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Acoustic properties of a porous glass (vycor) at hypersonic frequencies

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Abstract

Brillouin scattering experiments have been performed from 5 to 1600 K in vycor, a porous silica glass. The acoustic velocity and attenuation at hypersonic frequencies are compared to those of bulk silica and others porous silica samples. The experimental evidence for the influence of porosity on the scattering by acoustic waves is compared to calculations. The correlation between internal friction and thermal conductivity at low temperature is discussed.

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

1. Introduction

Vycor is a commercial porous glass¹ synthesized for industrial applications such as chemical separation and catalysis. It is also interesting from a physical point of view: due to its open porosity it is used as a matrix for testing the physical properties of liquids or phase transitions in confined geometries, especially for helium (Shapiro and Rudnick 1965, Fraser and Rudnick 1968, Clow and Reppy 1972, Kiewiet *et al* 1975, Adams *et al* 1984, Li *et al* 1991, Dimeo *et al* 1998). This material has been also used as a model for understanding thermal properties by comparison of bulk and porous glass (Tait 1975, Zaitlin and Anderson 1975, Hsieh *et al* 1981, Grace and Anderson 1986, Pohl *et al* 2002).

Questions about the interpretation of the plateau observed in the thermal conductivity at low temperature in glasses, not observed in crystals, have remained a motivation for many contributions over the last 30 years. This experimental behaviour is generally explained by excitations responsible for heat transport—those excitations being acoustic at low temperature—and their interactions with the disorder.

Two processes are often considered as limiting the phonon mean free path at low temperature. The first one is the interaction with tunnelling systems (TS), which yields a specific behaviour (Phillips 1972, Hunklinger and Arnold 1976, Pohl *et al* 2002). The parameters used to describe this interaction can be determined from acoustic properties (from the

¹ Vycor Brand Porous Thirsty glass N° 7930, Corning Glass Works, PO Box 5000, Corning, NY 14830.

slope of the temperature-dependent sound velocity $V(T)$, or from the plateau amplitude of the internal friction parameter Q^{-1}) and from thermal properties, from the power law for thermal conductivity $\kappa(T)$. A universal behaviour is observed for this contribution. The second process is usually and historically related to the hypothesis of phonon localization introduced in order to fit experimental data for the thermal conductivity $\kappa(T)$ in the temperature range of the plateau at a few K. More recently, fluctuations of the transverse elastic constants has also been invoked as the origin of the strong elastic scattering in the frequency regime of the boson peak (Shirmacher 2006). In this model, the plateau is essentially a harmonic behaviour, in agreement with simulations (Jund and Jullien 1999, Allen and Feldman 1993). The process at the origin of the hypothetical localization of acoustic waves is much debated (Foret *et al* 1996, Rufflé *et al* 2003, Benassi *et al* 1996, 2005). A scattering process, proportional to ω^4 (or q^4 , where q is the modulus of the scattering vector), was invoked long time ago (Zeller and Pohl 1971). A Rayleigh-like scattering mechanism was proposed as the origin of this process, but the determination of the amplitude of this process gave rise to contradictory results and interpretations. On the one hand, it was associated with local density fluctuations or dielectric constant or force constant fluctuations, but the spatial extension of the correlations associated with those physical properties is very difficult to estimate and has a huge impact on the amplitude of the scattering process. On the other hand, the direct evidence of an ω^4 or q^4 law for the contribution to the phonon mean free path was not possible using experimental techniques available a few years ago, because the frequencies involved are in the 100 GHz–1 THz range. Inelastic x-ray scattering provides data in the scattering vector or frequency range of interest but is limited to the THz range. More recently, the new inelastic UV scattering technique allows one to measure acoustic attenuation in the 100 GHz range (Masciovecchio *et al* 2006). New ‘coloured’ picosecond ultrasonic techniques are also available in the 100–250 GHz range (Emery and Devos 2007, 2006). All these new recent experimental data contribute to testing the different models explaining the thermal conductivity plateau. As the interpretation of old and new results is controversial (Foret *et al* 1996, Rufflé *et al* 2003, Benassi *et al* 1996, 2005, Masciovecchio *et al* 2006), this domain is an active field. Our contribution concerns the study of acoustic and thermal properties in porous materials (particularly in porous silica). It is worthwhile because it allows us to correlate structural modifications introduced by the porosity to previous models in non-porous amorphous solids. On the one hand, Q^{-1} measured at ultrasonic frequencies is hardly affected by changes of the porosity (de Goer *et al* 1989, Watson and Pohl 2003). One can infer that tunnelling systems (Watson and Pohl 2003) are only weakly modified by the porosity. On the other hand, the amplitude and temperature range of the plateau for the thermal conductivity are modified: the amplitude decreases and the plateau is shifted towards lower temperature when the porosity increases (Watson and Pohl 2003, de Goer *et al* 1989). There are two possible interpretations for those data, according to the porosity domain. For the most porous materials, fractality or hierarchical character of the structure is put forward to explain the localization of phonons when the wavelength becomes close to the size of the fractal aggregates. This is the case for phonons involved in Brillouin scattering in the more porous aerogels (Courten *et al* 1987). For the less porous ones (for example when the density is greater than 0.5 for silica aerogel), where the fractality of the structure is not noticeable, a good description of experimental results for thermal conductivity can be obtained with a mean free path of phonons including contributions from TSs in the bulk as well as a Rayleigh-like contribution by pores. The latter contribution can be calculated assuming different shapes for the pores (Grace and Anderson 1986), and the pore sizes obtained using these models can be compared to structural data.

