DOI: 10.1478/AAPP.98S1A3

AAPP | Atti della Accademia Peloritana dei Pericolanti
Classe di Scienze Fisiche, Matematiche e Naturali
ISSN 1825-1242

Vol. 98, No. S1, A3 (2020)

ON THE DEBYE-LIKE BEHAVIOUR OF THE SPECIFIC HEAT OF PERMANENTLY DENSIFIED SILICA GLASS

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ABSTRACT. The aim of this work is to review the main results about the vibrational dynamics of glasses and to clarify the effect induced by changes of the mass density on their thermal properties. In particular, we present the temperature dependence of the specific heat of permanently densified silica glass in comparison to that of crystalline α-quartz. We propose a very simple and schematic model to interpret the experimental results.

1. Introduction

The dynamics of glasses as well as their thermal properties have been the subject of an intense study in the last fifty years (Zeller and Pohl 1971; Galeener and Sen 1978; Fontana *et al.* 1980; Phillips 1981; Fontana *et al.* 1983; Galeener *et al.* 1983; Buchenau *et al.* 1984; Carini *et al.* 1984; Buchenau *et al.* 1986; Malinovsky *et al.* 1990; Benassi *et al.* 1991; Buchenau *et al.* 1991; Elliott 1991; Carini *et al.* 1993; Benassi *et al.* 1995; Duval and Mermet 1998; Engberg *et al.* 1998; Feldman *et al.* 1999; Fontana *et al.* 1999; Surovtsev *et al.* 2000; Surovtsev and Sokolov 2002; Scopigno *et al.* 2003; Novikov and Sokolov 2004; Benassi *et al.* 2005; Bove *et al.* 2005; Scopigno *et al.* 2005; Fontana *et al.* 2006; Schirmacher *et al.* 2007; D'Angelo *et al.* 2010; Orsingher *et al.* 2010a,b; Ruffle *et al.* 2010; D'Angelo *et al.* 2011; Crupi *et al.* 2015). The absence of periodicity characteristic of disordered systems such as glasses makes it difficult to describe their microscopic dynamics and the differences with respect to crystals pose several intriguing issues. One of the major achievements of the crystalline dynamics theory is the recognition that vibrations in crystals are phonons. In the low frequency range, say 20% of the Debye frequency, phonons follow a linear dispersion relation. Consequently, we would expect the density of states, $g(\omega)$, of glasses to have a $\sim \omega^2$ behaviour. In fact, in the Debye continuum theory, $g(\omega)$ is given by:

$$g(\omega) = \frac{3\omega^2}{\omega_D^3} = \frac{\omega^2}{6\pi n}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right) \tag{1}$$

where ω_D is the Debye frequency, $n = N/V$ is the number density, v_L and v_T are the longitudinal and transverse sound velocities. However, experiments have shown that the low-frequency density of states is very different from that expected by the Debye theory. All spectroscopic techniques indicate, in the 2-7 meV energy range, the existence of a bump, an excess of vibrational density of states with respect to the Debye expectation. This bump is known as boson peak (BP).

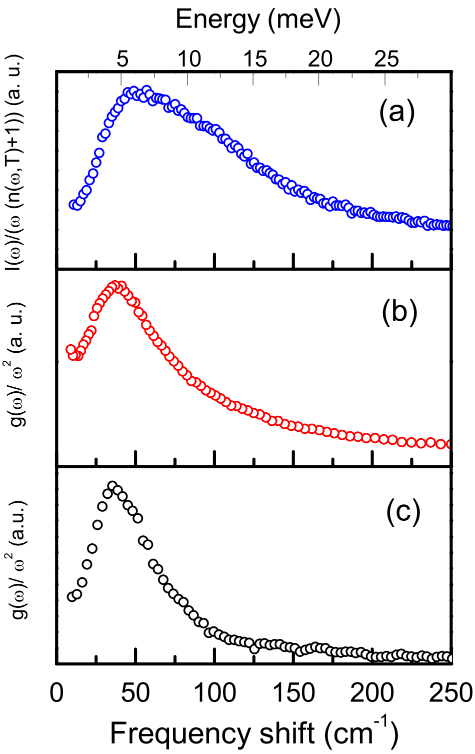

FIGURE 1. Reduced density of states by Raman (a), neutron (b), and X-ray (c) scattering measurements at room temperature. Raman and neutron data are taken from Fabiani *et al.* (2008) and X-ray from Chumakov *et al.* (2014).

