

## Acoustic Dissipation and Density of States in Liquid, Supercooled, and Glassy Glycerol

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Combined Brillouin spectra collected at visible, ultraviolet, and x-ray frequencies are used to reconstruct the imaginary part of the acoustic compliance  $J''$  over a wide frequency range between 0.5 GHz and 5 THz. For liquid, supercooled, and glassy glycerol,  $J''$  is found to be linearly dependent on the tagged-particle susceptibility measured by incoherent neutron scattering up to  $\approx 1$  THz, giving evidence of a clear relation between acoustic power dissipation and density of states. A simple but general formalism is presented to quantitatively explain this relation, thus clarifying the connection between the quasielastic component observed in neutron scattering experiments and the fast relaxation dynamics probed by Brillouin scattering.

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The dynamics of glass-forming systems spreads over a wide frequency range. While the structural ( $\alpha$ ) relaxation, ubiquitous in liquids, strongly slackens on cooling toward the glass transition, phononlike excitations in the gigahertz-terahertz frequency region are mainly affected by a fast relaxation dynamics. This dynamics appears as a broad and strongly temperature-dependent quasielastic contribution (QES) in depolarized light and neutron scattering spectra. Though the nature of this feature has been the motivation of many studies [1–20], no consensus has yet been achieved on its interpretation.

On a general ground, the available literature suggests a connection between the QES and the damping of the acoustic waves, although the existing theoretical and experimental investigations in most of the cases concern a narrow temperature region, usually confined to the glassy state, and rarely extend to the supercooled region. A limitation of the existing studies is due to the lack of experimental data for the acoustic attenuation in a frequency range wide enough to be compared directly to the QES data. Only recently have the development and improvement of spectroscopic techniques like inelastic x-ray and ultraviolet Brillouin scattering (IXS and IUVS, respectively) enabled measuring the acoustic attenuation in previously unexplored regions.

In this Letter—based on the combined use of Brillouin spectra collected on a sample of glycerol in the visible, ultraviolet, and x-ray frequency regions (BLS-IUVS-IXS) and incoherent neutron spectra (INS)—we are in a position to (i) demonstrate a linear relation between the acoustic dissipation and the density of states of the system, (ii) show a simple, model-independent, relation that quantitatively accounts for the obtained linear coefficients in terms of acoustic properties of the system, and (iii) verify this

relation in different aggregation states, i.e., liquid, supercooled, and glassy, and in the whole frequency region where QES is observed. These findings highlight under what general circumstances the connection presented here is expected to hold and clarify how the quasielastic component observed in neutron scattering is related to the fast relaxation dynamics probed by light scattering.

We discuss experimental results obtained on glycerol by means of four different techniques, namely, BLS, IUVS, IXS, and INS, recorded at several temperatures spanning the glass, the supercooled, and the normal liquid phases (glass transition temperature  $T_g = 189$  K, melting temperature  $T_m = 291$  K). The BLS measurements have been carried out at the optical laboratory in Perugia [21] and have already been presented [22]. The IUVS experiment has been performed at the Elettra facility [23]. The IXS experiment has been performed at beam line ID16 of the European Synchrotron Radiation Facility [24]. Finally, incoherent neutron scattering experiments have been carried out on partially deuterated glycerol  $C_3H_5(OD)_3$  at  $Q_{INS} = 1.09 \text{ \AA}^{-1}$  by using a wavelength of  $\lambda = 7 \text{ \AA}$  at the cold neutron time-of-flight spectrometer IN5 of the Institut Laue-Langevin [25]. These spectra are in agreement with those reported in the literature [26], where, in particular, it has been shown that, in the case of glycerol, the vibrational density of states scarcely depends on the isotopic composition up to  $\sim 1.2$  THz.