The fact that low-temperature acoustic properties and ultrasonic properties are weakly sensitive to porosity is in agreement with thermal conductivity results—which are very sensitive

to porosity—due to the fact that phonons associated with ultrasonic frequencies are ‘dominant’ at very low temperatures, much below the plateau. Typically, ultrasounds at 10 MHz are efficient at $T = 0.1$ mK.² This is very different for acoustic phonons involved in Brillouin visible light scattering whose frequencies (typically 10–40 GHz) are efficient in thermal conductivity for a few fractions of kelvin, which is precisely the temperature range where the plateau appears in porous materials. To be useful, Brillouin scattering data for the phonon mean free path should be available at low temperature because of contributions due to other processes such as thermally activated relaxational processes or anharmonicity at higher temperatures (Pelous and Levelut 2006). The interest in Brillouin scattering measurements in porous materials is three-fold: first, these measurements allow us to test models for wave scattering, secondly they allow us to understand the origin of processes responsible for sound damping, and finally they allow us to connect these data to thermal conductivity data (Grace and Anderson 1986).

Some Brillouin scattering data as a function of temperature can be found in the literature for porous media, but the relation with thermal properties is lacking, and a quantitative analysis of phonon scattering by pores has not yet been performed.

In this contribution, we present Brillouin scattering experiments in a large temperature interval ranging from a few kelvin up to the glass transition temperature of silica glass. As the typical pore size in vycor is about 4 nm and, in the frequency range investigated by Brillouin scattering experiments, the acoustic wavelength is near 200 nm, so Rayleigh sound scattering is expected to be strongly enhanced for this material compared to the bulk—non-porous—silica.

The influence of the high efficiency of the wave scattering in porous media on the acoustical properties is indeed demonstrated and the determination of the acoustic scattering by the porosity will be quantified. The influence of porosity for acoustic properties has been studied previously in xerogels or aerogels (Courtens *et al* 1987, Anglaret *et al* 1995, Terki *et al* 1998), and we will compare the data in vycor with these previous investigations. Modelization of the Rayleigh scattering and comparison with the characteristic sizes associated with Rayleigh scattering and with structural data for pore sizes will be discussed. Finally, this direct measurement of the mean free path of phonons allows us to compare this determination with those previously deduced from fits of the thermal conductivity data in the same material.

2. Experimental details

Vycor porous glass, commercially available and produced by Corning (code 7930), is used for its excellent absorbing properties and for filtration or separation of compounds as in chromatography³. It is prepared from a quaternary glass mixture (SiO_2 , B_2O_3 , Al_2O_3 and Na_2O) undergoing a phase separation process; the alkali borate phase is removed and a network of nearly pure silica remains; the final glass contains 96% silica (3% B_2O_3 remains). Vycor has a porosity of 28% with a narrow pore size distribution, a density of 1.5 and an internal surface area of 200–250 $\text{m}^2 \text{g}^{-1}$; the average internal pore diameter is typically around 4 nm but different mean size pores are available. Its structure has been extensively studied, and it keeps giving rise to controversial interpretations about the fractal character of the internal surfaces (Beamish *et al* 1984, Even *et al* 1984, Wiltzius *et al* 1987, Levitz and Drake 1987, Schaefer *et al* 1987, Höhr *et al* 1988, Benham *et al* 1989, Mitropoulos *et al* 1995, 1997, Agamalian *et al* 1997) or the presence of porosity at the micrometre scale (Kim and Glinka 2006). It is

² The correspondence between frequency and temperature can be found by introducing ‘dominant’ phonons, defined by $h\nu \propto kT$ with a proportionality factor close to 4.25 (Pohl *et al* 2002, Klitsner and Pohl 1987).

³ Vycor Brand Porous Thirsty glass N° 7930, Corning Glass Works, PO Box 5000, Corning, NY 14830.

now accepted that the presence of absorbing compounds smooths the surfaces and destroys the fractality (Kim and Glinka 2006).

Brillouin scattering experiments were performed in the backscattering configuration with a laser line excitation at 514.5 nm. The spectrometer has been previously described in detail (Vacher *et al* 1980, 1981, 2005). The high resolution of this set-up allows access to a precise determination of the acoustic properties at hypersonic frequencies, in particular the acoustic attenuation in the hypersonic regime. The shift position is obtained with a relative uncertainty of 5×10^{-4} , and the Brillouin linewidth with a 5–10% uncertainty. The Brillouin shift $\delta\nu_B$ is related to the longitudinal sound velocity V_1 by

$$\delta\nu_B = \frac{2nV_1}{\lambda} \sin(\theta/2), \quad (1)$$

where n is the refractive index, λ the wavelength of the incident light, and θ the scattering angle inside the sample. The frequency shifts probed are typically in the 20–40 GHz range in solids. The elastic constant M can be calculated from the sound velocity V_1 using $M = \rho \times V_1^2$, where ρ is the sample density. The acoustic longitudinal attenuation α can be deduced from the Brillouin full linewidth Γ using the formula

$$\alpha = \frac{2\pi\Gamma}{V_1}. \quad (2)$$

In the formalism of phonons, the acoustic attenuation corresponds to the inverse mean free path of phonons, $\ell^{-1} = \alpha$. A dimensionless quantity, the internal friction, Q^{-1} , defined as the ratio between the full linewidth and the frequency shift, is convenient for comparison of acoustic loss at various frequencies:

$$Q^{-1} = \frac{\Gamma}{\delta\nu_B}. \quad (3)$$

In order to deduce the velocity and the attenuation from Brillouin shift and linewidth data respectively, the refractive index values are needed; unfortunately these data versus temperature are not available for vycor. Nevertheless, it can be noted that the internal friction can be deduced without information on the refractive index.

3. Results

Brillouin shift versus temperature is reported in figure 1. The general trends looks similar to those observed in bulk silica glass. A minimum is observed but at higher temperature than in silica, as well as a positive slope for temperatures higher than room temperature; this is a characteristic of tetrahedrally coordinated glasses (Krause and Kurkjian 1968, Kul'bitskaya *et al* 1975). The positive slope of $V_1(T)$ for temperatures higher than room temperature appears higher in vycor than in bulk silica; this probably means that structural modifications and densification start at temperatures as low as 600 K. At high temperature, densification induces an increase of the Brillouin shift towards the value of silica glass (figure 2). The temperature at which the densification occurs coincides with the temperature at which a microscopic transformation under heat treatment is observed in xerogels by Raman scattering (Caponi *et al* 2002).