The $g(\omega)$ can be estimated by several experimental techniques such as Raman (Fontana *et al.* 1983; Benassi *et al.* 1991; Carini *et al.* 1993; Fontana *et al.* 1999), inelastic neutron (Galeener *et al.* 1983; Buchenau *et al.* 1986; Fabiani *et al.* 2008; Orsingher *et al.* 2010b; Zanatta *et al.* 2013) and X-ray scattering (Baldi *et al.* 2008; Benassi *et al.* 2015) measurements as well as infrared absorption (Kabeya *et al.* 2016). The Raman scattering intensity is given by (Galeener and Sen 1978):

$$I^R = \frac{|n(\omega,T)+1|}{\omega} C(\omega) g(\omega) \tag{2}$$

where $C(\omega)$ is called the light-vibration coupling function and $n(\omega,T)$ is the Bose-Einstein population factor for phonons. The neutron and X-ray scattering intensity, in the incoherent approximation (Egelstaff 1989; Baldi *et al.* 2008), can be written as:

$$I^{N,X} = \frac{|n(\omega,T)+1|}{\omega} g(\omega). \tag{3}$$

As an example, in Fig. 1 we report the reduced density of states, $g(\omega)/\omega^2$, measured by neutron and X-rays and the reduced Raman scattering intensity, $I(\omega)/\{\omega[n(\omega,T)+1]\}$, of vitreous $\mathrm{SiO_2}$. The shape of the BP is very similar for the three techniques and the frequency of the maximum, ω_{BP}, is centred at $\omega_{\mathrm{BP}} \sim 5$ meV. In Raman scattering, due to the presence of the coupling function, $C(\omega)$, the position of this maximum is shifted to $\omega_{\mathrm{BP}} \sim 6$ meV and the overall shape is slightly different. Indeed, $C(\omega)$ is roughly proportional to ω in this spectral region (Fontana *et al.* 1999; Surovtsev and Sokolov 2002).

Turning to the thermal properties, the T^3 behavior of specific heat (SH) of crystalline solids below $\sim 1-2$ K is well described by the Debye model. The SH is given by:

$$C_p \approx C_v = \int_0^\infty d\omega \frac{\partial n(\omega,T)}{\partial T} \hbar\omega g(\omega) \tag{4}$$

where C_{p} and C_{v} are the specific heats at constant pressure and at constant volume, respectively. The SH in the Debye low temperature limit is (Kittel 2004):

$$C_p \approx C_v = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3 \tag{5}$$

where k_{B} is the Boltzmann constant and the Debye temperature θ_{D} is given by $\theta_{\mathrm{D}} = \hbar\omega_{\mathrm{D}}/k_{\mathrm{B}}$. At higher temperature, in the $\sim 2-80$ K range, a deviation from the T^3 behaviour is typically observed in crystals. This deviation is attributed to the flattening of the dispersion curves. The broad bump is caused by the higher density of states of the lowest transverse acoustic branch near the edge of Brillouin zone (see Phillips 1981, and references therein). In glasses, the T^3 Debye regime is never reached (Zeller and Pohl 1971) and the SH is several order of magnitude greater than that of the corresponding crystal at low temperatures. This large SH is observed at temperatures below $\sim 1-2$ K and is generally ascribed to tunneling processes occurring between quasi-equivalent sites (two-level systems) (Phillips 1981). Moreover, the bump related to the dispersion of the transverse acoustic vibrations occurs at lower temperature and is almost one order of magnitude greater than the one seen in the corresponding crystal. The bump observed in the SH is also referred to as "boson peak" because it is related to the previously mentioned spectral feature.

