High Frequency Dynamics of Glass Forming Liquids at the Glass Transition

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The dynamic structure factor of the glass formers glycerol, *o*-terphenyl, and *n*-butyl-benzene has been studied by inelastic x-ray scattering across the liquid-glass transition. Data taken at selected temperatures in the $1-8$ nm^{-1} momentum transfer (Q) range show a propagating soundlike mode in both liquid and glass phases. The energy of this mode, studied at fixed Q (≈ 2 nm^{-1}) on a fine temperature grid, shows a cusp behavior in a region either comparable or higher than the macroscopic structural arrest temperature T_g. This suggests the existence of a correlation between the glass structure and the arrest taking place at the molecular scale. [S0031-9007(97)05023-0]

The study of the high frequency density fluctuations in glass forming liquids has received great attention, and one of its aims is to improve our understanding on the microscopic mechanisms responsible for the liquid-glass transition. Whether the liquid-glass transition must be considered as a classical phase transition is, in fact, a still highly debated topic. For example, the glass transition temperature T_g, associated to the macroscopic structural arrest, cannot be considered as a *critical* transition temperature because there are quantities showing anomalous behaviors at temperatures different from T_g: among others, the time scale dependence of the structural relaxations, and the ergodicity of the system. Similarly, an order parameter in the classical sense has not yet been identified, and there are properties that depend on the cooling rate. These issues have been the object of many theoretical models, extending from thermodynamic descriptions of the transition [1] to pure dynamical approaches as the mode coupling theory (MCT) [2].

The dynamics of the density fluctuations is addressed by the experimental determination of the dynamic structure factor, $S(Q, \omega)$. Laser light scattering experiments address the collective properties in the long wavelength limit, giving important information on the coupling between the sound waves and the structural relaxation processes [3]. At the level of intermolecular time and length correlations, traditionally, these determinations should be the domain of neutron spectroscopies. The inelastic *neutron* scattering techniques, however, due to kinematic limitations, are not easily applied to study collective excitations in disordered systems. On the contrary, they are successfully used to determine the nonergodicity factor from the quasielastic scattering energy region, and the excitations at large Q [4]. As shown by recent works on liquids and glasses [5,6], the neutron kinematic limitations can now be overcome using inelastic *x-ray* scattering (IXS) with meV energy resolution.

In this Letter, we study the high frequency dynamics in the glass transition region, and present measurements of the $S(Q, \omega)$ in three glass forming systems: glycerol (GLY), *o*-terphenyl (OTP), and *n*-butyl-benzene (NBB). In all these systems, we find a propagating longitudinal collective dynamics in a temperature range extending from the glass to the liquid phase well above T_g, and up to Q transfers approaching the inverse of the interparticle separation. This result confirms and generalizes previous findings obtained in a molecular liquid as water [5], and in other glasses as SiO_2, glycerol, and $LiCl:6H_2O$ [6]. Specifically, it shows that this dynamics is the high frequency continuation of the acoustic branch detected with ultrasound and Brillouin light scattering techniques. Moreover, at a given Q, we find that the temperature dependence of the excitation frequency, $\Omega(Q, T)$, is more pronounced in the liquid than in the glass, and has a cusplike behavior at a temperature T_x which we infer to be higher than T_g. We associate this behavior to the liquid-glass transition at the investigated frequencies, which manifests in a change of the collective dynamics likely to be due to the freezing of the microscopic diffusional processes. The common behavior among the considered systems may lead us to speculate on a more general origin of this property, and therefore to its validity also for other glass formers.

