Inelastic x-ray scattering from nonpropagating vibrational modes in glasses

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The inelastic x-ray scattering from glasses is interpreted by the vibrational modes of correlated rigid nanodomains separated by softer interfacial zones. The observed dispersion is interpreted by the proportionality of the inverse domain size to both transfer frequency and momentum. [S0163-1829(98)09337-0]

The recent experiments with inelastic x-ray scattering (IXS) arouse great interest in the propagating or the nonpropagating nature of the low-frequency vibrational modes in glasses. These modes present an excess of vibrational density of states, which manifests itself in the low-temperature specific heat and appears as the so-called ''boson peak'' in Raman and inelastic neutron scattering. These modes are directly related to the existence of a plateau in the thermal conductivity of glasses, revealing the inefficiency of these phonons in the conduction of heat. IXS measurements on several glasses showed that acoustic modes with frequencies ω close to or spanning the boson peak verify a linear dispersion versus transfer momentum Q, $\omega \propto Q$.[1–3] Among them, the important case of amorphous silica leads to differing interpretations: one supports the existence of a linear dispersion up to frequencies much higher than that of the boson peak[2,6] while the other stresses that the dispersion stops beyond a frequency that is lower than the boson peak position.[4,5]

The propagating character of the boson peak vibrational modes deduced in Refs. 2 and 6 is most likely to be effective over distances of only a few vibrational wavelengths. This is not in contradiction with the observation of the same modes by Raman scattering, as the propagation distances remain much smaller than the light wavelengths. However, it contradicts measurements of acoustic phonon attenuation in amorphous silica[7] [and in poly(methyl methacrylate) (PMMA) (Ref. 8)], from which it was deduced that the mean free path of longitudinal acoustic modes with frequencies lower than the boson peak is restricted to about one vibrational wavelength (Ioffe-Regel criterion). Such disagreement makes it obvious that the observation of a linear dispersion is not a sufficient criterion with which to conclude propagation. In an attempt to address this issue, we hereby present one possible interpretation of this apparent paradox, within which the concept of nonpropagation is not inconsistent with the existence of a linear dispersion. Our interpretation is based on the model of a glass nanometric inhomogeneous elasticity or inhomogeneous nanostructure, where nanometric, more cohesive domains (or islands), are separated by narrower and softer interfacial zones. The correlated vibrations of these domains, which are very similar to the vibrations of nanometer-sized objects and which we believe are responsible for the existence of the boson peak,[9,10] are predicted to give rise to inelastic scattering in the (ω, Q) region

matching the (meV, nm^{-1}) range. After exposing the in's and out's of our model, we relate it to already published IXS results on amorphous silica[2] and PMMA (Ref. 3) in order to assert its applicability.

The general expression for the dynamical structure factor $S(Q, \omega)$ is the following:

$$S(\mathbf{Q}, \omega) = (1/N) \int dt \exp(-i\omega t)$$
$$\times \left\langle \sum_{ij} \exp\{i\mathbf{Q}[\mathbf{R}_i(t) - \mathbf{R}_j(0)]\} \right\rangle, \quad (1)$$

where N is the number of particles and $\mathbf{R}_j$ the position vector of particle j. Assuming that the displacement of a particle induced by a vibrational mode is small in comparison with any difference $(\mathbf{R}_i - \mathbf{R}_j)$, one easily obtains Stokes scattering, disregarding the Debye-Waller factor:

$$S(\mathbf{Q}, \omega) = (kT/2MN)(Q^2/\omega^2)$$
$$\times \sum_m \left[\sum_i \exp(i\mathbf{Q} \cdot \mathbf{R}_i) \mathbf{e}_i(m) \right]^2$$
$$\times f(\omega - \omega_m, \delta\omega), \quad (2)$$

where M is the mass of a particle, T is the temperature, and $\mathbf{e}_i(m)$ and ω_m are, respectively, the eigenvector and the eigenfrequency corresponding to the mth vibrational mode. $f(\omega - \omega_m, \delta\omega)$ is the homogeneous spectral shape of the mth mode, with a width $\delta\omega$ related to the phonon lifetime.