The minimum observed near room temperature for the shift is correlated with a peak for acoustic attenuation observed from the Brillouin linewidth data shown in figure 3. The Brillouin shift and linewidth near room temperature appear to be different for two different sets of experiments. The differences are probably due to impurities absorbed on the internal surface of this porous sample and not completely removed by the cleaning procedure applied before any

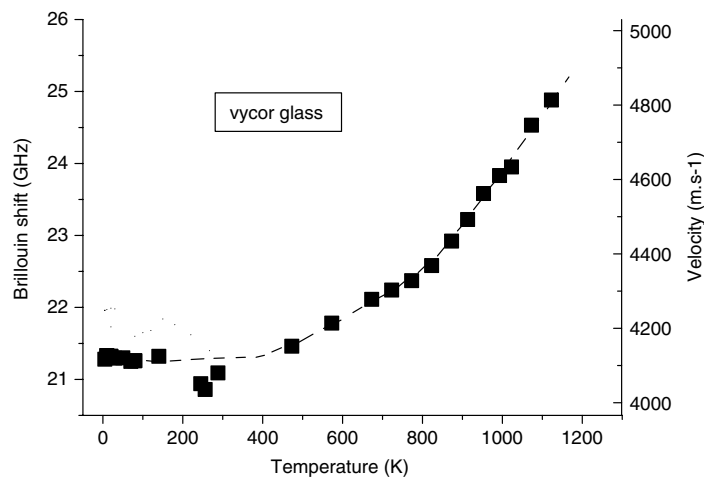


Figure 1. Brillouin shift (left axis) as well as longitudinal sound velocity (right axis) versus temperature in vycor glass.

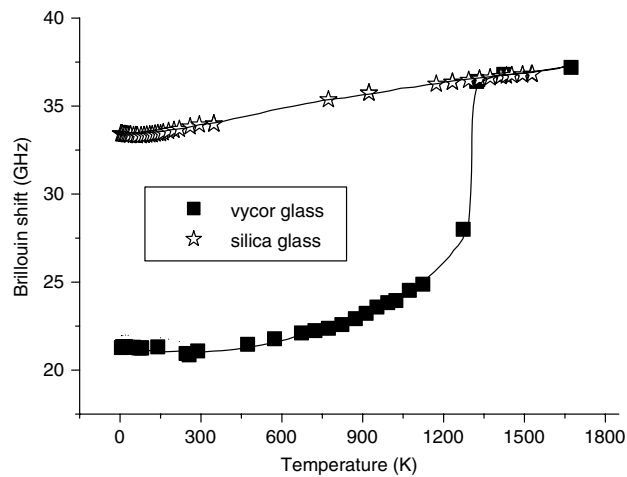


Figure 2. Comparison of Brillouin shift versus temperature in vycor and silica glass. The solid lines are to guide the eye.

experiment⁴. In order to examine this influence, various experiments were performed, and low reproducibility has been observed for measurements in the room-temperature range (figure 4); in contrast, a superimposition of the data for two different sets of experiments is observed at low temperature. Brillouin data at high temperature were also observed to be weakly sensitive to the presence of impurities (cleaning procedure) showing that the absorbed compounds are probably removed when the temperature increases.

Structural variations at high temperature also induce variations of refractive index. Those variations, $n(T)$, are usually smaller than the variation of the elastic constants. The sound velocity calculated using $n(T)$ constant is shown in figure 1. The sound velocity is lower than

⁴ Chemical as well as thermal procedures are possible. We used progressive heating (heating rate $<1\text{ }^{\circ}\text{C min}^{-1}$) up to a temperature of a few hundred $^{\circ}\text{C}$, sufficient to remove contamination by oxidation.

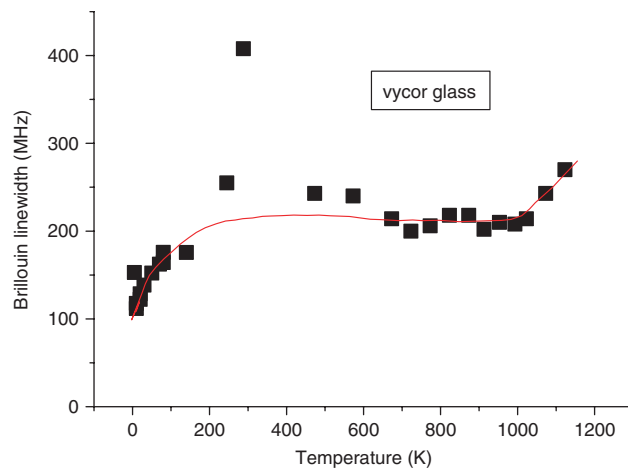


Figure 3. Brillouin linewidth versus temperature in vycor. The solid line is plotted to show the enhancement of the Brillouin linewidth near room temperature and to display the contribution not due to impurities.

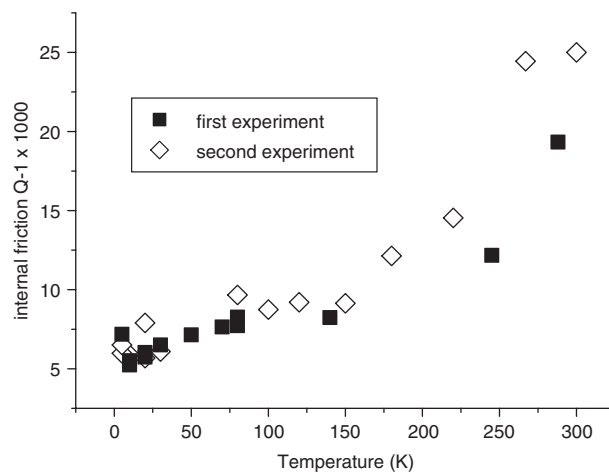


Figure 4. Comparison of the internal friction obtained by cooling the samples in two sets of experiments.

that of bulk silica glass as expected, due to porosity and lower density. It can be pointed out that, at room temperature, the ratio of sound velocities $V(\text{vycor})/V(\text{silica}) = 0.68$ is close to the ratio of the densities (0.72). Moreover, our values are significantly (12%) higher than previously published data of ultrasonic velocity (Grace and Anderson 1986, Pohl *et al* 2002). It has been checked that ultrasonic and hypersonic velocities are very close at these temperatures in sol-gel silica (Grace and Anderson 1986), so no dispersion is expected for vycor. This difference is higher than could be expected from pollution effects (about 1% on the sound velocity) and can be ascribed to a slightly different porous vycor samples.