The experiment has been carried out at the very high energy resolution IXS beam line (BL21-ID16) at the European Synchrotron Radiation Facility. The incident x-ray beam is obtained by the combination of a cryogenically cooled Si(111) double crystal monochromator and a very high energy resolution backscattering monochromator operating at the Si(11 11 11) reflection [7]. The scattered photons are collected by a spherical silicon crystal analyzer, also operating at the Si(11 11 11) back-reflection [8]. The monochromatic beam has an energy of $\approx 21\,748$ eV and an intensity of 2×10^8 photons/s. The total energy resolution, determined from the elastic scattering of a

Plexiglas sample at the maximum of its static structure factor, is 1.5 meV full width at half maximum. The momentum transfer, $Q = 2k_0 \sin(\theta_s/2)$, with k_0 the wave vector of the incident photon and θ_s the scattering angle, is selected between 1 and 8 nm^{-1} by rotating a 7 m long analyzer arm in the horizontal scattering plane. The total Q resolution has been set to 0.2 (0.4) nm^{-1} for $Q \leq$ ($>$) 2 nm^{-1}. Energy scans are done by varying the relative temperature between the monochromator and analyzer crystals. Each scan has taken about 130$'$, and each (Q, T)-point spectrum has been obtained from the average of two to five scans depending on the sample temperature. The data have been normalized to the intensity of the incident beam. The three high purity, anhydrous glass-former samples have been distilled in vacuum before loading the sample cell in an argon glove box. According to Angell's definition [9], glycerol is an "intermediate" glass former, while o-terphenyl and n-butyl-benzene are "fragile." To avoid crystallization of the undercooled liquids, the cell has been made out of a *pyrex*-glass tube [4 (10) mm inner (outer) diameter and 20 mm length], capped with two diamond single crystals disks, 1 mm thick, to reduce undesired scattering signals. In the Q-ω region of interest, empty cell measurements gave the flat electronic detector background of 0.6 counts/min (Eurisys-Mesures EPX-R). The cell length was chosen to be comparable to the x-ray photoabsorption length, and multiple scattering was negligible. The samples temperatures were changed with a typical 1 deg K/min rate, and no spectral changes were observed among different scans at the same temperature, or approaching the selected temperature from either above or below.

The IXS spectra were measured at different (Q, T) points. The Q dependence was studied in the 1–8 nm^{-1} Q region at the selected temperatures of 145, 175, 242, and 292 K in glycerol, and of 156, 223, 328, and 405 K in o-terphenyl. At the Q value of 2 nm^{-1} in GLY, and of 2.5 nm^{-1} in OTP and NBB, we studied the temperature evolution of the IXS spectra from $\approx$70 K, i.e., well inside the glass phase for the three systems, up to $\approx 2T_g$. Examples on the typical Q dependence of the IXS spectra are reported in Fig. 1(a) for liquid glycerol at $T = 292$ K ($T_g = 186$ K). The panel shows that the inelastic signal disperses with Q in a very similar fashion as previously reported for glycerol glass, and in other glasses [6]. The data obtained for o-terphenyl at $T = 328$ K ($T_g = 243$ K) show a similar behavior.

The energy position and the width of the excitations has been determined modeling the spectra with the function $F(Q, \omega)$, which consists of a Lorentzian for the quasielastic scattering, and a damped harmonic oscillator (DHO) [10] for the two side peaks:

$$F(Q, \omega) = I_c(Q) \frac{\Gamma_c(Q)}{\omega^2 + \Gamma_c(Q)^2} + [n(\omega) + 1]I(Q)$$

