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Vibrations at the boson peak: random- and coherent-phase contributions

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Abstract. Analysis of the dynamic structure factor, $S(Q, E)$, measured by means of inelastic neutron and x-ray scattering, for vibrations around the boson peak in glasses, demonstrates the presence of coherent- and random-phase contributions. It is found that systems with strong boson peaks have larger random-phase contributions to $S(Q, E)$. The results of the analysis are explained in terms of a model which relates the boson peak to scattering of acoustic-like vibrations by spatial fluctuations of elastic constants. Higher amplitude of the fluctuations leads to a higher boson peak and a larger random-phase contribution.

The most pronounced difference in dynamics between ordered crystals and disordered systems like glasses appears in the frequency range ~ 1 GHz to 1 THz. This region in ordered crystals is usually dominated by acoustic vibrations which show a Debye-like density of states $g_D(E) \propto E^2$. Two additional contributions show up in this frequency range for all glasses. One is an excess (in comparison with $g_D(E)$) density of vibrational states, $g_{exc}(E) = g(E) - g_D(E)$. Here $g(E)$ is the total vibrational density of states. The second is the anharmonic contribution which is traditionally ascribed to tunnelling systems or relaxation in double-well potentials [1]. The excess vibrations appear as a peak of $g(E)/E^2$ at frequencies around 0.3–1 THz. This is called the boson peak and is observed in neutron and Raman scattering spectra of glasses. The amplitude of the boson peak, defined as the ratio $g_{exc}(E)/g_D(E)$, is high for covalently bonded systems like SiO_2 or B_2O_3 , intermediate for hydrogen-bonded systems like glycerol and small for Van der Waals and ionic systems, like orthoterphenyl (OTP) and Ca-K-NO_3 (CKN) [2]. Moreover, the amplitude of the boson peak correlates with the degree of fragility of the system [2]. Fragility is a characteristic of the temperature variation of the viscosity (or α -relaxation time) around the glass transition temperature T_g . Recent investigations [3] revealed the existence of a boson peak in an orientational glass, i.e. in a crystalline solid with orientational disorder. Thus the boson peak is not something observed only in structural glasses. The nature of the excess vibrations and where they come from are currently subjects of intensive discussion.

The nature of the vibrations at the boson peak is revealed by analysis of the dynamic structure factor $S(Q, E)$. $S(Q, E)$ contains information about the type, propagation and localization of the vibrational modes. A significant advance in the measurements of $S(Q, E)$ for glasses was made following recent developments in high-resolution inelastic x-ray scattering spectroscopy (IXS). IXS makes possible Brillouin measurements in the Q -range $0.1\text{--}1 \text{ \AA}^{-1}$. These measurements reveal the existence of a linear dispersion between E and Q , for longitudinal vibrations, up to energies far above that of the boson peak [4–6]. The slope

of a dispersion curve gives a value for the velocity of sound in good agreement with the results of traditional light scattering Brillouin measurements [4]. Results from IXS measurements gave strong support for the proposal of an acoustic-like nature of the vibrations at the boson peak.

Traditionally, $S(Q, E)$ is measured using inelastic neutron scattering spectroscopy (INS). INS is not very efficient at Brillouin conditions due to kinematic limitations and is used most profitably around the first and second diffraction maxima, $Q \sim 1\text{--}5 \text{ \AA}^{-1}$. It was shown [7] that for random-phase motion of atoms $S(Q, E) \propto Q^2$, whereas for long-wavelength sound waves $S(Q, E) \propto Q^2 S(Q, 0)$. Here $S(Q, 0)$ is a static structure factor. In a plane-wave approximation $S(Q, E)$ for acoustic modes should oscillate in phase with $S(Q, 0)$ [7]. Analysis of the dynamic structure factor for SiO_2 clearly demonstrates an absence of oscillation near $Q = Q_{max} \sim 1.5 \text{ \AA}^{-1}$ [8]. This means that the random-phase contribution dominates $S(Q, E)$ at energies near the boson peak. The absence of oscillation is a strong argument against a sound-like picture for the vibrations at the boson peak in SiO_2 [8].

