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# Non-Debye normalization of the glass vibrational density of states in mildly densified silicate glasses

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## Abstract

The evolution of the boson peak with densification at medium densification rates (up to 2.3%) in silicate glasses was followed through heat capacity measurements and low frequency Raman scattering. It is shown that the decrease of the boson peak induced by densification does not conform to that expected from a continuous medium; rather it follows a two step behaviour. The comparison of the heat capacity data with the Raman data shows that the light-vibration coupling coefficient is almost unaffected in this densification regime. These results are discussed in relation to the inhomogeneity of the glass elastic network at the nanometre scale.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The so-called ‘excess’ of vibrational density of states (e-VDOS) in comparison with the Debye predictions for crystals, is one of the most distinctive properties of supercooled liquids and glasses, quite irrespective of their detailed chemical compositions. Experimentally, the e-VDOS is directly observed in inelastic neutron scattering and indirectly observed in the low temperature specific heat of glasses; it is also well known to be at the origin of the boson peak (BP) observed in the low frequency Raman scattering spectra from vitreous materials. Long debated, the e-VDOS in glasses has not yet been given a definite origin, although a growing consensus is currently building on key ingredients: (i) the breakdown of elastic continuity at the nanometre scale [1–3] which *de*

*facto* requires taking into account the role of nanometric inhomogeneities in the vibrational scheme of glasses [4] (ii) the transverse character of the boson peak excitations [5].

In order to explore the underlying specificity of the glass VDOS in relation to its structure, one approach is to perturb the inner structure of the glass by physical treatment and probe the related VDOS changes. Heat treatments such as quenching or annealing [6–9] have proved to be relevant approaches. However, the changes of the boson peak with thermal treatments are somewhat weak in comparison with densification effects. In this latter respect, most pressure experiments have dealt with permanently densified glasses recovered to ambient pressure [10–13], essentially because the application of large pressures (of the order of the GPa) are often technically incompatible with VDOS-probing experiments;

however, several *in situ* pressure experiments, using light or neutron spectroscopies, have been reported for different types of glasses [14–18].

*Qualitatively*, the most salient effects of densification on the VDOS of glasses have long been evidenced: upon increasing density, one observes (i) a significant decrease of the e-VDOS magnitude (although it is never completely suppressed) and (ii) a high energy shift of the e-VDOS maximum. The *quantitative* analysis of these changes is rather recent [16, 13, 17]. It has been suggested [13] that the e-VDOS pressure changes should be normalized with respect to the correlated changes of the Debye parameters of the glass. While a first study supported the idea that the densification effects between 0.2% and 6% densification rates of a silicate glass are entirely accounted for by the expected elastic behaviour of a continuous medium [13], a second one, performed on a polymer glass [17] up to 20% densification contradicted this finding. Furthermore, a recent paper [18], reporting *in situ* high pressure experiments on silica, demonstrated that the behaviour of silica up to 4.7 GPa is not consistent with the continuous medium model. In an effort to clarify this situation, we present results on a multicomponent silicate glass that was permanently densified up to about 2% through a high temperature high pressure treatment [19–21, 18]. The rather low investigated densification rates (as compared to comparable studies on silicate systems [14, 12, 13]) enables us to cover the region where the evolution of the VDOS definitely does not comply with the transformation of a continuously elastic medium [13]. Through low temperature specific heat measurements we show that a Debye renormalization fails to explain the decrease of the e-VDOS upon densification. The comparison of the Raman BP with the e-VDOS reveals that the Raman probe faithfully reproduces the e-VDOS changes, although with a reduced amplitude due to the light-vibration coupling coefficient.

## 2. Experimental details

The experiments were carried out on sodium borosilicate glasses (NBS),  $16\text{Na}_2\text{O}-10\text{B}_2\text{O}_3-74\text{SiO}_2$  glasses (in mol%), the preparation of which was detailed in a previous paper [19]. The melt was equilibrated for 10 min above  $T_g$  ( $\sim 853$  K) at high temperature (between 861 and 889 K) and under hydrostatic pressure: ambient pressure 0.1 MPa (NBS1), 100 MPa (NBS-100), 200 MPa (NBS-200), 400 MPa (NBS-400) and 500 MPa (NBS-500). The samples were then cooled under pressure with an approximately constant cooling rate ( $3.6-4.6$  K  $\text{min}^{-1}$ ) down to 730 K and then at rates lower than  $3$  K  $\text{min}^{-1}$  down to room temperature. The resulting glasses at room temperature exhibit permanent densification, with densities ranging from 2.448 up to  $2.504$  g  $\text{cm}^{-3}$  (table 1).