In Fig. 1, tagged-particle susceptibilities  $\chi''_{INS}(\omega)$ , obtained from incoherent neutron scattering spectra [27], are reported after normalization of the related density of states [28] and further scaling by a factor  $s$  (see below) that allows matching them to the light scattering susceptibilities  $\chi''_L(\omega)$ . These latter are obtained from isotropic Brillouin (BLS-IUVS-IXS)  $S(q, \omega)$  spectra via the relation

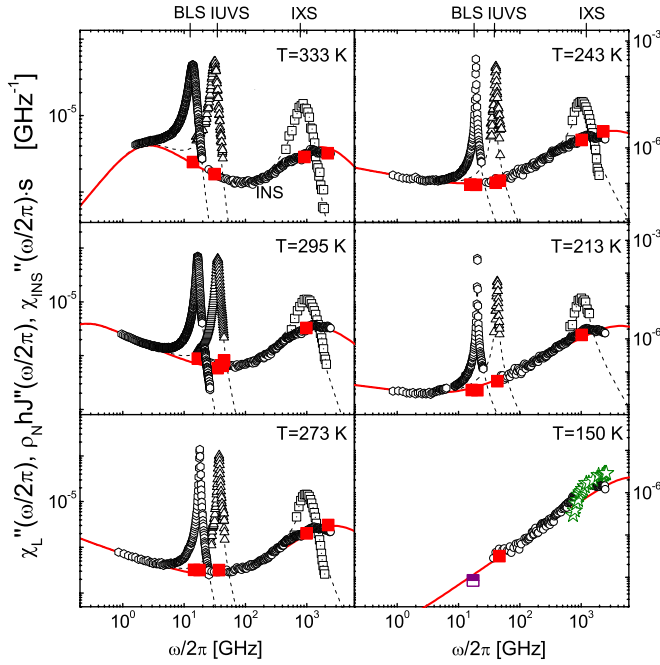


FIG. 1 (color online). Selection of susceptibility spectra in absolute units for different temperatures. Experimental BLS (open diamonds) [22], IUVS (open triangles), and IXS (open squares) data are shown together with INS data (open circles). The INS data have been scaled by a factor  $s$  (see the text) in order to match them to the  $\chi_L''(\omega/2\pi)$  data. Solid squares correspond to the imaginary part of the longitudinal compliance,  $J''(\omega_B/2\pi)$ , at the Brillouin frequency ( $\omega_B/2\pi$ ), after scaling by  $\hbar\rho_N$ ,  $\rho_N$  being the number density. Dashed and solid (red) lines are the Brillouin spectra joint-analysis fits and the corresponding  $\hbar\rho_N J''(\omega/2\pi)$  curves, respectively. The half-filled square is a longitudinal compliance value taken from Ref. [39], and the open stars are taken from Ref. [34].

$\chi_L''(\omega) = \pi S(q, \omega)/[n(\omega) + 1]$ , where  $n(\omega)$  is the Bose factor. In the same figure, we also reported scaled acoustic compliance data  $\hbar\rho_N J''$ , where  $\rho_N$  is the number density (average number of atoms per unit volume). Here the scaling factor  $\hbar\rho_N$  is used to allow for a proper comparison with the  $\chi_L''(\omega)$  data. The  $J''$  data have been evaluated as  $J''(\omega_B) = Q^2\Gamma/[\rho\omega_B(\omega_B^2 + \Gamma^2)]$ , where  $Q$  is the momentum exchanged in the scattering process,  $\rho$  the mass density, and  $\omega_B$  and  $\Gamma$  the angular frequency and linewidth, respectively, of the Brillouin peaks obtained by a damped harmonic oscillator fit of the Brillouin peaks [29].

In Fig. 1, we also draw the  $\hbar\rho_N J''(\omega)$  curves (red solid lines) obtained from a simultaneous full-spectrum analysis of the isotropic Brillouin spectra previously performed by some of us [22]. That analysis was based on a phenomenological model for the complex generalized elastic modulus  $M^*(\omega)$  that still is able to well represent the main contributions to the Brillouin spectra (dashed curves in Fig. 1). The used model includes only the  $\alpha$  process, described by a Cole-Davidson relaxation function, and a very fast (“instantaneous”) process [22]. The  $J''(\omega)$  data correspond to  $J''(\omega) = M''(\omega)/[M''(\omega)^2 + M'(\omega)^2]$ . In