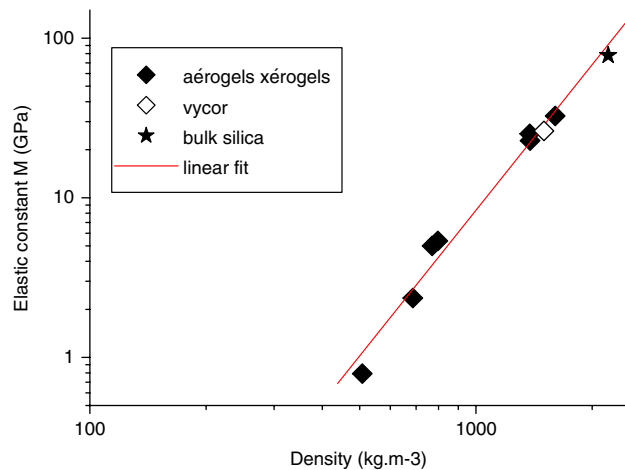


Figure 5. Comparison of the elastic constants versus density in bulk silica glass, xerogels, aerogels (from Terki *et al* 1998, Caponi *et al* 2004)) and vycor. The linear slope is 3 ± 0.1 and correspond to a power law.

4. Discussion

4.1. Comparison of acoustic properties of vycor and other porous silica glasses with bulk silica glass.

4.1.1. Elastic constant. The influence of the porosity on the elastic properties at hypersonic frequencies of silica glass has been previously studied (Courten *et al* 1987, Anglaret *et al* 1995, Terki *et al* 1998) for xerogels and aerogels. These materials are elaborated by the sol-gel process followed by densification; the most porous samples have been studied for their fractal properties (Courten *et al* 1987). To compare the data obtained for vycor and these porous materials we have plotted in a log-log scale the elastic constant versus density at room temperature in figure 5. Within the accuracy of the experiments, the data for vycor coincide with the xerogel data of the same density. This result was not expected *a priori*. Comparison of the structure of xerogels and aerogels, as well as the structural, textural changes and changes in elastic properties during densification of these highly porous materials, have been previously studied by small-angle x-ray scattering, small-angle neutron scattering or thermoporometry (Foret *et al* 1992, Anglaret *et al* 1995, Terki *et al* 1998, Dieudonné *et al* 1998, Calas and Semperé 1998, Calas *et al* 1998). Significant differences in the texture have been observed depending on the chemical parameters in the sol-gel process or the thermal conditions of densification. Our results demonstrate that the elastic properties do not depend on the elaboration process of the material and thus on the details of the shape and distribution of pores. The linear fit in figure 5 corresponds to a power law; M is proportional to the density to the power 3 ± 0.1 , which is equivalent to a sound velocity proportional to the density, as mentioned for vycor in section 3.

4.1.2. Internal friction. In figure 6, data for internal friction in vycor are calculated and compared with previous data in bulk silica (Vacher and Pelous 1976, Levelut *et al* 2006). As pointed out before, the prominent peak observed in vycor near room temperature can be explained by an additional contribution to the acoustic attenuation by moisture or impurities absorbed at the internal surfaces of the porous sample. It has also been pointed out previously

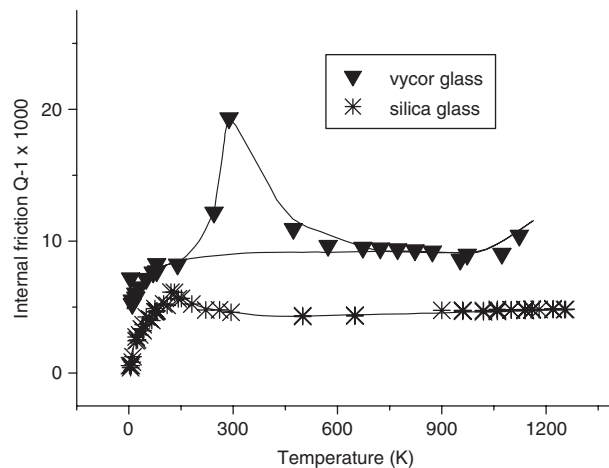


Figure 6. Comparison of the internal friction versus temperature in vycor and silica glass. The solid lines are guides to the eye.

in aerogels that the presence of organic radicals at the surface induces thermally activated relaxations which can be removed by heat treatment (Anglaret *et al* 1995). Coupling of acoustic waves with thermally activated defects as in bulk silica has been postulated to explain such a behaviour.