Unlike *in situ* experiments where micro-samples are buried in bulky multi-anvil presses, the so obtained permanently densified samples are relatively large, highly transparent and free of bubbles, therefore very suitable for optical analysis.

In order to determine the acoustic sound velocities of the different samples, Brillouin light scattering (BLS)

**Table 1.** Macroscopic parameters of the investigated samples: density  $\rho$ , relative density change with respect to the non-densified sample ( $\frac{\Delta\rho}{\rho_{\text{NBS1}}}$ ), refractive index  $n$  at  $\lambda = 543.5$  nm, transverse  $v_T$  and longitudinal  $v_L$  sound velocities.

	$\rho$ (g $\text{cm}^{-3}$ )	$\frac{\Delta\rho}{\rho_{\text{NBS1}}}$ (%)	$n$	$v_T$ (m $\text{s}^{-1}$ )	$v_L$ (m $\text{s}^{-1}$ )
NBS1	2.448	0	1.5175	3607	5935
NBS100	2.458	0.4	1.5186	3651	5997
NBS200	2.464	0.7	1.5209	3671	6040
NBS400	2.488	1.6	1.5230	3720	6118
NBS500	2.504	2.3	1.5262	3788	6234

experiments were performed in a  $90^\circ$  scattering geometry with a Sandercock triple-pass tandem interferometer using the YAG:Nd $^{3+}$  532 nm line ( $P = 180$  mW). The transverse ( $v_T$ ) and longitudinal ( $v_L$ ) sound velocities were derived from the corresponding Brillouin shifts, using the refractive indices  $n$  of the samples that were experimentally determined from M-line spectroscopy with a 4 digit precision (table 1). The sound velocities were found to increase by about 5% for the most densified sample.

The e-VDOS of the investigated samples were obtained through the measurement of the specific heat at low temperatures; these were performed on a Quantum Design PPMS (physical property measurement system) between 2 and 50 K. The method is a classical heat pulse technique with a typical temperature rise of about 2%. The samples, of masses ranging from 20 to 60 mg, were glued with a minute amount of Apiezon grease N to ensure good thermal contact with the sample holder. The added contribution to the total heat capacity was, for the smallest sample, of the order of 10% at 2 K, 4% at 20 K, and 8% at 50 K with an overall precision of a few per cent.

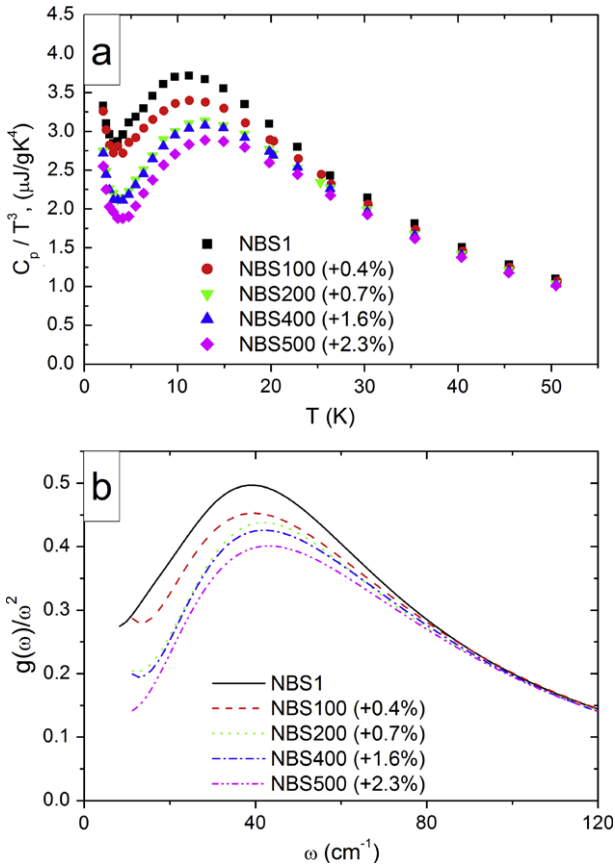
Low frequency Raman scattering spectra of the NBS samples were recorded with a high rejection rate quintuple monochromator, using the 514.5 nm line of a Ar $^+$  laser. In order to minimize the influence of the optical bands at 510 and 630  $\text{cm}^{-1}$ , only depolarized spectra are considered in the present study. All Raman spectra shown thereafter are so-called ‘reduced’ intensities  $I_R(\omega)$ ; these are derived from the direct Raman Stokes intensity [22],  $I(\omega)$ :

