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Low-Q Brillouin scattering from glasses

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A general framework for the understanding of Brillouin scattering spectra observed in glasses with light, X-rays, or neutrons is presented. Several sources of acoustic damping are discussed. Crossovers between different damping regimes can occur, depending on the glass and on the temperature. Generally, the damping of sound culminates in the THz frequency range with a Ioffe-Regel limit corresponding to a resonance with the boson peak. This limit should be of direct relevance to BRISP, as the instrument will mostly operate in that region.

Keywords: Brillouin scattering; Sound damping; Acoustic attenuation; Glasses; Ioffe-Regel crossover; Boson peak

In spite of the considerable recent activity on the acoustic properties of glasses [1], particularly since the advent of high-resolution inelastic X-ray scattering (IXS) [2], many issues were raised that remain unsettled. This contribution describes our current views [3–4] on the acoustic damping observed in various scattering experiments. We mostly consider momentum exchanges $\hbar Q$ of the order or larger than these of Brillouin light scattering (BLS), but small by usual neutron-scattering standards. BLS is capable of excellent accuracy in measuring the full width Γ of acoustic modes of frequency Ω (angular frequencies are used for Ω and Γ). This is illustrated in figure 1 which shows *typical* spectra acquired on the longitudinal acoustic (LA) mode of silica glass with a modern high-resolution BLS instrument [5]. The ratio Γ/Ω, known as the internal friction, is then determined to about 1 part in 10^4. The situation becomes much more difficult at higher Ω, whether using IXS or inelastic neutron scattering (INS). An example of what can be achieved using triple-axis INS on a glass selected for its low sound velocity was shown for Se in Ref. [6]. Although very useful information was thus obtained, in particular concerning Umklapp scattering, in no way do the spectra match the quality of BLS. This is unfortunate, as for $Q \approx 1\,\mathrm{nm}^{-1}$, or for $\Omega/2\pi \approx 1\,\mathrm{THz}$, dramatic changes in the acoustic modes are anticipated [7]. Indeed, thermal conductivity results predict that plane acoustic waves experience then a Ioffe-Regel (IR) crossover beyond which they cease to be useful approximations of thermal excitations. The crossover frequency, Ω_{co}, falls in the range of the *boson peak* (BP) at Ω_{BP}, which is a spectral feature common to glasses and associated with low-lying optic-like vibrations [8]. In this

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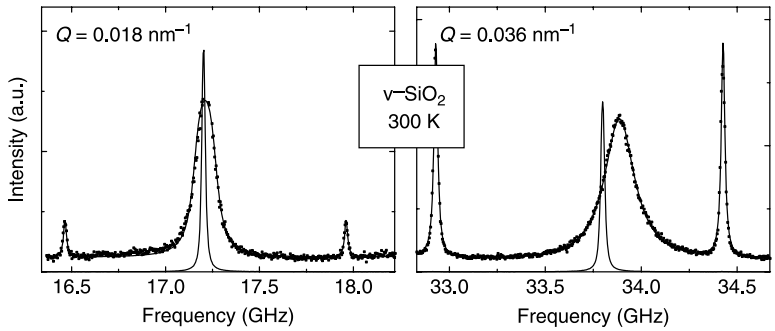

Figure 1. BLS Stokes spectra of the LA mode in vitreous silica at two scattering angles, $\theta = 60°$ (left) and $\theta = 180°$ (right). On each spectrum, the narrow elastic doublet marks the free-spectral range of the spherical Fabry-Perot. The superimposed narrow peak is a modulation signal that serves for calibration and whose shape is the instrumental response function. The line through the measured points is a damped harmonic oscillator fit.

paper, we show that several crossovers might occur between different sound-damping regimes, generally culminating with this IR crossover. The latter ought to be important to BRISP experiments which will mostly operate in that spectral region.