Fig. 1, it is clearly shown that  $\chi_L''(\omega)$  coincides with  $\hbar\rho_N J''(\omega)$  in the low-frequency part of the spectrum, the so-called Mountain region [29]. In the liquid and for frequencies around 10 GHz, the acoustic dissipation is dominated by the  $\alpha$  relaxation that progressively gets slower on cooling. In the high-frequency range, the fast relaxation gives rise to a second maximum in  $J''(\omega)$  centered at a few thousand gigahertz. Furthermore, the excellent superposition between  $J''(\omega)$  and the scaled  $\chi_{INS}''(\omega)$  suggests that there exists a proportionality between these two quantities at all temperatures and in the whole explored frequency range. Interestingly, the proportionality factor  $s$ , defined as  $\hbar\rho_N J''(\omega) = s\chi_{INS}''(\omega)$ , comes out to be almost temperature-independent. This highlights a remarkable correspondence between  $J''(\omega)$  and  $\chi_{INS}''(\omega)$  independently of any theoretical consideration.

The physical meaning of this connection can be understood if one recalls that, in mechanical experiments,  $\omega J''(\omega)$  is proportional to the energy dissipation per unit time [30]. On the other hand, in incoherent neutron scattering experiments,  $\omega\chi_{INS}''(\omega)$  is proportional to the Fourier transform of the velocity autocorrelation function  $g(\omega)$ . In the glass and in vicinity of the glass,  $g(\omega)$  strictly corresponds to the vibrational density of states [27]. Our results in Fig. 1 thus suggest a direct connection between  $g(\omega)$  and the dissipation of acoustic energy.

Increasing attention has been recently devoted to the relation between  $g(\omega)$  and the acoustic properties in glasses, especially in the region of the boson peak [31]. Our findings here point out that this relation holds—and even more accurately—also at lower frequencies. To rationalize this result, we recall that a standard field-theory approach allows deriving a simple and general relation between the density of states and the longitudinal and transverse dynamic susceptibilities  $\chi_L$  and  $\chi_T$ , respectively [31]:

$$g(\omega) = \left(\frac{2M\omega}{3\pi\hbar}\right) \sum_{k < k_D} \frac{1}{k^2} \text{Im}\{\chi_L(k, \omega) + 2\chi_T(k, \omega)\}, \quad (1)$$

where  $M$  is the average atomic mass and the sum over  $k$  corresponds to an integration up to the Debye cutoff  $k_D = [6\pi^2\rho_N]^{1/3}$ . From this relation, by performing an expansion in the variable  $\Gamma/\omega_B$  as in Ref. [31], it is possible to derive a generalized relation between  $g(\omega)$  and  $\Gamma(\omega)$  under the following assumptions: (i) The approximation  $\omega_B \gg \Gamma$  holds (low acoustic absorption); (ii) the longitudinal and transverse moduli have the same temperature and frequency dependence; and (iii) the longitudinal acoustic attenuation is simply proportional to the transverse one,  $\alpha$  being the proportionality factor. Under the conditions above, one obtains

$$g(\omega) \simeq g_D(\omega) + g_{\text{rel}}(\omega) = \frac{3\omega^2}{\omega_D^3(\omega)} + \frac{\Gamma(\omega)}{\omega_0^2}, \quad (2)$$

where  $g_D(\omega)$  is the Debye density of states, with  $c_D(\omega) = \{[c_L^3(\omega) + 2c_T^3(\omega)]/3\}^{(-1/3)}$  and  $\omega_D(\omega) = k_D c_D(\omega)$

frequency-dependent generalizations of the Debye sound velocity and frequency, respectively, and with  $c_L$  and  $c_T$  the longitudinal and transverse sound velocities, respectively, and where  $g_{\text{rel}}(\omega)$  is the relaxational contribution to  $g(\omega)$ , with  $\omega_0$  an interaction parameter describing the coupling between sound waves and relaxations. Equation (2) can be alternatively written as a relation between  $[g(\omega) - g_D(\omega)]$  and  $J''(\omega)$  by recalling that, in the case of small damping,  $\Gamma(\omega) = \rho\omega c_L^2(\omega)J''(\omega)$ . Moreover, the coupling coefficient  $\omega_0$  has the following expression in terms of acoustic properties:

$$\omega_0^2 = \frac{\pi k_D^2 c_L^2(\omega)}{2} \left[ 1 + \frac{2}{\alpha} \left( \frac{c_L(\omega)}{c_T(\omega)} \right)^4 \right]^{-1}. \quad (3)$$

In the following, we use  $\alpha = 3$  in accordance with the recent finding that a generalized Cauchy-like relation  $M' = A + \alpha G'$  holds in several systems, including glycerol, with  $\alpha$  close to 3, not only in the glass and in vicinity of the glass [32] but also in the viscoelastic range [33]. For glycerol, we use  $A = (3.61 \pm 0.85)$  GPa, with  $\alpha = 3$ .