$$I_R(\omega) = \frac{I(\omega)}{\omega[n(\omega, T) + 1]} = \frac{C(\omega)g(\omega)}{\omega^2}, \quad (1)$$

where  $n(\omega, T)$  is the Bose factor applied at room temperature,  $g(\omega)$  is the glass VDOS and  $C(\omega)$  is the light-vibration coupling coefficient.

## 3. Results

Figure 1(a) shows the results of the low temperature heat capacity measurements performed between 2 and 50 K for the five different samples. The broad maximum observed in the  $C_p/T^3 = f(T)$  plots expresses the e-VDOS; it is a feature of glasses. According to the relationship between  $C_p$  and the VDOS,  $g(\omega)$ , the  $C_p/T^3$  plots can be converted into  $g(\omega)/\omega^2$  plots that directly express the e-VDOS. The

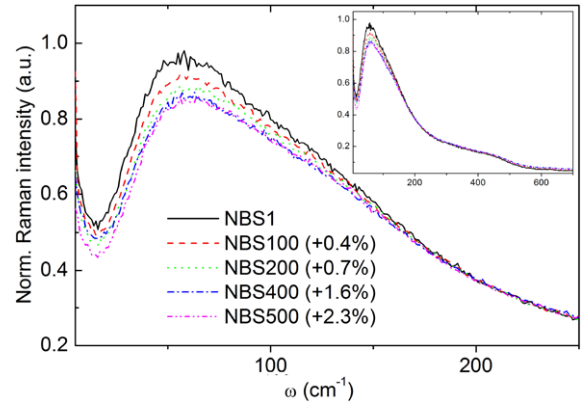


**Figure 1.** Evolution with densification of (a)  $C_p/T^3 = f(T)$  plots, (b)  $C_p$ -derived e-VDOS ( $g(\omega)/\omega^2$ ) plots. Values in brackets are  $\frac{\Delta\rho}{\rho}$ .

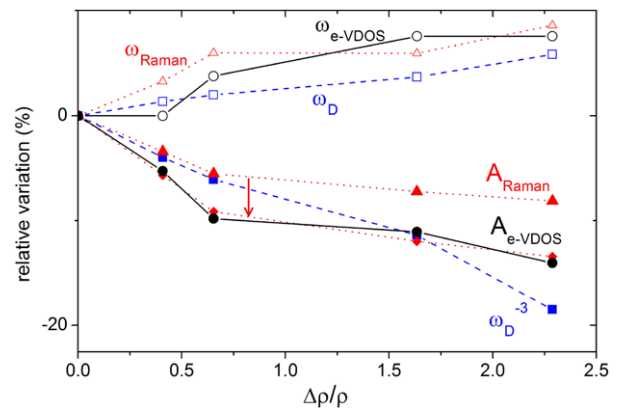
procedure used for this conversion is described elsewhere [23]; the results are displayed in figure 1(b). As already observed with many other glasses, the e-VDOS magnitude decreases while shifting to higher energies upon densification. The same qualitative behaviour is observed for the Raman BP (figure 2). While the  $C_p$  data provide absolute values of the e-VDOS, the comparison of different Raman spectra from different samples requires a normalization with respect to a reference. All spectra were normalized with respect to the region near  $200\text{ cm}^{-1}$ , in a similar fashion to that naturally obtained from the  $C_p$  measurements near 50 K. In the following, we quantitatively analyse these results.