$$\times \frac{\omega \Gamma(Q)^2 \Omega(Q)}{[\Omega(Q)^2 - \omega^2]^2 + \Gamma(Q)^2 \omega^2}. \quad (1)$$
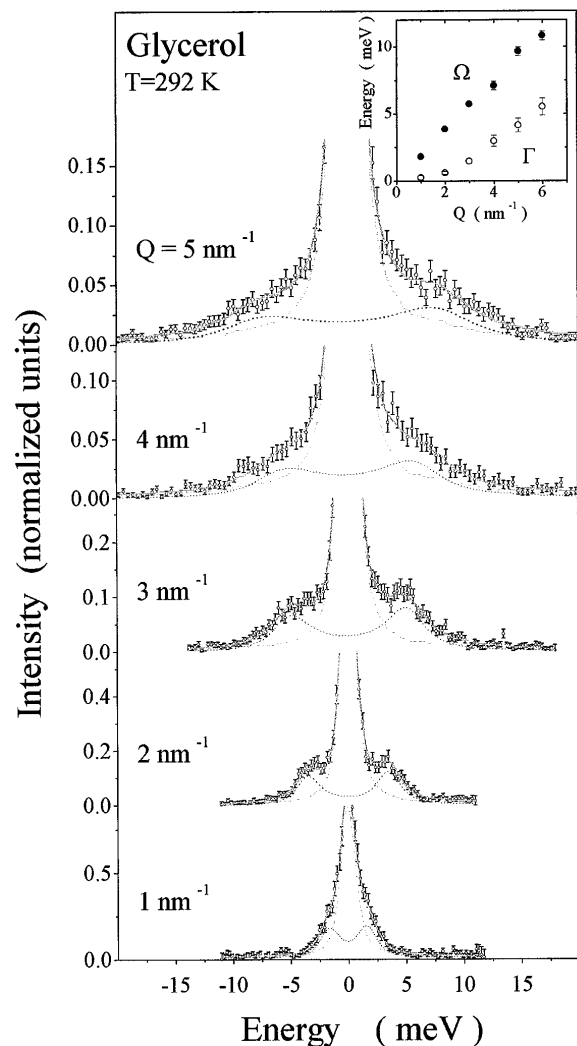

FIG. 1. IXS spectra of glycerol (GLY) at 292 K and at the indicated Q values. The data ($\circ$), shown with the error bars, are superimposed to the fit (solid line) as explained in the text. The dashed (dotted) lines represent the quasielastic (inelastic) contributions to the total fits. The data are normalized to the central peak intensity, corresponding to 250, 400, 650, 900, and 900 counts for $Q = 1$ to 5 nm^{-1}. The typical counting time was 300 s/point. The inset reports the values of Ω ($\bullet$) and Γ ($\circ$) as derived from the fit.

Here $I_c(Q)$ and $I(Q)$ are, respectively, the intensities of the central peak and of the inelastic contribution, $\Omega(Q)$, $\Gamma(Q)$, and $\Gamma_c(Q)$ refer to the central frequency and to the energy widths of the side and central lines, and $n(\omega)$ is the Bose factor. The spectrum is fitted to the convolution of $F(Q, \omega)$ with the instrument resolution function using standard χ^2 minimization. The arbitrary choice of the DHO is made because it contains the basic features of the inelastic part of the $S(Q, \omega)$ of a disordered system, and allows us to determine the spectroscopic parameters and their Q, T dependences independently of specific theories [11] as demonstrated on other real and simulated systems [5,6,12].

The individual contributions to a typical fit are shown by the dashed and dotted lines in Fig. 1. The inset reports

the values obtained for $\Omega(Q)$ and $\Gamma(Q)$. The full set of parameters derived from the fits and the Q and T dependencies of the corresponding dispersion curves will be discussed elsewhere [13]. We emphasize here the dispersion of the excitation energies, and, therefore, the propagating nature of the collective dynamics in these liquids up to Q values comparable to $Q_m/2$, where Q_m is the position of the first maximum in the static structure factor. Similarly, this indicates that the dynamics in the liquid phase is similar to that of the glass.