We now consider that the structure of the glass consists of built-in cohesive nanometric domains whose ill contours are materialized by significant cohesion drops that characterize what we term the ''soft interfacial zones.''[9,10] Both soft zones and cohesive domains are amorphous in nature; they only differ in the strength of the elastic constants distributed within each of them. Obviously, the cohesive domains cannot be considered as independent from each other as they are bound together by the soft interfacial zones. This is all the more true in polymeric systems as one macromolecular chain is expected to be involved in more than one domain. Therefore, one can reasonably assume that there exist in the glass ''coherent regions'' that contain several domains of approximately the same size, inside which the vibrational motions of the domains are correlated; the size of the coherent regions

defines the correlation length along which a phase relationship between the domain vibrations is conserved. We believe that the collective modes probed in the (ω, Q) region covered by IXS are precisely the correlated fundamental modes of the cohesive nanodomains. These fundamental modes are very similar to dilatational (or breathing-type) modes of nanometer size objects; the frequency of such a mode ω_l is related to the domain size d_l through the relation:[11,12]

$$\omega_l = S 2\pi (C_{11}/\rho)^{1/2}/d_l \tag{3}$$

where $C_{11} = B + 4G/3$, in the case of isotropic medium inside the domains, with B and G, respectively, being the bulk modulus and the shear modulus. S is a shape factor and ρ the density of the domain.

Even if the elasticity or cohesion fluctuations giving rise to such noncontinuous structure are not associated to clear-cut contrasts in static density fluctuations, the fundamental mode of a rigid domain induces an oscillating electron density fluctuation, whose size is that of the vibrating domains. Therefore, within one coherent region, one has an oscillating repeat distance a_l, which is the distance between next-nearest-neighbor correlated l domains. a_l is close to and related to the size d_l: $a_l = \alpha d_l$ ($\alpha \geqslant 1$; $\alpha \simeq 1$ when the sizes of the soft zones are small compared to those of the domains). As a result, at the fixed frequency ω_l corresponding to the vibrations of domains with size d_l, a correlation peak in the structure factor will appear at $Q = Q_l$, such that

$$Q_l = 2\pi/a_l. \tag{4}$$

It follows from Eq. (3)

$$\omega_l = \alpha S (C_{11}/\rho)^{1/2} Q_l. \tag{5}$$

Because of this latter relation, the Q line shape of the correlation peak observed at fixed frequency $\omega = \omega_l$, $F(Q - Q_l, \Delta Q)$, has a counterpart spectral line shape $F(\omega - \omega_l, \Delta\omega)$, where the frequency width $\Delta\omega$ corresponds to the width ΔQ through Eq. (5). The width ΔQ is governed by the extent of correlation between domains of size d_l.

It follows from this picture that the dynamic structure factor at a given Q describes the correlated vibrations of domains of a particular size, so that the m mode in expression (2) becomes the fundamental mode of a domain l of size d_l. It therefore involves two spectral shapes, one arising from the correlation length associated to the size of the coherent regions and the other coming from the lifetime of the domain vibration, so that the dynamical structure factor in the spectral range of the boson peak can be written as

$$S(\mathbf{Q}, \omega) \propto (kT/2M)(Q^2/\omega^2)\delta(Q - Q_l)$$
$$\times F(\omega - \omega_l, \Delta\omega) \otimes f(\omega - \omega_l, \delta\omega), \tag{6}$$

where $\otimes$ denotes a convolution product. The domains l, which are correlated over a length equal to a few inter-domain distances a_l, have same size d_l.