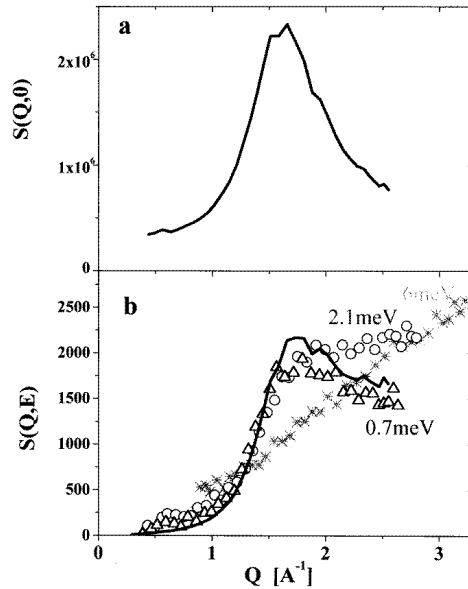


Figure 1. Neutron scattering data for $S(Q, E)$ for B_2O_3 at $T = 100 \text{ K}$, from [10]. (a) The static structure factor. (b) Symbols—the dynamic structure factor, measured at the values of E given in the figure. $E_{BP} \approx 2 \text{ meV}$. The curve in (b) shows the dynamic structure factor expected for sound waves, $S(Q, E) \propto Q^2 S(Q, 0)$.

Recent analysis of $S(Q, E)$ for polybutadiene (PB) [9] and B_2O_3 [10] reveals oscillations near the first diffraction maximum. Figure 1 presents $S(Q, E)$ for B_2O_3 at low temperature where quasielastic scattering is weak. At energies below the boson peak $S(Q, E)$ is similar to $Q^2 S(Q, 0)$ expected for sound waves. This means that the coherent-phase contribution dominates $S(Q, E)$ at this energy range. However, the oscillation becomes less pronounced with increase of E and nearly disappears at energies above that of the boson peak (figure 1(b)). The ratio of the random-phase contribution to the coherent-phase contribution increases with the energy. The authors of [10] decomposed $S(Q, E)$ into two parts and estimated the density of vibrational states for both phases (figure 2). At the energy of the boson peak, the coherent-phase contribution exceeds the expected Debye level for the sound waves (figure 2). However,

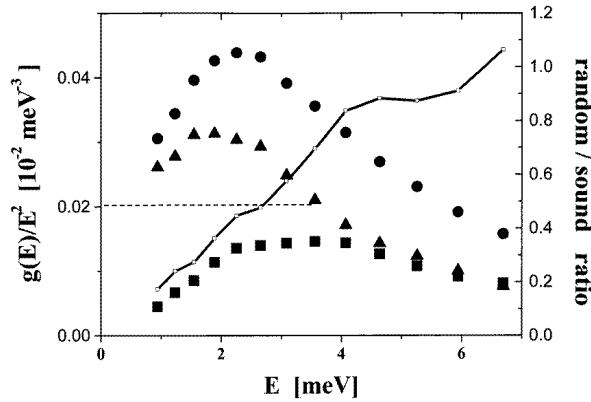


Figure 2. Total (●), coherent-phase (▲) and random-phase (■) parts of the vibrational density of states in B_2O_3 at $T = 100$ K, from [10]. The dashed line shows the Debye level. The ratio of the random-phase contribution to the coherent-phase contribution increases with E , as shown by the solid curve.

the ratio of the random-phase contribution to the coherent-phase contribution increases rapidly with energy.

Comparison of $S(Q, E)$ for different systems demonstrates that the ratio of the random-phase contribution to the coherent-phase contribution at E near the boson peak varies: it is very high for SiO_2 , which has an extremely high amplitude of the boson peak, $g_{exc}(E)/g_D(E)$, and it is much lower for B_2O_3 and PB, which show some intermediate strength of the boson peak. Does the amplitude of the boson peak correlate with the amount of the random-phase contribution? Analysis of $S(Q, E)$ for fragile systems with relatively weak boson peak (like CKN or OTP [2]) can help to answer this question.