The internal friction of bulk silica presents a plateau at low temperature and low frequencies up to the ultrasonic range (Jäckle 1972, Hunklinger and Arnold 1976, Pohl *et al* 2002). This plateau can be described by the interaction of mechanical waves (or phonons) with tunnelling systems (Anderson *et al* 1972, Phillips 1972), characteristic for the disorder. The amplitude of the plateau is theoretically equal to $Q^{-1} = \pi C/2$, where $C_i = \frac{\bar{P}\gamma_i^2}{\rho V_i}$, \bar{P} is the spectral density of the tunnelling states, γ_i a coupling constant coefficient, and V_i the sound velocity, where the subscript i stands for longitudinal or transverse waves. C is usually defined and calculated for numerous glasses and disordered materials. It can be inferred from this comparison that determinations using thermal properties are in reasonable agreement with determinations from acoustic properties. Moreover, the C values are very similar for all samples, showing a universal behaviour of this property, beyond the amorphous nature of materials. With increasing frequency, the plateau shifts at higher temperature; its amplitude is frequency independent at low frequencies. However, a slight increase of the amplitude, not expected by the theory, is observed when the frequencies are in the ultrasonic range. Simultaneously, the temperature extension of the plateau decreases. At hypersonic frequencies no plateau is observed at low temperature in silica glass; this is again confirmed in the porous silica glass but the value at 5 K is identical in the MHz and in the GHz range⁵. In contrast, another plateau observed in bulk silica at high temperature is also observed in the vycor glass up to temperatures where structural rearrangements transform the porous sample in bulk glass (figure 2). Anharmonic interactions of acoustic phonons with the bath of phonons have been proposed as an explanation for this high-temperature part (Vacher *et al* 1981, 2005, Levelut *et al* 2006) in bulk glasses.

The main feature of the comparison is that the internal friction of vycor is larger than that of the bulk sample, and the enhancement is nearly constant in the large range of temperature

⁵ For bulk silica at 5 K, Q^{-1} measured by Brillouin scattering is identical to that measured using ultrasounds (Vacher *et al* 2005).

investigated. Such an additional temperature-independent contribution can be interpreted as a geometrical effect due to scattering of acoustic waves by the inhomogeneous structure. This contribution has nearly the same amplitude as dynamical contributions responsible for internal friction in bulk silica at room temperature. This result is, to our knowledge, the first in which the existence of a geometrical contribution of the acoustic attenuation at hypersonic frequencies can be simultaneously observed and clearly separated from other dynamical contributions. This result confirms and extends the existence of a geometrical contribution of the acoustic attenuation at hypersonic frequencies observed in other more porous silica glass (Courtens *et al* 1987, Anglaret *et al* 1995, Caponi *et al* 2004). Moreover, in the case of vycor, the existence of rather monodisperse well-defined pores makes it possible to quantify the contribution of Rayleigh sound scattering. As structural information is available for vycor and other porous silica (aerogels or xerogels), we will compare our results to calculations on vycor and in more porous samples in section 4.2.

Before that, it is interesting to compare values of internal friction obtained at hypersonic frequencies in vycor to that, taken from the literature, obtained for amorphous silica and other porous silica-based glasses (xerogels and aerogels) for densities higher than 500 kg m^{-3} . For such high densities, the bulk structure is not fractal, so no specific formalism is needed. (Courtens *et al* 1987). *A priori* for vycor, the fractal character (largely discussed in the literature) appears in the surface at such a scale for the modulus of the scattering vector, q , that no interaction with acoustic waves occurs. For more porous materials, the geometric contribution is expected to dominate at all temperatures, but for less porous ones, if the comparison is taken at 300 K, dynamical contributions (mostly thermally activated relaxational contributions or anharmonic contributions) also take place and can blur out the geometric scattering due to the porosity. At 5 K, whatever the porosity, only the two level systems' contribution and the geometric scattering contribution—which is essentially independent of the temperature—can subsist.

Table 1 compiles data from the literature (together with data of the present paper) about the internal friction measured in porous silica at ultrasonic and hypersonic frequencies. From those data, it is observed that the more porous (but non-fractal) silica, the aerogel with density 690 kg m^{-3} and the xerogel with density 510 kg m^{-3} display Brillouin linewidth, and thus internal friction, similar at 300 and 5 K, in contrast to what is observed for vycor and *a fortiori* for non-porous silica. Moreover, the values of internal friction are about one order of magnitude larger in more porous materials. In order to identify the physical origin of those differences, it is useful to compare data at different frequencies.

The comparison of values of data for internal friction at low temperature in silica glass or vycor and other porous materials at hypersonic frequencies to data obtained at lower (ultrasonic) frequencies has been partly discussed in the literature (Tielbürger *et al* 1992, Pohl *et al* 2002). On the one hand, at ultrasonic frequencies, the internal friction is weakly dependent on the porosity (de Goer *et al* 1989, Watson and Pohl 2003); the values vary by less than a factor of two, even for most porous materials. On the other hand, for vycor, the internal friction measured by ultrasonic measurements is much lower than the value measured by Brillouin scattering, by a factor of 5 to 10. Also for aerogels (non-fractal), Q^{-1} measured by Brillouin scattering is 50 to 100 times higher than the low-frequency Q^{-1} . The efficiency of geometric scattering shows up when the size of the homogeneities is no longer negligible compared to the wavelength of sound waves.

In order to calculate the geometric scattering contribution to Q^{-1} , we took into account the fact that the contribution due to TS is independent of the porosity (as shown by ultrasonic

Table 1. Data taken from the literature and from our results for porous silica: density, Brillouin frequency shift, Brillouin linewidth and Brillouin internal friction, comparison with ultrasonic internal friction and estimate of the part ascribed to Rayleigh scattering. The errors in the measured Brillouin shift and Brillouin linewidth are 0.1% and 10%, respectively. An additional error of 0.5 for the determination of Rayleigh part $1000 \times Q^{-1}$ has been taken into account due to imprecision of the determination of the TS contribution.