Now, a question arises: why the continuum approximation, underlying the Debye model, does not apply to glasses? At low frequency, in $g(\omega)$, or low temperature, in C_{p}, one would have predicted this approximation to hold also for glasses, since defects and disorder are increasingly less important as the wavelength of the phonons increases. Hence, the excess of excitations has been generally attributed to the presence of new oscillatory degrees of freedom, more or less localized, caused by the topological disorder of glasses, which couple to acoustic wave-like vibrational modes (Buchenau *et al.* 1986). Nevertheless, the possibility of performing inelastic scattering measurements with X-rays (Sette *et al.* 1998; Matic *et al.*

2001; Scopigno *et al.* 2005) free from any kinematic limitation that are present in neutron scattering (Galeener *et al.* 1983; Orsingher *et al.* 2010b; Zanatta *et al.* 2013), has led to discover the existence of phonon-like excitations and of a pseudo-Brillouin zone also in glasses (Sette *et al.* 1998; Scopigno *et al.* 2005; Baldi *et al.* 2008, 2014).

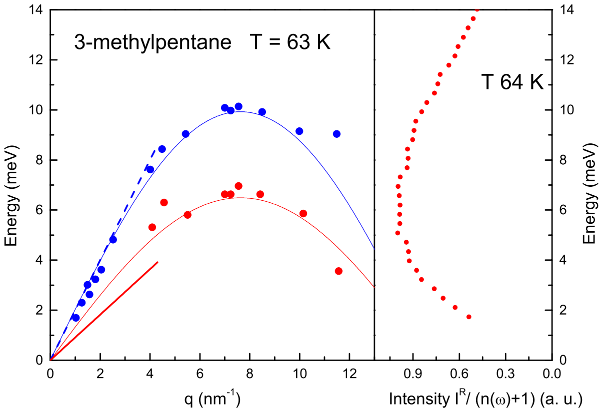

FIGURE 2. Revised data from Baldi *et al.* (2017). (Left panel) Dispersion curves: the upper data (full blue circles) are the ω_L parameters and the lower data are the ω_T parameters (full red circles). The continuous lines are the best fit of Eq. (6) to the two different data sets, as described in the text. The linear lines correspond to the linear dispersion at the macroscopic scale, expected from the longitudinal (blue), $v_L = 2868$ m/s and transverse (red), $v_T = 1354$ m/s sound velocities. (Right panel) Low frequency density of states from Raman data with the assumption that $C(\omega) \propto \omega$, see Eq. (2).

As an example, the longitudinal and transverse acoustic branches measured by X-ray scattering in organic glassy 3-methylpentane (3MP is a structural isomer of hexane, molecular formula C_6H_{14}) (Baldi *et al.* 2017) are shown in Fig. 2. The values of $\omega_L(q)$ exhibit a linear trend in the low q region with a sound velocity that matches the sound velocity measured by Brillouin light scattering. At larger q, the acoustic branch bends and presents a maximum, located in the range $6-9$ nm^{-1}. Also the transverse branch presents a maximum even if the mode is measurable only above 4 nm^{-1} and it has, at low q, a much less pronounced propagation trend with respect to the longitudinal one. We fitted the data using a sinusoidal law of the form (Kittel 2004):

$$E = \hbar\omega(q) = A\left|\sin\left(\frac{qa}{2}\right)\right|. \tag{6}$$

Here q is the exchanged wavevector and a reflects in the direct space the periodicity of the pseudo-Brillouin zone. It should be noted that this simple model describes surprisingly well the experimental data. The dispersion curves (Pilla *et al.* 2003; Benassi *et al.* 2015; Baldi *et al.* 2017) in glasses bend over and flatten for $q_0 \sim q_m/2$, where q_m corresponds to the position of the first structure factor peak, FSDP, in a similar way to what the acoustic phonon dispersion curves do when reaching the Brillouin-zone boundary in a crystal. The *lattice parameter* $a = \pi/q_0$ describes the extension of the local order.