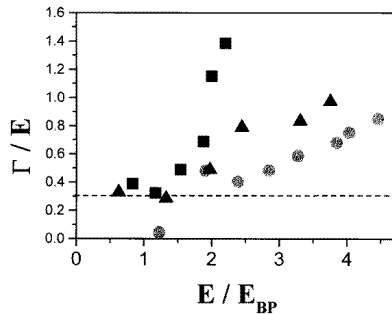


Figure 3. The internal friction for the Brillouin line in IXS measurements versus energy scaled with respect to the energy of the boson peak maximum, E_{BP} . ■: SiO_2 at $T = 1100$ K [4], $E_{BP} = 5$ meV; ▲: glycerol at $T = 292$ K [5], $E_{BP} = 2.9$ meV; ●: OTP at $T = 156$ K [6], $E_{BP} = 1.45$ meV. The dashed line marks the level $\Gamma = E/\pi$, i.e. $L = \lambda$.

Can one also identify the random-phase contribution in Brillouin scattering measurements? In general, this random phase will give strong broadening of the Brillouin line and a flat background under the Brillouin line. The broadening is often characterized by an internal friction defined as $Q^{-1} = \Gamma/E$. Here Γ is the full width at half of the maximum. Figure 3 presents the internal friction data versus energy scaled with respect to the energy of the boson

peak E_{BP} , for a few different systems. First of all, the broadening increases with the energy of the mode. This is consistent with the conclusion drawn from the analysis of the INS. The random-phase contribution increases with increase of E (figures 1, 2). Even more important is the comparison of different systems. SiO_2 has the largest and OTP has the smallest broadening, while that for glycerol is intermediate. This broadening correlates with the amplitude of the boson peak [2]. Thus the analysis of IXS and INS data leads us to a consistent picture: the higher the boson peak, i.e. the higher $g_{exc}(E)/g_D(E)$, the larger the random-phase contribution to the dynamic structure factor. At energies below that of the boson peak, vibrations have sound-like character, but random-phase contributions strongly increase with the energy of the vibration (figures 2, 3). Does every vibrational mode have both random and coherent parts in its response or one can separate the modes into purely coherent and purely random modes (as suggested in the vibration-relaxation model [9])? The results presented here do not answer this question. Results of computer simulations [11] seem to show the presence of a random phase for every mode.

What kinds of vibration are the modes at the boson peak? Earlier it was noted [12] that temperature variations of the boson peak frequency usually follow temperature variations of the sound velocity. That was an argument in favour of acoustic-like vibrations. Recent IXS data gave additional support to this point of view. Results of computer simulations [13] also indicated acoustic-like character for the vibrations near the boson peak, although the presence of a weak optic-like character for the vibrations was noted.

Recent analysis of INS and specific heat data for ethanol demonstrates that the boson peak can appear for orientational glass [3]. The peak was found to be identical to the boson peak for the structural glass of ethanol. This result demonstrates that fluctuations of elastic constants are sufficient for the appearance of the boson peak. The same conclusion can be drawn from the recent theoretical analysis presented in [14]. The authors demonstrate that fluctuations of the elastic constants of a simple cubic lattice (i.e. once again of a crystalline solid) lead to the appearance of an excess $g(E)$ at small energies similar to the boson peak for glasses. The amplitude of the peak increases with increase of the amplitude of the fluctuations of the elastic constants [14].

The results presented above agree well with the model approach which relates the boson peak to strong scattering of acoustic-like vibrations by fluctuations of elastic constants [2, 15]. This scattering leads to a shift of the vibrational response to lower frequencies. As a result an excess $g(E)$ appears in the low-frequency range. Higher amplitude of the fluctuations leads to a stronger scattering process and a larger shift of the vibrational response. As a result $g_{exc}(E)/g_D(E)$ will be higher [2]. Strong scattering will also give a larger random-phase contribution to every vibrational mode. That explains the observed relation between the amplitude of the boson peak and the size of the random-phase contribution (figure 3). It is also evident that vibrations with wavelengths λ much longer than the characteristic size of the fluctuations of the elastic constants are scattered very weakly. Decrease of λ leads to stronger scattering. As a result, the random-phase contribution will increase with increase of the energy of the vibration.