	Density	T (K)	$\delta\nu$ (GHz)	Γ (MHz)	Q^{-1} (Brillouin) $\times 1000$	Q^{-1} (US) $\times 1000$	Rayleigh part in $1000Q^{-1}$ Brillouin
Aerogel ^a	0.690	300	8.0 ± 0.008	500 ± 50	62.0 ± 6.2		
		5	8.0 ± 0.008	500 ± 50	62.0 ± 6.2	0.5 ^a	61.0 ± 6.7
Aerogel ^b	0.760	300	8.0 ± 0.008	480 ± 48	60.0 ± 6.0		
		5 ^f				1.0 ^g	54.3 ± 6.0
Xerogel ^a	0.510	300	5.2 ± 0.0052	300 ± 30	60.0 ± 6.0		
		5	5.2 ± 0.0052	300 ± 30	60.0 ± 6.0		59 ± 6.5
Xerogel ^c	0.900	300	9.3 ± 0.0093	200 ± 20	18.0 ± 2.4		
		5 ^f					12.3 ± 0.6
Xerogel ^b	1.380	300	21.4 ± 0.0214	152 ± 15.2	7.5 ± 0.75		
		5 ^f					1.8 ± 0.7
Vycor	1.500	300	21.2 ± 0.0212	200 ± 20	9.5 ± 0.95		
		5	21.2 ± 0.0212	100 ± 10	4.8 ± 0.48	1.0 ^g	3.8 ± 1.0
Silica ^d	2.200	300	34.0 ± 0.034	150 ± 15	4.4 ± 0.44		
		5	34.0 ± 0.034	14 ± 1.4	0.4 ± 0.04	0.5 ^h	

^aCaponi *et al* (2004).

^bCaponi *et al* (2003).

^c Unpublished work.

^dVacher *et al* (1980, 1981, 2005).

^e Density $\rho = 880$, frequency = 1 kHz, from reference 68 of (Watson and Pohl 2003).

^f Estimated value.

^g Frequency 88 kHz (Watson and Pohl 2003).

^h Frequency 66 kHz, references 57 and 64 from Watson and Pohl (2003).

measurements; see table 1) and is lower than 1×10^{-3} for Q^{-1} .⁶ Temperature-dependent dynamical contributions, that are responsible for differences between high and low (5 K) temperatures values of Q^{-1} in vycor and in silica are also assumed to depend weakly on the porosity because they are related to the silica-based matrix structure. Moreover, one can note that for the most porous silica, no difference is observed between values at 5 and 300 K within the uncertainty for the Brillouin scattering linewidth. The Rayleigh part of internal friction has been estimated using two different methods, depending on the temperature range of the available internal friction data. For samples in which low-temperature measurements have been done, i.e. bulk silica, vycor, xerogel with density 510 kg m^{-3} and aerogel with density 690 kg m^{-3} , the Rayleigh contribution has been estimated by subtracting the TLS contribution from the experimental determination at 5 K. A value of 1×10^{-3} has been taken for the TLS contribution in all samples, as the experimental (ultrasound) determinations depend only weakly on the porosity. For samples where only measurements at room temperature exist in the literature (aerogel with density 0.760, xerogels with density 0.900 and 1.380), a dynamical contribution has first to be estimated. This dynamical part is deduced from the level of the high-temperature plateau (above room temperature) for the internal friction, also weakly dependent on the porosity and method of preparation of the sample (Levelut *et al* 2006), from which the low-temperature value at 5 K is subtracted. The dynamical contribution can be estimated to

⁶ For bulk silica at 5 K, Q^{-1} measured by Brillouin scattering is identical to that measured using ultrasounds (Vacher *et al* 2005).

Table 2. Structural characteristic pore size L_p and values calculated from Q^{-1} for D_s , D_c and ξ using equation (4), (5) and (9) defined in the text. The error bars on the characteristic distances are equal to 10%.

	Density (kg m ⁻³)	Porosity	L_p (nm)	D_s (nm)	D_c (nm)	ξ (nm)
Aerogel	690	0.69	14	46	45.6	7.04
	760	0.65	12	44.4–44.6	43.4–43.7	6.69–6.71
Xerogel	510	0.77	12.3	45.3	43.8	7.2
	900	0.59	7.6	27.3–27.8	221.2–21.8	3.97–4.05
Vycor	1390	0.365	9.75	15.5–17.3	9.5–11.2	1.93–2.15
	1500	0.318	7.5	20.3	14.4	2.4

$4.4 \times 10^{-3} - 0.4 \times 10^{-3} = 4 \times 10^{-3}$ in bulk silica and to $9.5 \times 10^{-3} - 4.8 \times 10^{-3} = 4.7 \times 10^{-3}$ in vycor. Therefore it also depends weakly on the porosity and is mainly due to the silica backbone. We assumed that it is independent of the porosity and we used the value obtained for vycor for all the porous samples. Taking into account the rather large error bars (10%) on internal friction determined by Brillouin scattering, subtracting a slightly different dynamical contribution would not affect our conclusion. Indeed the experimental uncertainty is about $\pm 6 \times 10^{-3}$ for three out of six porous samples (two aerogels and the xerogel of density 510 kg m⁻³), about $\pm 2 \times 10^{-3}$ for xerogel of density 900 kg m⁻³ and about $\pm 0.7 \times 10^{-3}$ for xerogel of density 1380 kg m⁻³. The Rayleigh part is then deduced from the room-temperature experimental value by subtracting the dynamical contribution (4.7×10^{-3}), as well as the TLS contributions (1×10^{-3}). The last column of table 1 gives the Q^{-1} values assigned to geometrical scattering, which are useful for the calculations developed in the next paragraph.

4.2. Modelization of geometric scattering of acoustic waves

It is possible to deduce from Q^{-1} Brillouin measurements a structural characteristic distance associated with a geometrical scattering process of phonons. Two models are available, and they have been thoroughly used for the interpretation of the plateau in the thermal conductivity.

The first model, introduced for the first time by Pohl (Zeller and Pohl 1971), is based on the scattering by point defects related to atom vacancies, which is extended to pores. The use of this model allowed Anderson *et al* (Grace and Anderson 1986) to describe properly the thermal conductivity above 1 K for porous silica (sol-gel silica or vycor) by ascribing the scattering of phonons to cylindrical or spherical pores. Within this framework, the mean free path of phonons is given respectively by

$$\ell^{-1} = 65pD_s^3(\delta\nu)^4/V^4 \quad (4)$$

for scattering by spheres of diameter D_s , and

$$\ell^{-1} = 13.6pD_c^2(\delta\nu)^3/V^3 \quad (5)$$

for scattering by cylinders of diameter D_c (p is the porosity, $\delta\nu$ the Brillouin frequency and V the velocity of sound).