In the case of isotropic spherical clusters and dilatational modes, S takes the value of 0.8.[12] In the case of our domains, one cannot assign a precise value to S because (i) their shapes are most likely to be poorly defined, (ii) the modes involved may have mixed characters (and IXS allows us to

probe only their dilatational component), and (iii) the domains are, by hypothesis, not free from each other. At any rate, S cannot exceed unity and in a rough approximation one can take $S = 0.8$. On the other hand, α must be slightly larger than 1. $(C_{11}/\rho)^{1/2}$ corresponds to a ''sound'' velocity, although it does not strictly refer to the propagation of a classical sound wave. Our suggestion is that the apparent linear dispersion observed by IXS, at least for silica and PMMA, is given by expression (5): measuring $S(Q, \omega)$ at $Q = Q_l$ implies probing the vibrational mode of a particular domain with size $d_l = 2\pi/\alpha Q_l$ and scanning the Q space implies scanning the size distribution of domains. The ''apparent'' sound velocity deduced from the proportionality between ω_l and Q_l is then given by $V_{app} = \alpha S (C_{11}/\rho)^{1/2}$. As a consequence, it appears that the ''apparent'' sound velocity V_{app} is not far from the bulk longitudinal sound velocity $\sqrt{C_{11}/\rho}$.

Acoustic vibrations with wavelengths longer than d_l can propagate, so that for $Q < 2\pi/d_l$ the dynamical structure factor would be that of propagating modes.[1,2,4] In consequence, according to our picture, we expect the dispersion to display a changeover that should be all the more pronounced as αS differs from 1: at low Q's the dispersion reflects a ''true'' propagation (with a ''true'' sound velocity $\sqrt{C_{11}/\rho}$), while at Q's corresponding to energies above the boson peak maximum, the dispersion reflects vibrations of correlated domains with different sizes (with an ''apparent'' sound velocity $\alpha S \sqrt{C_{11}/\rho}$).

The objection that is often formulated against such a type of nanostructure stems from the nonobservation of any correlation peak in small-angle x-ray or neutron scattering. However, as described above, we wish to emphasize that the main assumption of our model does not lie on the existence of pronounced heterogeneous *density* fluctuations in a single-component glass; it only involves an inhomogeneous distribution of elastic constants within the bonding network, and most likely within the intermolecular bonding network. This makes the glass ''medium'' range order rather subtle when looking at the time-averaged atomic positions, while we expect it to be more acute at the level of cohesion parameters like restoring force constants. Therefore, only snapshots of this type of structure at frequencies matching the domain vibrational frequencies would allow its visualization. The nonpropagating vibrational modes we think are probed by IXS resemble those belonging to an acoustic branch at the edge of a Brillouin zone: while atoms within domains belonging to one coherent region move in-phase according to the fundamental mode, they move in counterphase with respect to atoms in the soft interfacial zones. In the framework of such an analogy, one could assimilate our picture of cohesive domains within coherent regions to a ''quasiperiodic'' network of domains that extends over a correlation length that includes several of them. Still along these lines, the dispersion $d\omega/dQ$ of the correlated fundamental modes is zero, the same as for modes at the edge of a Brillouin zone. As a consequence, these modes are unable to transport energy, in agreement with the thermal conductivity plateau. If the glass were made of domains of the same size, one would indeed observe a flat dispersion. Our point is that because of the existence of a size distribution of domains, one observes a

dispersion with an ''apparent'' sound velocity close to that corresponding to the propagation of acoustic sound waves.