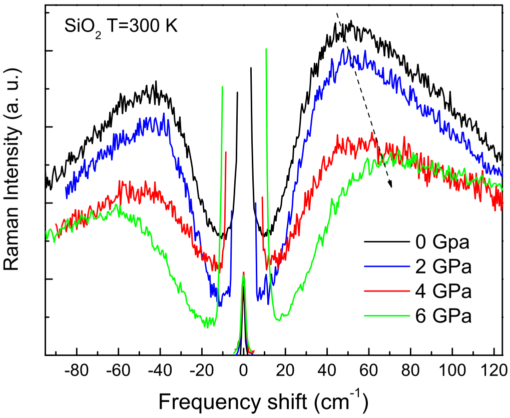

FIGURE 3. Revised data from Zanatta *et al.* (2010). Stokes and anti-Stokes reduced Raman spectra for the normal and permanently densified samples. From top spectrum to bottom one: 0 GPa correspond to a density $\rho = 2.2$ g/cm^3 (black line), 2 GPa to $\rho = 2.210$ g/cm^3 (blue line), 4 GPa to $\rho = 2.255$ g/cm^3 (red line) and 6 GPa to $\rho = 2.406$ g/cm^3 (green line). The arrow highlights the boson peak shift with increasing sample density. The intensity on the peak decreases of about a factor two from 0 GPa to 6 GPa.

The BP evolution as a function of temperature (Fontana *et al.* 1999; Caponi *et al.* 2007), pressure (Mermet *et al.* 1998; Niss *et al.* 2007; Hong *et al.* 2008; Wang *et al.* 2015), as well as thermal history (Surovtsev *et al.* 2000) and density (Orsingher *et al.* 2010b; Zanatta *et al.* 2010; Baldi *et al.* 2013) of glasses has been widely investigated. Indeed, the BP is very sensitive to the elastic properties of the system. In all samples studied so far a BP shift to higher frequencies and an intensity decrease take place with a hardening of the elastic medium and vice versa if the process makes the glass softer. The evolution of BP on some systems as silicate glasses (Baldi *et al.* 2009), or in epoxy-amine mixture (Caponi *et al.* 2009) are explained with elastic medium changes, while in other systems such as v-SiO$_2$, v-GeO$_2$, and in polymeric glasses (Niss *et al.* 2007; Hong *et al.* 2008) the shift of the BP frequency, ω_{BP}, is greater than the ω_{D} increase. As an example of density change, we report in Figs. 3 and 4 the low frequency Raman scattering measurements in the permanently densified v-SiO$_2$ and the low temperatures SH measurements in the permanently densified v-GeO$_2$ respectively. It could be argued that the changes are related to a suppression of low-frequency excess of modes with increasing density because the system becomes more compact. However, the BP intensity decrease is only apparent and is a consequence of the BP shift towards higher frequencies. It is worth to underline that we are reporting the reduced density of states and C_{p}/T^3.

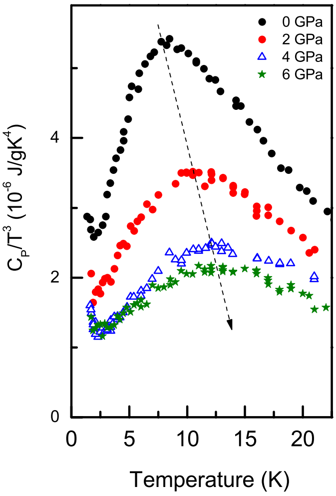

FIGURE 4. Revised data from Orsingher *et al.* (2010b). Dependence of C_p/T^3 for GeO_2 permanently densified glasses at 2, 4, and 6 GPa. 0 GPa indicates the glass prepared at atmospheric pressure. From top to bottom: $\rho = 3.66$ g/cm^3 (full black circles), $\rho = 3.99$ g/cm^3 (full red circles), $\rho = 4.21$ g/cm^3 (open blue triangles), and $\rho = 4.52$ g/cm^3 (full green stars) with a densification of $\sim 23\%$. The arrow highlights the T_M shift at increasing pressure. At the highest density, the T_M position is twice the one of the normal GeO_2 and its intensity is only $\sim 40\%$.