One should carefully distinguish the wave-vector *exchange* Q from that of a *plane-wave excitation*, noted q. Correspondingly, ω is used for the angular frequency variable in a spectrum, while Ω is reserved for modes. At sufficiently low Ω, sound propagates in glasses as in a continuum. Brillouin scattering is *momentum conserving*. This implies that $q = Q$ for excitations of sufficiently well defined momentum $\hbar q$. For acoustic modes of phase velocity v, one has then a dispersion curve $\Omega = v(q)q$. When the experimentally selected Q matches modes of well defined q, the linewidth Γ truly reflects an inverse lifetime. The energy decay length ℓ directly relates then to the *homogeneous* linewidth $\Gamma_{\rm hom}$, $\ell^{-1} = \Gamma_{\rm hom}/v$. In this case, the damped harmonic oscillator (DHO) model gives an excellent representation of the spectral shape. In the opposite limit, where q is *ill-defined* at a given mode frequency Ω, a spectrum $S(Q, \omega)$ at constant $\omega = \Omega$ just reflects an average spatial profile of the excitation packets at Ω [9]. Conversely, a spectrum $S(Q, \omega)$ at constant Q is then the sum of contributions of all the modes with $\Omega = \omega$ at this particular Q. This is *inhomogeneous* broadening. There is no basis for using the DHO in this case, while there are good reasons to believe that other line shapes should apply [9]. Only when the inhomogeneous linewidth $\Gamma_{\rm inh}$ is sufficiently small can the DHO remain a useful approximation, in which case $\ell^{-1} \cong \Gamma/v$ is the inverse energy decay length of a hypothetical plane wave that would be launched in the glass. The failure of the DHO above $\Omega_{\rm co}$ is illustrated in figure 2 by IXS spectra for two different glasses.

Several mechanisms have been identified that contribute to Γ. At very low temperatures T, it is known that resonant and relaxational couplings with two-level systems dominate acoustic damping [11]. This quantum regime will not be discussed here. However, two-level systems are just one aspect of the structural defects that occur in glasses, as emphasized by the successful soft-potential model [12]. At higher T, these defects produce *thermally activated relaxation* (TAR), characterized by $\Gamma_{\rm rel} \propto \Omega^2$ for $\Omega\tau_{\rm rel} \ll 1$, and by $\Gamma_{\rm rel} \propto \Omega^0$ for $\Omega\tau_{\rm rel} \gg 1$, where $\tau_{\rm rel}$ is a characteristic relaxation time of the defects in the strain of the sound wave. Usually, there is a distribution of $\tau_{\rm rel}$ which is a strong function of T, leading to a peak in $\Gamma_{\rm rel}(T)$ where the mean $\tau_{\rm rel}(T) \approx 1/\Omega$. The amplitude of this peak is proportional to Ω. TAR usually dominates the damping in the sonic and ultrasonic regimes [13].

A second damping mechanism, the most usual one in crystals, is the *anharmonic interaction of sound with thermally excited vibrations*. This was invoked for glasses already

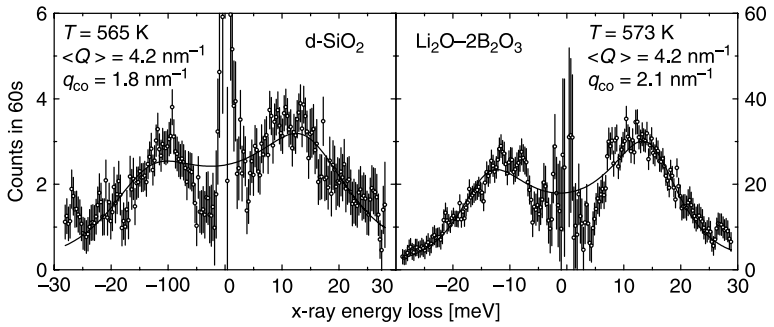

Figure 2. Best DHO fits to the inelastic part of IXS spectra above Ω_{co}. Left: densified silica from [10]; right: lithium diborate from [4]. One notices similar dips near the origin, a hallmark of inhomogeneous broadening [9].