#### 4. Analysis

In the context of continuous medium physics, comparing the vibrational properties of different solids requires prior normalization through the Debye frequency  $\omega_D$  ( $\omega_D \sim \rho^{1/3}v$ , where  $v$  is the orientationally averaged sound velocity). Figure 3 compares, on one hand, the relative variations of both e-VDOS and Raman BP maximum frequencies with those of the Debye frequency and, on the other hand, the relative variations of both the e-VDOS and Raman BP integrated intensities (from 15 to  $200\text{ cm}^{-1}$ ) with those of the inverse cube of the Debye frequency.



**Figure 2.** Evolution with densification of the depolarized Raman BP. The inset shows the same spectra over a broader spectral range.

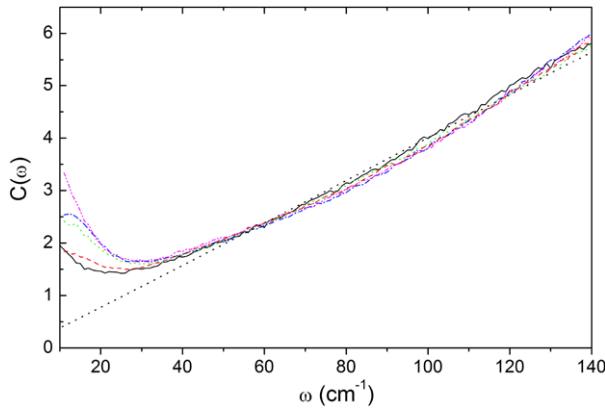


**Figure 3.** Comparison of the densification induced relative variations of the e-VDOS maximum frequency (O) and of the Raman BP position ( $\Delta$ ) with the Debye frequency  $\omega_D$  ( $\square$ ); and of the e-VDOS ( $\bullet$ ) and Raman BP ( $\blacktriangle$ ) integrated intensities with  $\omega_D^{-3}$  ( $\blacksquare$ ). The lozenge symbol curve is the Raman one multiplied by 1.65.

Comparing the frequency positions of the e-VDOS and of the Raman BP, one observes that the high frequency shifts induced by densification are slightly stronger than those of the Debye frequency (or those of the BLS sound velocities since the contribution of the density relative variations are negligible).

If one now compares the evolution of the e-VDOS integrated intensity with that of the Raman BP, one finds that the amplitude of the variations are smaller in the Raman case, yet they homothetically scale with the e-VDOS (using a multiplying factor of 1.65, figure 3). This shows that in spite of the Raman coupling coefficient, the light probe faithfully reproduces the e-VDOS variations, although with a lower amplitude. Both probes show that the first two densification stages account for about 70% of the observed changes. This two step behaviour hardly complies with the behaviour of the Debye level ( $\omega_D^3$ ), which predicts a monotonic decrease with increasing densification.

From the ratio between the reduced Raman intensities  $I_R(\omega)$  and the e-VDOS  $g(\omega)/\omega^2$  (equation (1)), one can investigate the evolution of the frequency dependence of the Raman coupling coefficient with densification. The results



**Figure 4.** Light-vibration coupling coefficient  $C(\omega)$  for the different samples (same legends as figure 1). The dotted black line is a linear fit with equation  $0.037\omega^{1.019}$ .

displayed in figure 4 show that: (i) the frequency variation observed for  $C(\omega)$  is close to linear, as observed for many glasses [24]; (ii) below  $30 \text{ cm}^{-1}$ , its spectral dependence is strongly influenced by the quasielastic contribution; this comes from the fact that the e-VDOS was obtained from low temperature measurements where the contribution from anharmonic motions is negligible, whereas Raman data were recorded at room temperature, where scattering from anharmonic motions is no longer negligible. Far from the quasielastic region (i.e.  $60\text{--}200 \text{ cm}^{-1}$ ) where scattering by harmonic vibrations prevails, one observes that only the non-densified sample significantly (though slightly) differs from all the other densified samples: the light coupling strength decreases with densification, as previously observed with pure densified silica [25]. Below about  $30 \text{ cm}^{-1}$ , the coupling coefficient strongly *increases* with densification leading to significant deviations from the linear behaviour. Rather than an increase of the coupling coefficient for anharmonic motions, this behaviour is due to the strong decrease of the harmonic contribution in this spectral range with increasing densification. In fact, this observation shows that the effect of mild densification is most important on the lowest frequency part of the vibrational spectrum.