Several different models have been proposed to explain the origin of the BP. Without going to discuss all the models here, we mention a few of those that have been more discussed over the years. Parshin *et al.* (2007) suppose that the BP arises from the hybridization of the acoustic modes with quasi-localized excitations characteristic of the disordered structure; Buchenau *et al.* (1986) hypothesized the existence of librating molecular units; Grigera *et al.* (2003) interpreted the BP as the precursor of a dynamical instability expected in a disordered structure; Shintani and Tanaka (2008), performing numerical simulations, suggested that the BP frequency is due to the Ioffe–Regel limit for transverse excitations, above which such excitations no longer propagate. Other models include the theory suggested by Schirmacher *et al.* (2002, 2007), where the BP is associated to disorder in the force constants distribution, and the work by Taraskin *et al.* (2001), who proposed a relation between the BP and the lowest energy van Hove singularity of the corresponding crystal (Pilla *et al.* 2003). However, most of the proposed models search for an explanation of the existence of BP and generally do not give predictions about BP behaviour when thermodynamic parameters such as temperature, pressure or density of the system vary. At present, there is no theory able to predict the experimental results that have been accumulated in the literature. The aim of this paper is to present the results of the temperature dependence of the specific heat of permanently densified v-SiO$_2$ glass in comparison to that of α-quartz and a very simple model, based on the idea of Taraskin *et al.* (2001), to interpret such experimental results.

2. Experimental results and discussion

The main results of this work is shown in Fig. 5: the excess of specific heat, reported as C_p/T^3, of normal v-SiO$_2$, of permanently densified SiO$_2$ glass, and of α-quartz (Chumakov *et al.* 2014). The temperature, T_M, of the maximum of the characteristic bump shifts from $T_M \sim 10$ K in the normal v-SiO$_2$ to $T_M \sim 20$ K in the densified sample, while $T_M \sim 23$ K in the crystal. Moreover, the bump magnitude decreases and becomes equal to that of the crystal. The result is that the SH in the densified glass and in quartz not only are very similar in shape, position, and intensity but, more importantly, the SH reaches the Debye value at low temperature also for densified silica as it happens in the crystal. Consequently, the densified silica sample represents an example of a glass where there is no excess of states with respect to the Debye level. Moreover, the bump observed in C_p/T^3 is very similar in the glass and in the crystal with corresponding mass density. Similar results have been found also in v-B$_2$O$_3$ (Surovtsev *et al.* 2000). This observation answers the question posed in the introduction: the Debye model also works well in glasses. The fact that the SH in normal silica does not reach the Debye level is a consequence of at least two factors. The first is that in normal v-SiO$_2$, T_M is located at a lower temperature than that of the crystal, the second is that the SH peak is very broad. Another important element, which contributes

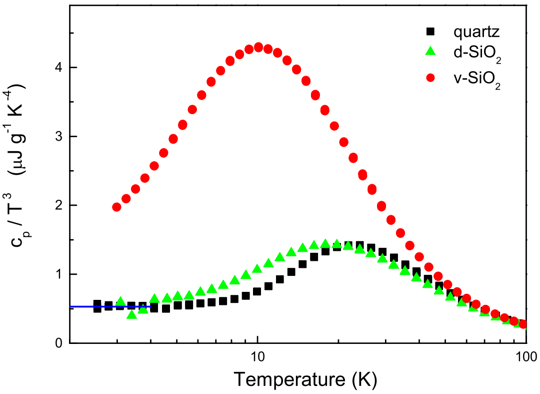

FIGURE 5. Revised data from Chumakov *et al.* (2014). Plot of the temperature behaviour of C_p/T^3 for normal (red circles), permanently densified at 8 GPa (green triangles) (Buchenau *et al.* 1986; Malinovsky *et al.* 1990; Surovtsev *et al.* 2000; Surovtsev and Sokolov 2002) silica glasses and crystalline α-quartz (black squares). The graph is reported in a semi-logarithmic scale in order to highlight the low temperature behaviour. Normal silica has a mass density $\rho = 2.2$ g/cm^3, SiO$_2$ densified at 8 GPa has a density $\rho = 2.67$ g/cm^3 very similar to that of α-quartz, $\rho = 2.65$ g/cm^3.

to this discrepancy, is the fact that at low temperatures in glasses there are relaxation modes and tunnelling between almost equivalent sites not present in crystals (Phillips 1981).