A relation very similar to Eq. (2) between  $g(\omega)$  and  $\Gamma(\omega)$  has been recently reported by Schirmacher, Ruocco, and Scopigno [31]. We have here basically derived a more general expression to include the dependence on frequency of  $c_D(\omega)$ . This enables us to extend the comparison between  $g(\omega)$  and  $\Gamma(\omega)$  over the whole frequency and temperature range and independently of any model as far as  $\omega_B \gg \Gamma$ . Moreover, the experimentally verified validity of the Cauchy relation allows us to fix  $\alpha = 3$ , while, in the original paper by Schirmacher and co-workers [31], the value  $\alpha = 2$  was fixed based on the assumption that the longitudinal Lamé coefficient  $\lambda$  is a constant and the shear modulus  $G$  is a spatially fluctuating quantity, these two quantities being related to the longitudinal modulus by the relation  $M = \lambda + 2G$ .

To test the derived relations against our experimental data, we calculate the parameters required by Eqs. (2) and (3) at the specific frequency of each Brillouin spectrum, using the values of  $c_L$  directly measured by Brillouin scattering and those of  $c_T$  calculated via the Cauchy-like relation. As is well known indeed, the transverse dynamics in disordered systems is basically not experimentally accessible in the frequency range of interest here. We find that the proposed model works well at BLS and IUVS frequencies and at all temperatures apart from the highest one and the highest-frequency IXS data; see Fig. 2. In these cases, however, the hypothesis that  $\omega_B \gg \Gamma$  does not hold any more, and Eq. (2) cannot be applied any longer. In this regime one has to go back to Eq. (2) in order to investigate the relation between the vibrational density of states and the dynamic susceptibilities, as successfully shown in Ref. [34]. Thus our model, within the limits of its applicability, provides a valuable description of our experimental results. In particular, the choice  $\alpha = 3$  comes out to give a better description of our experimental results than the choice  $\alpha = 2$ , consistent with the experimentally verified validity of the Cauchy-like relation [33].

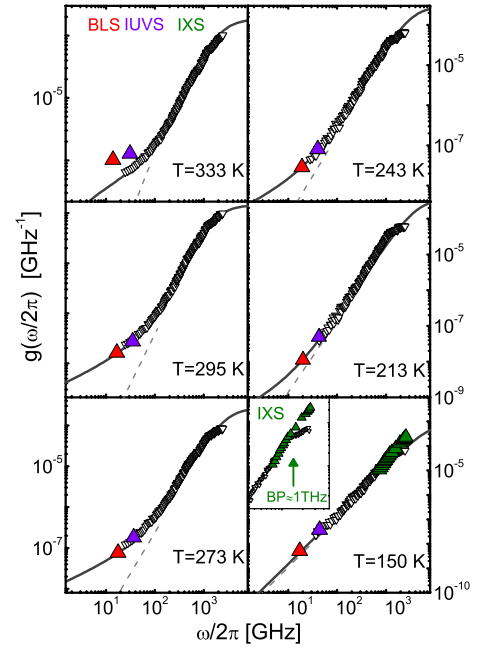


FIG. 2 (color online). Experimental  $g(\omega/2\pi)$  from INS (open down triangles) shown together with calculated  $g(\omega/2\pi)$  (full up triangles) at the Brillouin peak frequency of BLS (red), IUVS (violet), and IXS measurements (olive [34]) using Eqs. (2) and (3).  $J''(\omega/2\pi)/s$  curves multiplied by  $\omega/2\pi$  are also reported as solid lines, where  $s$  has the same values as in Fig. 1. The Debye level is indicated as well (dashed lines) for reference. In the inset, the high-frequency data for the glass are emphasized, and the boson peak position is indicated by the arrow.