a long time ago [14]. In the Akhiezer description, sound modulates the population of modes in the thermal bath [15]. The relaxation within this bath, characterized by a mean thermal relaxation time τ_{th}, leads to sound damping. The time τ_{th} is usually very short, so that $\Omega\tau_{th} \ll 1$ for frequencies up to at least hundred GHz, leading to $\Gamma_{anh} \propto \Omega^2$. This power is nearly independent of T as long as $\Omega\tau_{th} \ll 1$, so that Γ_{anh} is prone to exceed Γ_{rel} as Ω increases sufficiently. This can lead to a dynamical crossover [16]. In the case of silica, this Ω^2-dependence was confirmed for Q-values up to $0.12\,\mathrm{nm}^{-1}$ using ultraviolet BLS [17]. In the approximation that transition probabilities are additive the total homogeneous linewidth Γ_{hom} is then $\Gamma_{hom} = \Gamma_{rel} + \Gamma_{anh}$.

A third possible mechanism is the scattering of sound waves by frozen-in density or elastic modulus fluctuations. This is an inhomogeneous mechanism called *Rayleigh scattering*. For fluctuation sizes small compared to the sound wavelength λ, it leads to $\Gamma_{Ray} \propto \Omega^4$. In view of this high power dependence, it was thought that Γ_{Ray} could lead to the IR crossover. However, more quantitative estimates [18] indicate that Γ_{Ray} is somewhat small to explain the plateau observed in the thermal conductivity $\kappa(T)$. Conversely, a study of Si–Ge crystalline alloys, in which the density fluctuations are extremely large owing to the widely different masses of Si and Ge, revealed the absence of a $\kappa(T)$ plateau [19]. For these reasons, we believe that one should generally disregard Γ_{Ray} as a mechanism contributing appreciably to Γ below Ω_{co} in "homogeneous" glasses—as opposed to fractal substances.

A fourth broadening mechanism is the *hybridization* of acoustic modes with low-lying optic modes [20]. It can arise from a bilinear coupling between acoustic strains and optic displacements. To the extent that the uncoupled optic modes feel the glass inhomogeneity and are rather local, this hybridization produces inhomogeneous broadening of the acoustic modes, while it delocalizes the optic ones. In this model, the redistribution of optic modes creates the BP which necessarily relates to Ω_{co} [20]. We have sufficient experimental information to actually verify that $\Omega_{co} \cong \Omega_{BP}$. To be specific, we *define* Ω_{co} as that frequency Ω where $\Gamma = \Omega/\pi$. With $\ell^{-1} \cong \Gamma/v$, this implies that $\ell \cong \lambda/2$. Although a peak in a DHO spectrum can still be identified for $\Gamma = \Omega/\pi$, one should recognize that a plane wave whose energy decays by the factor $1/e^2$ over a wavelength corresponds well to the concept of a IR limit, justifying this definition. The data in figure 3 are values of Γ/Ω vs. Ω obtained from DHO fits of IXS spectra for nine different glasses. For each glass, the points are arbitrarily interpolated with a straight line. Its intercept with the horizontal line $\Gamma/\Omega = 1/\pi$ gives an estimate for Ω_{co}. Only for $Li_2O{-}2B_2O_3$ and d-SiO_2 (densified silica) are high-quality data available below Ω_{co} [4,10]. In the seven other cases, the data seem sufficient to estimate Ω_{co} within the indicated error margins. On the other hand, the hatched vertical bars illustrate for each glass the region of Ω_{BP}. It is evident that $\Omega_{co} \cong \Omega_{BP}$ in all