D_s and D_c have been calculated using equations (4) and (5) starting from the Rayleigh contribution extracted from the experimental determination for Q^{-1} (last column of table 1), for vycor and other porous silica, using $\ell^{-1} = Q^{-1} \times 4\pi \times n/\lambda$, where n is the refractive index, and λ the incident wavelength of the laser in Brillouin experiment. Table 2 gives the values used for figures 7 and 8.

Figure 7 shows D_s and D_c as a function of apparent density ρ of samples. Taking into account that D_s depends on Q^{-1} to the power 1/3, the uncertainty in the Q^{-1} values leads

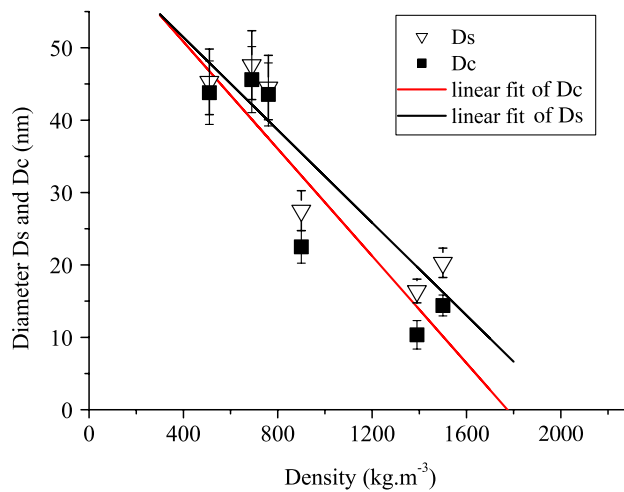


Figure 7. Pore diameters, calculated for spherical and cylindrical pores, from experimental values for Q^{-1} measured using Brillouin scattering and equations (4) and (5), respectively.

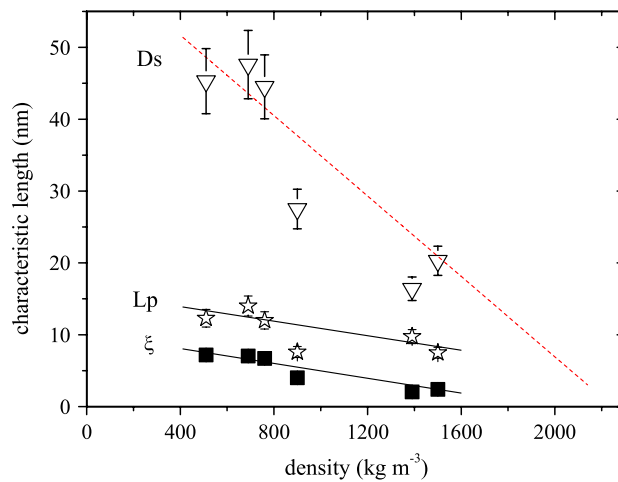


Figure 8. Comparison of the characteristic pore sizes determined from structural data (L_p) on the one hand and from internal friction data on the other hand (D_s using the model for spherical pores and equation (4) and ξ using a fluctuation model and equation (9)).

to a very narrow range for the characteristic length D_s . A straight line fits D_s and D_c versus ρ rather well, and the two pore sizes corresponding to two different hypotheses for the shape of the pores are rather close to each other. As expected, it can be noted that the extrapolation towards $D_s = 0$ gives a value very close to the density of bulk silica, showing that the model is self-consistent. In contrast, as expected, the model of cylinders appears inadequate at low porosities.

Another model, which has been largely used for non-porous silica, considers scattering by the disorder. Fluctuations of density, elastic constant, sound velocity or force constant at the atomic scale have been proposed (Zeller and Pohl 1971, Morgan and Smith 1974, Jäckle 1976, Walton 1977, Jones *et al* 1978, Graebner *et al* 1986, Grace and Anderson 1986, Raychaudhuri

1989). In that case, the mean inverse free path due to Rayleigh scattering can be written as

$$\ell_R^{-1} = \frac{D\hbar^4\omega^4}{k^4}, \quad (6)$$

where

$$D = \frac{8k^4 G \xi^3}{\hbar^4 V^4}, \quad (7)$$

$$G = \left\langle \left(\frac{\Delta V}{V} \right)^2 \right\rangle. \quad (8)$$

$\langle \Delta V^2 \rangle$ is the mean square velocity fluctuation, and ξ the spatial extent of the correlation of these fluctuations.

Equation (8) can be extrapolated to porous samples assuming that the contrast of velocity between the silica part and the pores is of order of unity ($G \simeq 1$).⁷ Then ξ can be deduced from the part of the Brillouin linewidth which is ascribed to geometrical scattering (which can be approximated by the difference between the linewidth values of porous vycor and bulk silica glass):

$$\xi = \frac{\lambda}{(8\pi n)} (Q^{-1})^{1/3}. \quad (9)$$

In figure 8, data for the characteristic length ξ are compared to data for D_s : a linear variation also fits with the values and ξ is clearly smaller than D_s . This difference can be due to the hypothesis that pores are independent for the calculation of D_s and that the interconnection between pores has been neglected. Indeed the existence of interference effects, which are expected to be more important for higher porosity, should lead to an inaccurate estimation for D_s (or D_c).