## 5. Discussion

The investigation of the NBS samples densified at medium densification rates (compared to GPa densifications) shows that at nanometric lengthscales, which are relevant to the e-VDOS, the glass does not behave as a continuously elastic medium, at least upon densification. This is proved by the differing behaviours of both the e-VDOS and the Raman boson peak magnitudes with respect to the Debye level. In other words, the Debye frequency dependence of the glass VDOS cannot be described by a simple expression such as  $g(\omega) = G(\omega)/\omega_D^3$ , where  $G(\omega)$  would be a phenomenological frequency dependence inherent to glasses, analogous to (yet different from) the  $\omega^2$ -behaviour for crystals.

As mentioned in section 1, the role of nanometric elastic heterogeneities is increasingly being considered as

an important factor in the anomalous (i.e. non-crystal-like) behaviour of the low frequency vibrational pattern of glasses. Among recent [4] developments of an early proposed model based on such conception of the glass elastic network [26], the e-VDOS (or the Raman BP) is due to the hybridization between extended acoustic modes with optical-like eigenmodes of cohesive elastic nanodomains (note that the considered nanodomains need not be considered crystalline, they are expected to be ill-defined and interpenetrating within a less cohesive, elastically weaker, matrix). According to this scheme, the BP frequency is given by the lowest frequency (and predominantly transverse) eigenmode of the nanodomains:

$$\omega_{\text{BP}} \approx \frac{v_T}{\langle D \rangle c}, \quad (2)$$

where  $\langle D \rangle$  is the average nanodomain size ( $\sim 1 \text{ nm}$  in silicate systems, in agreement with simulation works) and  $c$  is the speed of light (for wavenumber units). The early bending of the phonon dispersion curve  $\omega(Q)$  ( $Q$  phonon momentum) generated by such hybridization induces a mode pile-up close the BP frequency, as attested by the e-VDOS. Clearly, the hybridization scenario is not compatible with the classical Debye treatment, which is valid for crystals where elastic continuity holds down to the atomic scale.

In the hybridization scheme, applying a hydrostatic pressure to the glass primarily acts on the softest interface regions between nanodomains, thus lowering the elastic contrast, which in fact is the very origin of the boson peak; in other words the elastic network of the glass becomes more homogeneous upon densification. This results in a weaker hybridization which manifests as a decrease of the e-VDOS magnitude with densification. Moreover, it is very likely that densification induces a slight reduction of the average nanodomain size [27], so that according to equation (2) the high frequency shift of the boson peak with densification has two origins:

$$\frac{\Delta\omega_{\text{BP}}}{\omega_{\text{BP}}} = \frac{\Delta v_T}{v_T} - \frac{\Delta\langle D \rangle}{\langle D \rangle}. \quad (3)$$

This may explain the fact that the experimentally observed shift of the BP frequency is systematically slightly larger than that of the sound velocities [17] (or that of the Debye frequency).

## 6. Conclusion

The excess VDOS, or boson peak, of multicomponent silicate glasses densified at medium densification rates was studied through the low temperature heat capacity and low frequency Raman scattering. It was observed that the e-VDOS hardly follows a monotonic decrease with densification, as is expected for the Debye level; it rather shows a two step behaviour: over a  $0\text{--}2.3\%$  densification range, densification up to  $0.7\%$  accounts for about  $70\%$  of the e-VDOS decrease. Following up this evolution through Raman scattering proves to reproduce the changes observed from the e-VDOS, though with an amplitude reduced by about  $40\%$ . In comparison with the e-VDOS magnitude, the changes of the light coupling coefficient in the harmonic regime are small.



The non-Debye normalization of the boson peak changes with densification appears as further confirmation of the elastic nano-heterogeneity of the glass. According to the hybridization scenario between localized eigen-like modes of cohesive nanodomains and propagating acoustic modes, the decrease of the e-VDOS with densification is a sign of a progressive dehybridization due to a more homogeneous elastic network. Although the inhomogeneity of the glass is not suppressed even at high densification rates, the improved compactness induced by densification should improve the agreement with Debye macroscopic parameters, as already observed [13]. To check this, NBS samples with densification rates larger than 2.3% will be studied in the near future.

## Acknowledgment

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