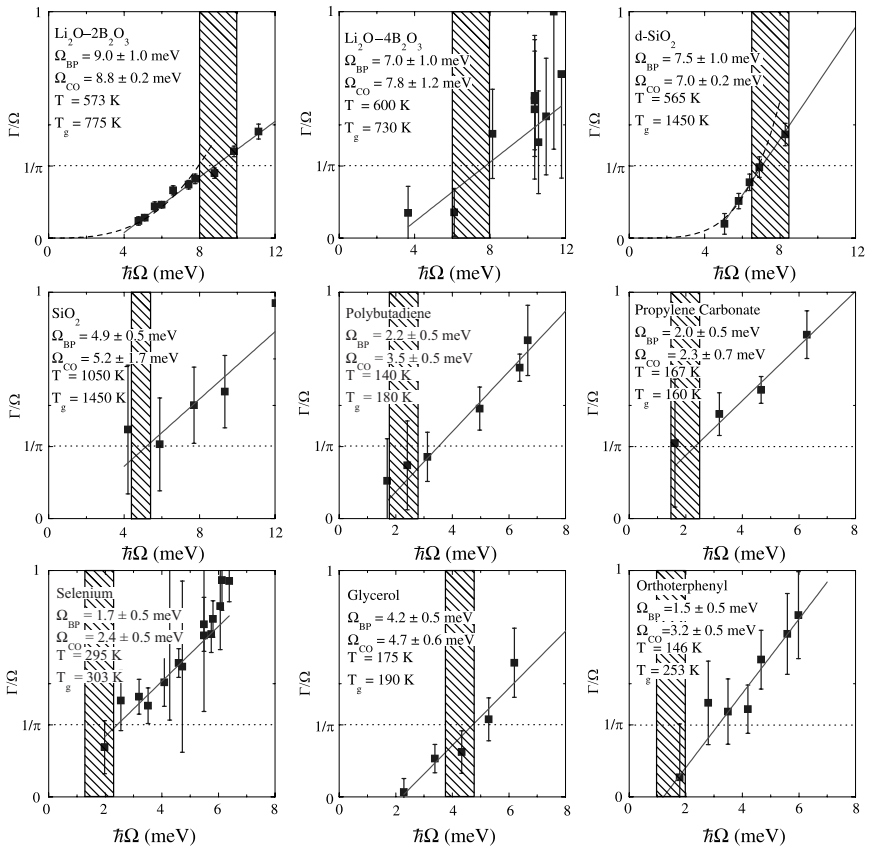

Figure 3. Determination of Ω_{co} for nine different glasses and comparison with Ω_{BP}. References for the experimental points and for the BPs are: $Li_2O–2B_2O_3$ [4,21]; Li_2O-$4B_2O_3$ [22,21]; *d*-SiO_2 [10,23]; v-SiO_2 [24,8]; polybutadiene PB [25]; polycarbonate PC [26]; selenium [27,6]; glycerol [2,28]; orthoterphenyl OTP [29]. In the case of Li_2O-$2B_2O_3$ and *d*-SiO_2, the dashed curves represent $\Gamma/\Omega \propto \Omega^3$, which is the approximate behavior observed below the IR-crossover [4,10]. The positions and ranges of the BPs are discussed in [30].

cases, except OTP. This strongly supports the hybridization model [20], as already advocated on different grounds in Ref. [18]. The case of OTP might be special as there could be several low-frequency optic modes [29], those dominating the BP and mostly coupling to transverse acoustic modes, and others hybridizing with the observed LA mode.

Except for the nearly universal IR-crossover, the strength of the other important broadening mechanisms—namely TAR and anharmonicity—strongly depends on the particular glass *and* on the measuring temperature *T*. Figure 4 illustrates this for two glasses. In v-SiO_2, for $\Omega/2\pi$ below ~ 10 GHz, TAR dominates the damping [3]. However, depending on *T*, TAR gives very different apparent slopes α in $\Gamma_{rel} \propto \Omega^{\alpha}$. The reason is explained in Ref. [3], where it is also shown that such power laws are not really justified for TAR. Above ~ 10 GHz, anharmonicity takes over, and at 300 K it dominates the damping beyond ~ 30 GHz. The large difference in the strength of Γ_{anh} between 100 and 300 K is mainly due to the strong *T*-dependence of τ_{th}: around 1 THz, Γ_{anh} is motionally broadened and τ_{th} at 300 K is more than an order of magnitude shorter than at 100 K [3]. As Ω is increased, there occurs a dynamical crossover between TAR-dominated and anharmonicity-dominated