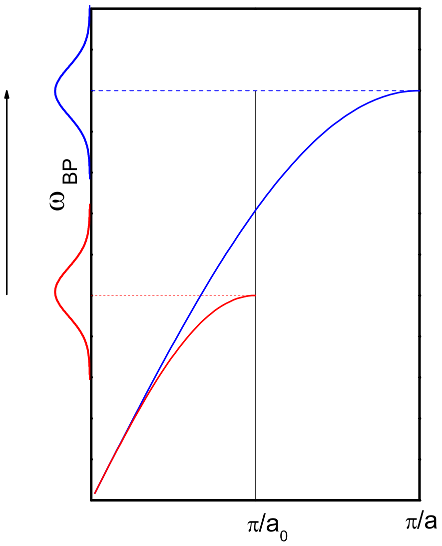

FIGURE 6. Sketch of two dispersion curves with different Brillouin zone sizes

The essence of these experimental data is that the excess of specific heat is related not to the structural disorder but to the mass density of the system. This result suggests that, since in crystals the peak is due to the transverse acoustic van Hove singularity, the SH excess in glasses as well as the BP measured by spectroscopic techniques (see Fig. 2, right panel) are also caused by the same mechanism. Let us now try to be quantitative. The pseudo-Brillouin zone is characterized by the lattice parameter $a = 2\pi/q_{\mathrm{m}}$ already mentioned. The idea is simply that, when the mass density of the system increases, a decreases and this causes a variation in the pseudo-Brillouin zone size of the glass: by decreasing a, *i.e.*, in denser samples, the pseudo-Brillouin zone size increases. Hence, the ω_{BP} increases as shown in Fig. 3 and the maximum of C_{p}/T^3 shifts to higher temperature, as shown in Figs. 4 and 5. This idea is sketched in Fig. 6. Here, we show two dispersion curves with the same sound velocity that bend defining two pseudo-Brillouin zones. These differ only for the lattice parameter a. The arrow highlights the BP shift. The vibrational dynamics of a glass can be envisioned as similar to that of a polycrystalline system with very small grains (Baldi *et al.* 2013) as already suggested by a pioneering study performed by Galeener *et al.* (1983) by coherent neutron scattering measurements. The model we propose, although phenomenological, allows us to take into account the presence of a BP and to predict the behaviour of the high q excitations varying the thermodynamic parameters such as temperature, pressure and density. It should however be mentioned that the quantitative agreement between the expected variation of the lattice parameter a and the effective variation of the BP position is not always verified and the connection between the two needs further investigation.

3. Conclusions

In conclusion, the experimental observations show that the specific heat of glasses and crystals with matched densities is essentially the same. This eliminates the rebus of the excess of specific heat in glasses with respect to the Debye expectation. In crystals, the peak in the $g(\omega)/\omega^2$ as well as in C_p/T^3 is due to the acoustic van Hove singularity. It results from a piling up of the vibrational states near the Brillouin zone edge. Hence, the striking qualitative and quantitative similarities in SH for glasses and corresponding crystals suggest that the boson peak is caused by the same mechanism.

Acknowledgments

We would like to acknowledge A. Chumakov for the many fruitful discussions and for help with the specific heat data on silica.

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Paper contributed to the international workshop entitled “Glasses and polymers: the science of disorder“, which was held in Messina, Italy (15–16 November 2018), under the patronage of the *Accademia Peloritana dei Pericolanti*

Manuscript received 4 June 2019; published online 1 October 2020