As a further step, in order to explain the direct connection empirically found between  $\chi''_{\text{INS}}(\omega)$  and  $J''(\omega)$ , we now consider that  $\chi''_{\text{INS}}(\omega) = [\pi\hbar Q_{\text{INS}}^2 e^{-2W} g(\omega)]/(2M\omega)$ , and starting from Eq. (2), we can write

$$\chi''_{\text{INS}}(\omega) = \frac{\pi\hbar Q_{\text{INS}}^2 e^{-2W}}{2M} \left[ \frac{3\omega}{\omega_D^3} + \frac{\rho c_L^2(\omega)}{\omega_0^2} J''(\omega) \right], \quad (4)$$

$e^{-2W}$  being the Debye-Waller factor. The first term on the right side of Eq. (4) is related to the Debye contribution. We find that, in the BLS and IUVS range, on increasing temperature it contributes less and less to the total value of  $\chi''_{\text{INS}}(\omega)$  and that actually at the highest probed temperatures it is truly negligible. In that condition, the ratio  $\hbar\rho J''(\omega)/\chi''_{\text{INS}}(\omega)$  from Eq. (4), which is only weakly frequency-dependent, corresponds to the empirically obtained scaling factor  $s$ . This then explains the large proportionality of  $\chi''_{\text{INS}}(\omega)$  and  $J''(\omega)$  in the log-scale representation of Fig. 1.

Finally, the coupling coefficient  $\omega_0^2$  obtained from Eq. (3) is reported in Fig. 3 together with that determined from Eq. (2) using the experimental values of the vibrational density of states at the IUVS Brillouin frequency, showing a 50% decrease with temperature in the explored temperature range. It is worth noting that this temperature dependence closely follows that of the Debye frequency,

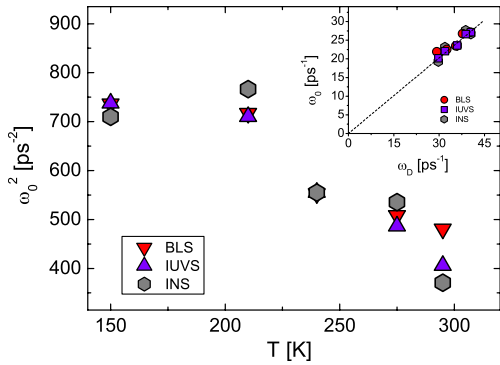


FIG. 3 (color online). Temperature dependence of the square of the coupling coefficient  $\omega_0^2$  between sound waves and relaxation processes, expected by the model Eq. (3) (triangles) and directly obtained at the IUVS Brillouin frequency from experimental  $g(\omega)$  via Eq. (2) (hexagons). The inset emphasizes how  $\omega_0$  remains a fixed fraction of the Debye frequency, independent of the temperature.

as shown in the inset in Fig. 3. In other terms,  $\omega_0$  turns out to be close to  $\omega_D$ , namely,  $\omega_0 \approx 0.7\omega_D$ , with their ratio being temperature-independent. Keeping in mind that in the explored temperature range the relaxations affecting the broadening of the Brillouin peaks include both the structural and the fast one, this leads to the interesting observation that the coupling coefficient  $\omega_0$  is independent of whether structural or fast relaxations are considered.

In conclusion, we have reported on the scaling of collective over single particle scattering spectra in the frequency region of the quasielastic scattering, which intriguingly works in both liquid and supercooled glycerol while it becomes worse below the glass transition in the region where the boson peak becomes prominent. In this region, more complex mechanisms may contribute to the acoustic attenuation in the glassy state and in proximity of the boson peak [34–38]. We have modeled the observed scaling by using a simple relation between acoustic loss and generalized density of states, proposing the use of the Cauchy-like model for deriving the shear modulus from the bulk one. This relation successfully describes the experimental data in the glass up to the boson peak and establishes a clear connection between the quasielastic component observed in neutron scattering experiments and the fast relaxation dynamics probed by Brillouin scattering.

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