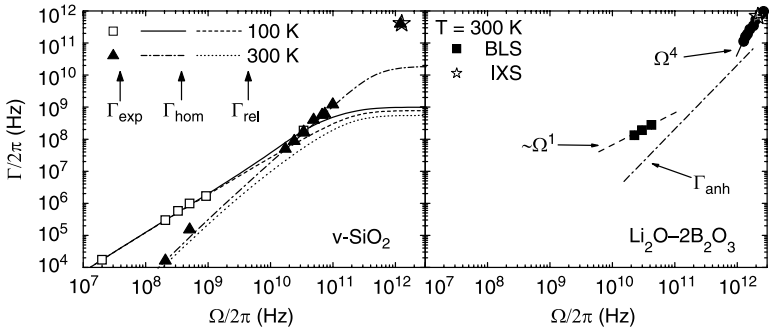

Figure 4. Frequency dependence of the LA linewidth for v-SiO_2 (left) and $Li_2O-2B_2O_3$ (right). The lines for v-SiO_2 are calculated from the model in Ref. [3]; in order of increasing Ω, the data points below 300 MHz are from figure 1 of [3b], those between 300 MHz and 1 GHz are from [31], three data points at 300 K and one at 100 K are from our own BLS measurements, four points are from [17]. The star shows Γ_{co} vs. Ω_{co} obtained from figure 3. It nearly coincides with a data point taken from [32]. For $Li_2O-2B_2O_3$ the references to the data are found in Ref. [4]. The star is similarly derived from figure 3, while the line of slope 2 for Γ_{anh} is an estimate explained in Ref. [4].

regimes. However, the visibility of this crossover in $\Gamma(\Omega)$ will strongly depend on T. Particularly at 300 K, where both mechanisms lead approximately to similar Ω^2 dependences, this crossover is hardly apparent. We also note that Γ_{hom} saturates for $\Omega/2\pi \sim 1$ THz. We have drawn in figure 4a a measured IXS point near 1 THz, and the point $\Gamma = \Omega_{co}/\pi$ extracted from figure 3. These two points which nearly superpose are clearly above the curve $\Gamma_{hom}(\Omega)$. This suggests that the broadening due to the hybridization with the BP has there taken over. The datum measured near 1 THz, taken from Ref. [31], is the one reliably measured at the *lowest* Ω out of a very large number of available IXS experimental reports. So far, IXS has unfortunately not been able to reach lower Ω-values in v-SiO_2. However in *d*-SiO_2, where the IR-crossover is substantially higher, the approach of Ω_{co} from below could be measured [10]. It revealed a law approximately in $\Gamma_{inh} \propto \Omega^4$, as illustrated by the dashed curve in figure 3. One expects thus a second dynamical crossover, around 400 GHz in v-SiO_2, between Γ_{hom} and Γ_{inh}. This was already pointed out in Ref. [33], although the inhomogeneous broadening was there attributed to Γ_{Ray}. The IR-crossover is thus the third—and possibly the highest—crossover on plots of $\Gamma(\Omega)$. Indeed, beyond Ω_{co} the linewidth cannot be strictly defined for reasons explained above. It is however conceivable that in cases where the density of states in the BP would be small, or if the interaction would be too weak, the acoustic modes could approximately recover their plane-wave nature at higher frequencies, beyond the BP. It is also possible that at these higher Ω values Γ_{Ray} dominates then the damping.

Figure 4b illustrates for comparison the case of $Li_2O-2B_2O_3$ at 300 K [4]. The frequency distribution of TAR is then so broad that it dominates the BLS linewidth. It happens to be near the maximum of the defect distribution, in which case $\Gamma_{rel} \propto \Omega$. An estimate for Γ_{anh} is also drawn [4], showing that it hardly ever dominates the broadening. On the opposite, in the case of *d*-SiO_2 it is the anharmonicity which totally dominates BLS, while TAR appears to be negligible [3]. Figure 4b also shows the approach of Ω_{co} with the dependence $\Gamma_{inh} \propto \Omega^4$ [4], terminating at the IR-crossover.

To summarize, there exist several sound-damping mechanisms in glasses whose strength generally depends on the material and on T. At least three crossovers are expected in $\Gamma(\Omega)$ and a single law $\Gamma \propto \Omega^2$ is generally not meaningful. The analysis of sound-damping requires high quality measurements over a broad range of Ω. A near universal property of glasses seems to be the presence of a IR-crossover at resonance with the BP.