Selected IXS spectra of glycerol, taken at $Q = 2$ nm^{-1} and at the indicated T values, give in Fig. 2 an example of the temperature dependence of the excitations. Using the same fitting procedure as for the data reported in Fig. 1, we derived the temperature dependence of $\Omega(Q,T)$ and $\Gamma(Q,T)$ at the considered Q values. These relations are reported in Figs. 3(a)–3(c) for the three samples. In this figure, we also indicate the T_g's for each glass former. The temperature behaviors are quite similar for the three samples. The parameter $\Gamma(Q,T)$, related to the energy spread of the excitation, has a monotonic behavior in the considered temperature region within its statistical determination. On the contrary, the parameter $\Omega(Q,T)$, which
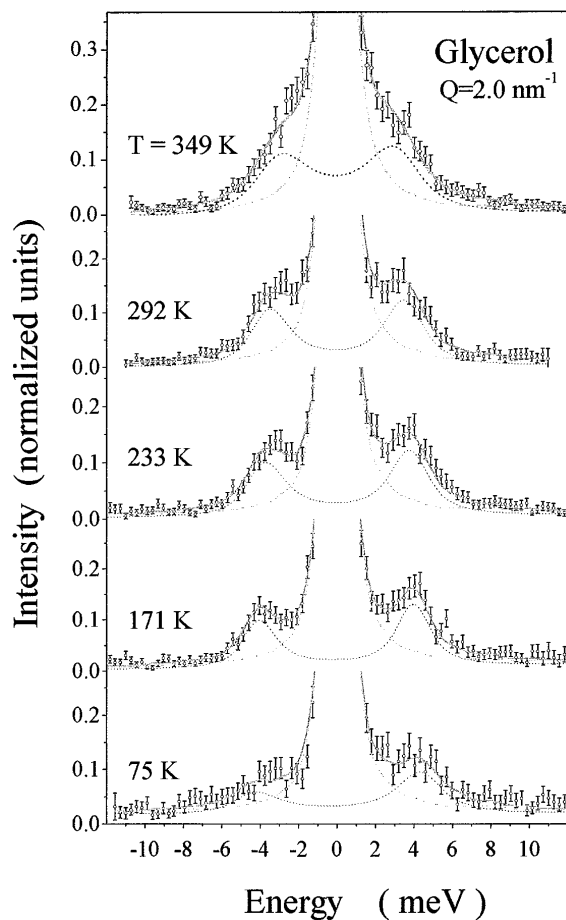
represents the maximum of the longitudinal current correlation function in the DHO model of the $S(Q,\omega)$, exhibits a clear temperature dependence with a slope change in a temperature region not far from T_g. A quantitative description of this observation is obtained using the values of $\Omega(Q,T)$ at temperatures below T_g, i.e., well inside the glass phase, and at high temperatures, i.e., well inside the liquid phase, to estimate two linear functions. The whole set of data is then well represented by these two linear relations that cross each other at a temperature indicated as T_x. The best fit to the high- and low-temperature
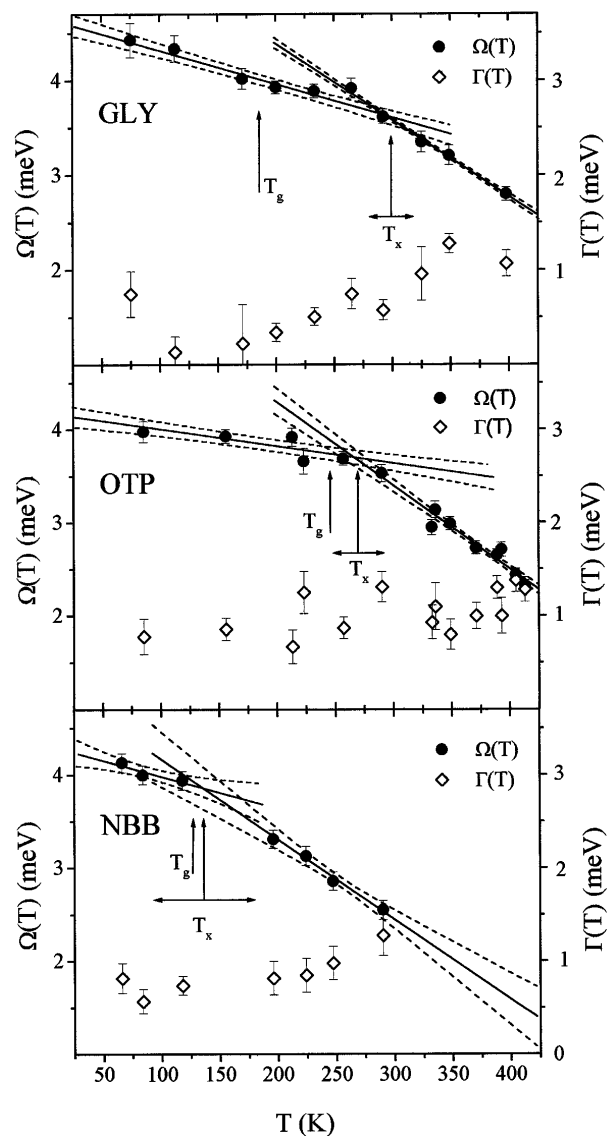

FIG. 2. IXS spectra of GLY at $Q = 2$ nm^{-1} and at the indicated temperatures. The symbols are as in Fig. 1, and the counts on the maxima in $\approx$300 s are 300, 350, 400, 400, and 400 counts for $T = 75$ to 349 K.