According to this picture, the correlation of the fragility of the systems with the boson peak amplitude can be interpreted as a correlation with the heterogeneity of the sample. Fragile systems have more homogeneous structure. As a result the boson peak is rather weak. This interpretation seems to be reasonable if one compares the structure of strong versus fragile systems. Strong systems usually have rigid covalently bonded structure which can support strong fluctuations of elastic constants. Fragile systems, in contrast, have Van der Waals or ionic structure where any strong fluctuations will be smoothed out.

Another simple consequence of the suggested picture is stronger localization of the

vibrational modes in systems with higher heterogeneity. It is very difficult to measure the localization of the vibrations at the frequency of the boson peak. One can estimate the localization length from the width of the Brillouin lines in IXS measurements (figure 3). The dashed line in figure 3 shows the level at which the mean free path $L \sim \lambda$. It is clear from figure 3 that the vibrations in SiO_2 have the shortest mean free path. At all energies around and above that of the boson peak, L is shorter than the wavelength. There is intensive discussion in the literature about the propagative/localized character of the vibrations at the boson peak in SiO_2 [4, 16]. The above estimates lead us to speculate that the modes in SiO_2 are neither propagating nor localized, because $L \leq \lambda$ but still has a finite value. The term ‘quasilocal vibration’ seems appropriate. In the case of glycerol, L becomes comparable with λ near the boson peak energy, whereas in the case of OTP, L reaches λ at E nearly twice E_{BP} (figure 3). This result contradicts the widely accepted view that the localization of the vibrations meets the Ioffe–Regel criterion just at the boson peak frequency.

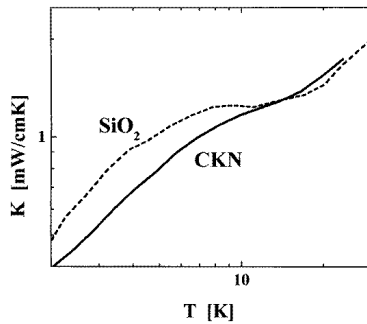


Figure 4. Thermal conductivity of SiO_2 and CKN, from [17]. No ‘plateau’ is observed for CKN.

One can also get rough estimates of L from the thermal conductivity κ . The energy range of the boson peak corresponds to the well-known ‘plateau’ in κ at temperatures between 1 and 10 K [1]. Stronger scattering of the vibrations should give a more pronounced plateau in κ . This suggestion is, indeed, consistent with the literature [17]: the plateau is usually well pronounced for strong glasses which have a high boson peak and the plateau does not appear for a fragile system like CKN which has a very weak boson peak (figure 4).

In conclusion, the combined analysis of the IXS and INS data demonstrates the presence of random- and coherent-phase contributions to $S(Q, E)$. The random-phase contribution increases strongly with the energy of the vibration. Moreover, it is found that the systems for which the amplitude of the boson peak, $g_{exc}(E)/g_D(E)$, is higher have larger random-phase contributions to $S(Q, E)$. This observation can be explained with a model which assumes that strong scattering of sound waves by spatial fluctuations of elastic constants is the main cause of the boson peak in disordered systems. It is clear that more detailed analysis of the dynamic structure factor for different glass-forming systems is needed in order to check the suggested relation between the random-phase motion and the amplitude of the boson peak. More detailed theoretical investigations of the vibrational modes in disordered systems are also important. The approach used for analysis of the dynamic structure factor [7] gives predictions for long-wavelength sound waves with mean free paths much longer than the wavelength. For most of the modes near the boson peak, however, the mean free path is of the order of or even shorter than the wavelength (figure 3). It is not clear how the predictions of the model [7] will be changed in the case of a strong localization, i.e. when the mean free path is shorter than the wavelength.

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