4.3. Comparison with structural data

Structural data on porous media are usually obtained by x-ray or neutron scattering as a function of the modulus of the wavevector or by nitrogen adsorption–desorption experiments. An average characteristic pore size is determined by x-ray or neutron scattering, whereas nitrogen adsorption–desorption experiments yield the maximum value of the size distribution. For the samples presented in table 1, either the average size or the maximum value of the pore size is reported, depending on the data available from the literature; they are shown in table 2 and plotted in figure 8 as a function of the apparent density. A linear fit accounts well for the results, and one can take note that, even though the absolute values of L_p and ξ differ by a factor of 2 to 3, the fitted values of slopes for L_p versus ρ and ξ versus ρ are equal within experimental accuracy. In order to explain the differences, for the comparison between D_s and ξ , it should be noted that the determination of characteristic sizes in scattering models using Q^{-1} values as well as the structural determinations of pore size do not take into account the polydispersity of pores. In addition, calculation of Rayleigh scattering neglects interference effects due to interconnections between pores. This interference effect increases with increasing porosity. Moreover, the structural determination by nitrogen adsorption–desorption gives only the maximum value of the size distribution. Finally, the Rayleigh scattering calculation is more suitable for vycor than for more porous samples.

⁷ This relation has been established for $q\xi\langle(\frac{\Delta V}{V})\rangle \ll 1$, where q is the modulus of the acoustic wavevector (Pekeris 1947). This condition is fulfilled at hypersonic frequencies.

4.4. Inverse mean free path of acoustical phonons and thermal conductivity

Anomalous thermal properties in glasses are correlated to properties of phonons (Kittel 1996, Zeller and Pohl 1971). Moreover, it has been demonstrated that acoustic phonons are responsible for thermal transport at low temperature (Zaitlin and Anderson 1975), and the thermal conductivity $\kappa(T)$ can be calculated to describe experimental data using the kinetic formula

$$\kappa(T) = \frac{1}{3} \int C(\omega, T) V \ell(\omega) d\omega, \quad (10)$$

where $C(\omega, T)$ is the specific heat, V an average velocity of the thermal carriers (phonons) and $\ell(\omega)$ the mean free path of phonons. As pointed in section 1, to describe quantitatively the data not only for temperatures lower than 1 K but also up to the end of the low-temperature plateau (typically 10 K), many theoretical processes of acoustic attenuation should be considered to determine $\ell(\omega)$: interaction of phonons with tunnelling systems (TS) dominant in the low-temperature part, a process of strong scattering such as Rayleigh scattering with a ω^4 dependence, to explain the plateau, and a cutoff limit at atomic scale. In bulk glass, such as silica, the existence of this strong scattering regime is speculative, and only indirect observation comes from inelastic scattering (Foret *et al* 1996, Rufflé *et al* 2003, Benassi *et al* 1996, 2005) or fits of thermal conductivity (Morgan and Smith 1974, Jäckle 1976, Walton 1977, Jones *et al* 1978, Graebner *et al* 1986, Raychaudhuri 1989). In both cases interpretations are controversial. Many authors have tried to calculate the Rayleigh scattering due to fluctuations of density, elastic constant or microscopic force constant (Morgan and Smith 1974, Jäckle 1976, Graebner *et al* 1986, Raychaudhuri 1989). Additional controlled pores in bulk glass has been successfully used (Zaitlin and Anderson 1975) to prove first that acoustic phonons are indeed responsible for heat transfer in glasses at low temperature and second that the efficiency of Rayleigh scattering of phonons can explain the modifications of thermal conductivity κ compared to the porous case. Comparison of data in bulk and porous glasses below 0.1 K shows a superimposition of the data; this corresponds to the regime where $\kappa(T)$ is nearly proportional to T^2 and $\ell(\omega)$ is dominated by interactions with TS and confirms that this contribution does not depend on the porosity. Such a regime in T^2 can extend up to 1 K in usual glasses. When the temperature increases, as porosity yields a strong increase of the phonon scattering, the inverse mean free path increases and the plateau is shifted towards low temperature. Thus thermal conductivity decreases by more than an order of magnitude in vycor compared to bulk silica (Grace and Anderson 1986). $\ell(\omega)$ can be deduced from the measured thermal conductivity by using equation (10) assuming, as in (Grace and Anderson 1986), that ℓ^{-1} is the sum of a first term due to phonon scattering by TS and a second term due to Rayleigh scattering.

From the curves fitting $\kappa(T)$ for vycor (Grace and Anderson 1986), $\ell(\omega)$ can be estimated at the Brillouin frequency 21 GHz: $\ell \simeq 8 \times 10^{-6}$ m. Using $V_1 = 4100$ m s⁻¹, this value is equivalent to a Brillouin full linewidth of $\Gamma \simeq 82$ MHz. In fact, both transverse and longitudinal phonons are involved in thermal conductivity, so an average velocity is used in the model, which leads to an overestimated value of the mean free path corresponding to the same measured value of the thermal conductivity, and thus to an underestimate of the linewidth deduced from equation (10) compared to the measured longitudinal attenuation⁸. On the other hand, Brillouin scattering data give a direct measurement of the longitudinal attenuation in the frequency range of interest. The experimental value deduced from our measurements (100 MHz) is in very good agreement with the calculation.

⁸ Transverse and longitudinal attenuations are generally similar at a given frequency (Pohl *et al* 2002, Vacher *et al* 1981).

5. Conclusion

Brillouin scattering investigations of the acoustic properties of vycor confirm a scaling variation of the elastic constant with density in porous silica glass, whatever the details of the preparation of the samples are. Moreover, a temperature-independent plateau for the internal friction Q^{-1} is observed in a large temperature range, from room temperature to the temperature of densification of vycor. The efficiency of geometrical scattering of acoustic waves in porous glass is demonstrated, which confirms the efficiency of this process postulated for long time ago to explain the mean free path of phonons and the thermal conductivity at low temperature. Quantitative agreement of the calculations from models for Rayleigh scattering by pores can explain the inverse mean free path of phonons, especially for low porosities. Direct measurements of the acoustic attenuation agree with the model of Rayleigh scattering of phonons to explain the plateau of thermal conductivity for vycor and other porous silica samples.

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