FIG. 3. Temperature dependence of the $\Omega(Q,T)$ and the $\Gamma(Q,T)$ derived from the fits at the indicated Q values for glycerol (GYL), o-terphenyl (OTP), and n-butyl-benzene. The error bars correspond to $\pm 1\sigma$ statistical error. The full lines are the best fits to the points in the low- and high-temperature regions; they cross at the indicated temperatures T_x. The dashed lines indicate the limits of the $\pm 1\sigma$ prediction bands. The uncertainty on each T_x, indicated by the horizontal bar, is derived from the intersection of the prediction bands. The glass-transition temperature T_g is also indicated.

points is reported in Fig. 3, together with their $\pm 1\sigma$ prediction bands. With this procedure, we derive T_x and its error from the crossing of the two fits. We find that the values of T_x are in a range systematically above the glass transition temperatures T_g. In the case of glycerol, $T_x = 300 \pm 20$ K is definitively higher than T_g, while in OTP, $T_x = 270 \pm 25$ K is only slightly above T_g. In NBB ($T_x = 180 \pm 40$ K) T_x and T_g have comparable values within an uncertainty larger than in the other two systems.

The much steeper change of the excitation energy in the liquid phase ends at T_x. We suggest, therefore, that in the considered high frequency limit, T_x marks the microscopic transition between two different dynamical regimes, respectively, characteristic of the glass and liquid phases. In view of the considered Q-ω region, this transition can then be interpreted as the freezing of the diffusional degrees of freedom at the molecular level. If these findings would be confirmed in other glass forming systems, one could speculate on the existence of a general behavior of the excitation frequencies above and below T_x.

Finally, we observe that the ratio T_x/T_g is ≈ 1 in NBB, ≈ 1.1 in OTP, and ≈ 1.6 in GLY, indicating a correlation between this ratio and the fragility of the glass. A similar correlation has been found in many glass formers for the ratio T_c/T_g [14], where T_c is the MCT critical temperature marking the microscopic transition from a nonergodic to an ergodic system. It will be of great interest to evaluate the possibility to identify the T_x determined by the present IXS with the MCT T_c. We note, however, that there is a possible important disagreement between our results and the MCT predictions for the ergodicity parameter, $f = 1 - c_0^2/c_\infty^2$. In fact, if one identifies c_∞ with our $\Omega(Q,T)/Q$, and assumes that c_0, the zero frequency sound velocity, does not have anomalies around T_c, our results would indicate for f a temperature dependence below T_x opposite to the theoretical predictions. This can be reconciled considering that the identification of $\Omega(Q,T)/Q$ with c_∞ can be incorrect because of structural effects inducing the bending of the Ω-Q dispersion relation and/or dynamical effects as the high frequency tail of a relaxation process. A detailed study on the determination of c_∞ from the whole dispersion curve and on the issue whether other relaxation processes are activated in the considered temperature and momentum transfer region will be the subject of a forthcoming publication [13].

In conclusion, we have shown in three glass forming systems that (i) in the high frequency limit, there is the persistence of propagating collective excitations in the whole liquid-glass transition temperature region; (ii) we derived a characteristic temperature T_x, which is higher than, or comparable to the macroscopic structural arrest temperature T_g, depending on the fragility of the glass [9]. T_x, therefore, may mark the microscopic liquid-glass transition. This study, more generally, demonstrates a strong correlation between the liquid-glass transition and the high frequency dynamics, and opens intriguing questions that may shed new interest on the microscopic processes associated to the glass transition.

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