The inset of fig. 3(a) shows temperature and wave number dependences of the third mode coupling parameter V_s. The Q-dependence exhibits a marked peak at 1.2 Å^{-1}, which is the value of the first maximum of the static structure factor in this system, revealing the narrowing of the quasielastic α-peak together with the increasing of its intensity. On decreasing temperatures, V_s increases monotonously reflecting the growth of the α-peak. At the identified transition, the Debye-Waller factor for $\phi_s(Q,t)$, which reads $f_s^c(Q) = 1 - 1/(V_s(Q)f_c)$, is $f_s^c = 0.858$ at 1.2 Å^{-1}.

In spite of an analysis restricted to energy values between 10 μeV and 10 meV, the correlation times of the α-process that can be inferred from the computed spectra at the first maximum of the static structure factor are completely in agreement with structural relaxation times provided by viscosity measurements $\tau_\alpha \propto \eta_s/T$ [14] as clearly shown in fig. 3(b). This result strongly supports the relevance of the parameters provided by the schematic MCT model used.

At much lower Q-values, polarized light scattering experiments close to the backscattering geometry also probe the dynamical structure factor if the anisotropic contribution arising from molecular orientational motions is very much lower than the longitudinal density fluctuation component. For $Na_{0.5}Li_{0.5}PO_3$, the anisotropic part is at least two orders of magnitude lower than the isotropic one at all the temperatures investigated. The usual model which describes the isotropic spectrum of a relaxing fluid is derived from generalized hydrodynamic theory and takes the following form when the thermal diffusivity is neglected:

$$S(Q \sim 0, \omega, T) = \frac{I_0}{\omega} \mathrm{Im}\{\omega_0^2(T) - \omega^2 - \omega m_B(\omega, T)\}^{-1}, \qquad (2)$$

where $C_0 = \omega_0/Q$ is the relaxed adiabatic sound velocity and $m_B(\omega, T)$ a complex memory function arbitrarily chosen to describe the stretched structural relaxation in supercooled liquids. It is now well known that this kind of analysis provides acceptable fits within a rather

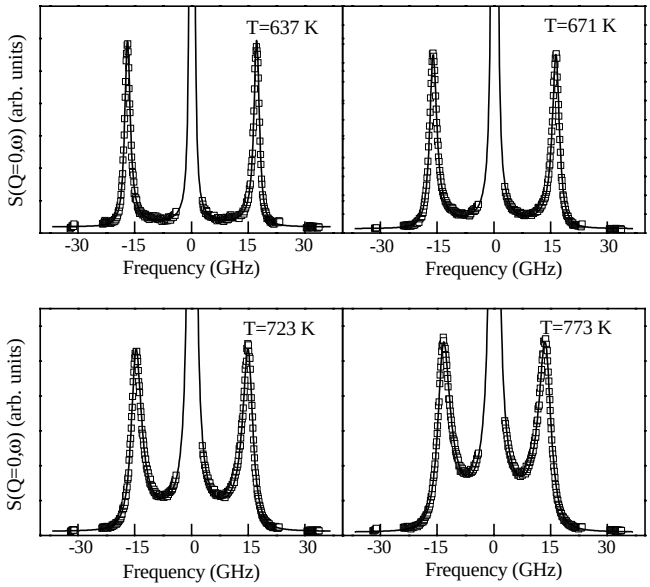

Fig. 4. – Brillouin spectra in $Na_{0.5}Li_{0.5}PO_3$ at four selected temperatures compared to the spectra obtained with eq. (2) as discussed in the text.

wide variation of the numerous adjustable parameters [15]. This is due to the fact that Brillouin lines are obtained just over one decade in frequency while the structural relaxation often covers more than three. It is then necessary to draw an independent characterization of the memory function, which should also include the β-relaxation. That is exactly what we have done in assuming that the memory function $m_{\rm B}(\omega, T)$ appearing in eq. (2) was simply proportional to the memory function $m_{\rm s}(\omega, T)$ provided by the schematic MCT model, $m_{\rm B}(\omega, T) = \gamma m_{\rm s}(\omega, V_{\rm s}(T))$, with only one free parameter at each temperature, $V_{\rm s}$, whereas the other parameters Ω, ν, $\Omega_{\rm s}$, $\nu_{\rm s}$, $V_1(T)$ and $V_2(T)$ were taken from the neutron scattering results. Furthermore, the temperature dependence of ω_0 have been extrapolated from higher-temperature measurements, above 1000 K where $\omega_0(T) = C_0(T)q = (3020 - 0.726T) \times 2.830 \times 10^7$. Therefore, the three adjustable parameters left in the fits at each temperature where I_0, γ and $V_{\rm s}$ leading to an accurate description of the Brillouin lines at all the temperatures, as shown in fig. 4. The continuous decrease *vs.* temperature of the Brillouin shift frequency $\omega_{\rm B}$ which finally joins with ω_0 at high temperatures as well reproduced as the progressive damping $\gamma_{\rm B}$ which shows a maximum around 850 K in this system.

In this letter, we have achieved for the first time a consistent analysis of coherent neutron scattering and Brillouin scattering spectra in a nonfragile glass-forming liquid. A two-component schematic MCT model with few parameters has been used to describe all the spectra in the whole supercooled liquid range. In particular, it stresses that it is not necessary to invoke another relaxation process in order to describe the acoustic behaviour. A smooth drift *vs.* temperature of the coupling parameters leads to a good description of the temperature evolution of the data revealing a crossover temperature $T_{\rm c}$ around 620 K in this system. These results strongly suggest that, even for nonfragile supercooled liquids, the MCT scenario gives an accurate physical picture of the structural dynamics. A more refined MCT schematic model that would take into account the particular dynamics of these systems is then simply needed.

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