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References

[1] See, e.g. J. Phys. Condens. Matter **15** 11 (2003), or phys. stat. sol. (c) **1** 11 (2004).
[2] F. Sette, *et al.*, Science **280** 1550 (1998).
[3] E. Rat, *et al.*, Phys. Rev. B **72** 214204 (2005); R. Vacher *et al.*, Phys. Rev. B **72** 214205 (2005).
[4] B. Rufflé, *et al.*, Phys. Rev. Lett. **96** 045502 (2006).
[5] Updated version of a spectrometer described by R. Vacher *et al.*, Rev. Sci. Instrum. **51** 288 (1980).
[6] M. Foret, *et al.*, Phys. Rev. Lett. **81** 2100 (1998).
[7] R.C. Zeller and R.O. Pohl, Phys. Rev. B **4** 2029 (1971); J.E. Graebner *et al.*, Phys. Rev. B **34** 5696 (1986).
[8] U. Buchenau, *et al.*, Phys. Rev. B **34** 5665 (1986); B. Hehlen *et al.*, Phys. Rev. Lett. **84**, 5355 (2000).
[9] R. Vacher, *et al.*, Phil. Mag. B **79** 1765 (1999).
[10] B. Rufflé, *et al.*, Phys. Rev. Lett. **90** 095502 (2003).
[11] J. Jäckle, Z. Phys. **257** 212 (1972).
[12] V.G. Karpov, *et al.*, Sov. Phys. JETP **57** 439 (1983).
[13] S. Hunklinger and W. Arnold, *Physical Acoustics* (Academic Press, N.Y., 1976), Vol. XII, pp. 155–215.
[14] T.N. Claytor, *et al.*, Phys. Rev. B **18** 5842 (1978); R. Vacher *et al.*, J. Non-Cryst. Solids **45** 397 (1981).
[15] A. Akhiezer, J. Phys. USSR **1** 277 (1939).
[16] T.C. Zhu, *et al.*, Phys. Rev. B **44** 4281 (1991).
[17] C. Masciovecchio, *et al.*, Phys. Rev. Lett. **92** 247401 (2004); P. Benassi *et al.*, Phys. Rev. B **71** 172201 (2005).
[18] D.A. Parshin and C. Laermans, Phys. Rev. B **63** 132203 (2001).
[19] A. Béraud, *et al.*, Physica B **350** 254 (2004).
[20] V.L. Gurevich, *et al.*, Phys. Rev. B **67** 094203 (2003).
[21] J. Lörosch, *et al.*, J. Non-Cryst. Solids **69** 1 (1984).
[22] A. Matic, *et al.*, Phys. Rev. Lett. **86** 3803 (2001).
[23] M. Foret, *et al.*, Phys. Rev. B **66** 024204 (2002).
[24] R. Dell'Anna, *et al.*, Phys. Rev. Lett. **80** 1236 (1998).
[25] D. Fioretto, *et al.*, Phys. Rev. E **59** 4470 (1999); U. Buchenau *et al.*, Phys. Rev. Lett. **77** 4035 (1996).
[26] J. Mattsson, *et al.*, J. Phys. Condens. Matter **15** S1259 (2003).
[27] T. Scopigno, *et al.*, Phys. Rev. Lett. **92** 025503 (2004).
[28] J. Wuttke, *et al.*, Phys. Rev. E **52** 4026 (1995).
[29] G. Monaco, *et al.*, Phys. Rev. Lett. **80** 2161 (1998); A. Tölle, Rep. Prog. Phys. **64** 1473 (2001).
[30] B. Rufflé, *et al.*, Phys. Rev. Lett. (to be published).
[31] C.K. Jones, *et al.*, Phys. Lett. **8** 31 (1964).
[32] C. Masciovecchio, *et al.*, Phys. Rev. B **55** 8049 (1997).
[33] R. Vacher, *et al.*, Phys. Rev. B **56** R481 (1997).