The first two papers on the IXS of silica were simultaneously published.[2,4] In Ref. 4 the data analysis indicates an acoustic localization edge at $\simeq 1$ THz, and in Ref. 2 the experimental results show a linear $\omega(Q)$ dispersion up to 4 THz, which is interpreted by a propagation of acoustic modes. As recalled in the introduction, the propagation of acoustic modes with frequencies higher than 1 THz is in disagreement with other results showing that in silica these modes should be localized on distances equal to or less than their corresponding wavelengths.[7] It also disagrees with a recent Raman study in which it was shown that the dependence of the boson peak intensity on the scattering angle cannot be inferred from propagating modes.[13] To overcome this contradiction one could argue that the assumed propagating modes only have a weak contribution to the total number of modes involved in the boson peak. However, such an argument goes against very new IXS measurements made on silica as a function of temperature.[6] Indeed, in this latter work, it was demonstrated that the modes probed with IXS show identical thermal behaviors to those of the boson peak observed in Raman and inelastic neutron scattering. Besides, this common thermal behavior differs from that of longer wavelength phonons ($\lambda \approx 200$ nm) detected by Brillouin light scattering. This clearly identifies the IXS observed modes with those of the boson peak. Such a result prompts us to apply the concept of an inhomogeneous glass nanostructure and its inherent concept of nonpropagating correlated domain modes to interpret the IXS data, as it was already successfully used to explain the boson peak origin[9,14] and other related glassy nanostructure specificities.[15,16] The comparison of expression (5) with the IXS experiment[2,6] leads to an ''apparent'' sound velocity $V_{app} = \alpha S (C_{11}/\rho)^{1/2} \simeq 4800$ m/s at 295 K and 5800 m/s at 1050 K. The longitudinal sound velocity deduced from Brillouin light scattering[6] is 5800 m/s at 295 k and 6050 m/s at 1050 K. The apparent sound velocity V_{app} is thus smaller than the longitudinal sound velocity. Assuming that $\sqrt{C_{11}/\rho}$ in the rigid domains is equal to the macroscopic longitudinal sound velocity, it would be found that αS is equal to 0.83 at 295 K and 0.96 at 1050 K. While a thermal variation of S is not physical, an increase of α, i.e., an increase of the distance a_l between domains with increasing temperature appears very plausible. It is also possible that the steeper thermal variation of V_{app} compared to that of the macroscopic sound velocity indicates that the ratio C_{11}/ρ inside the rigid domains is not exactly equal to the corresponding macroscopic ratio. Concurrently, their respective evolutions as a function of temperature would not be identical. Such different nanoscopic and macroscopic behaviors would not be surprising from a thermodynamical point of view.

The dispersion $\omega(Q)$ was also observed by IXS in amorphous PMMA, up to more than $Q = 2$ nm^{-1}.[3] There again, the measured apparent sound velocity is slightly smaller (2400 ± 300 m/s, deduced from Lorentzian data fits) than the longitudinal sound velocity determined by Brillouin light scattering (2750 m/s). From measurements on the attenuation of longitudinal acoustic modes in this material,[8] it was seen that the corresponding mean free path is shorter than the vibrational wavelength for $\omega > 300$ GHz or for $Q > 0.75$ nm^{-1}. Therefore, the interpretation of IXS by propagating modes in PMMA leads to the same inconsistency as for silica, so that again the interpretation of IXS by rigid domain modes appears to be adequate. This is supported by the successful description of the vibrational density of states excess in PMMA with the concept of a noncontinuous nanostructure.[10] Further support in this direction was provided by the investigation of the pressure dependence of the inelastic-elastic x-ray scattering spectra of this same material.[3] A pronounced break at 1.6 kbar in the pressure dependence of the elastic scattering, specific to Q values lower than 5 nm^{-1}, revealed the sensitivity of the static density fluctuations to the existence of a disruption in the nanometer scale structure. This experimental result provides strong indication that the nanostructure of such glass is noncompact, as is assumed in our model.

We do not claim that the interpretation of IXS we give here is universal for all glasses. Obviously, it is aimed at being valid for glasses whose structure is characterized by a nanometric inhomogeneous elasticity. As developed in previous papers,[9,14,17] such a nanostructure is believed to be at the origin of the boson peak, and thus only applies to acoustic modes involved in the boson peak.

In conclusion, we have proposed a model within which the linear dispersion $\omega(Q)$ observed in glasses like amorphous silica[2] or in poly(methyl methacrylate) (Ref. 3) can be interpreted by fundamental modes of more cohesive domains whose existence is derived from an inhomogeneous nanoscale elasticity. Thanks to their soft interfaces, these modes are correlated over a length equal to a few interdomain distances. We give credit to this model beyond its consistency with phonon attenutation results and the exsitence of a plateau in the thermal conductivity; it agrees with the notion of ''cooperative rearranging regions,''[18] with the existence of rigid aggregates used to interpret the dynamics or viscosity of supercooled liquids,[19–21] and with light-scattering observations.[22,23]

The proposed model will be developed to account for the observed Q dependences of the IXS intensity and peak linewidth.

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