PHYSICAL REVIEW B VOLUME 56, NUMBER 2 1 JULY 1997-II

Mean free path of high-frequency acoustic excitations in glasses with application to vitreous silica

René Vacher, Jacques Pelous, and Eric Courtens
Laboratoire des Verres, UMR 5587 CNRS, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France
(Received 27 February 1997)

Direct spectroscopic information on the frequency and temperature dependences of acoustic-phonon damping in vitreous silica is reconsidered. It points to the essential role played by Rayleigh scattering of the phonons, in quantitative agreement with thermal properties at low temperatures. A picture is proposed that consistently unifies thermal properties with all the available spectroscopic results. [S0163-1829(97)51326-9]

Glasses exhibit well documented anomalies of their thermal properties that are fairly specific and apparently universal.[1,2] At temperatures T of the order of 10 K, they show a sizable hump in C_p/T^3, where C_p is the specific heat. This corresponds to an *excess* over the Debye density of vibrational states, which is confirmed by neutron scattering when the data are analyzed with some variant of the incoherent approximation.[3,4] At roughly the same low temperatures, the thermal conductivity $\kappa(T)$ shows a plateau. Its likely explanation is a crossover in the damping of the *dominant* acoustic modes which are propagating plane waves at low T and would become strongly scattered at high T.[1,5] The excitations that must be involved in both anomalies have frequencies $\omega/2\pi$ well above 100 GHz, reaching into the THz range. This is a difficult region for direct spectroscopic observation of *acoustic* modes, which probably explains why the question is still unsettled. Also unsettled is the origin of the ''boson peak,'' another universal feature of glasses that appears both in Raman and neutron spectroscopy in the same frequency range, and this in experiments where the *momentum* q of acoustic phonons (if the concept made sense) could not be conserved.[6,7] Of course, if this momentum had lost its significance owing to strong elastic scattering of the excitations both the boson peak and the $\kappa(T)$ plateau might be explainable in one sweep. In glasses, strong scattering can be expected to occur at sufficiently high frequency owing to the intrinsic structural disorder.[1,8,9] This implies that before strong scattering sets in at a crossover frequency ω_{co}, the linewidth of plane waves, $\Gamma(\omega)$, might eventually become dominated by elastic scattering, in which case it should obey the Rayleigh law, $\Gamma \propto \omega^4$. Such a damping contribution in a glass would of course be T independent for $T \ll T_g$, where T_g is the glass-transition temperature. However, what is mostly reported over rather broad T and ω ranges, is that $\Gamma \propto \omega^2$. For example, in vitreous silica, v-SiO_2, an ω^2 dependence is found from $\approx$100 K to $\approx$1000 K. At room T, it applies from $\approx$1 MHz to well over 100 GHz.[10–12] The interest in this question is constantly being revived by new experimental capabilities. In particular, for v-SiO_2, there exist now Brillouin data obtained with small-angle inelastic neutron scattering (INS) as well as inelastic x-ray scattering (IXS).[13,14] These in principle considerably extend the previously measured ω and q ranges. Although the behavior observed both in INS and IXS can be analyzed in terms of strong scattering,[13,15] the IXS data seem also to be described adequately by a simple damped harmonic oscillator (DHO).[14] With the latter hypothesis one finds approximately $\omega \propto q$ and $\Gamma \propto q^2$ at frequencies well into the THz range.[14] This surprising result prompted us to reconsider the entire available spectroscopic and thermal information in the light of the recent data.

This paper shows that one is able to present a fully consistent picture that is able to qualitatively account for the thermal anomalies as well as for the spectroscopic information, including the boson peak. We concentrate the analysis on v-SiO_2 for two reasons: (i) some relevant results were recently reported for this glass,[13–15] and (ii) experience shows that the low-frequency vibrational modes of v-SiO_2 do not depend significantly on the particular choice of sample.[16,17] The latter point is important to meaningfully compare data from different sources.

In Fig. 1, three high-resolution Brillouin scattering measurements of the inverse mean free path ℓ^{-1} of the longitudinal acoustic (LA) waves in v-SiO_2 are combined, covering a T range from 0.3 to 1300 K.[18–20] These were all obtained using the 5145 Å Ar-laser excitation in backscattering geometry. This corresponds to a phonon frequency $\omega_{LA}/2\pi \simeq 35$ GHz. The energy mean free path relates to the half-width at half-height $\Gamma/2\pi$ by $\ell^{-1} = 2\Gamma/v_{LA}$, where $v_{LA} \simeq 5960$ m/s is the LA velocity.[19] Four distinct regimes (I–IV) are recognized. Below 3 K (I), Γ is mostly produced by the resonant absorption of phonons by two-level systems (TLS's).[21,2] From $\sim$4 to $\sim$20 K (II), it is relaxational absorption by TLS that takes over. These two regimes were analyzed in detail in Ref. 18. To achieve a satisfactory agreement between the TLS prediction, ℓ_{TLS}^{-1}, and the measured ℓ^{-1}, it was necessary to postulate an additional T-independent absorption, $\ell_0^{-1} = 50$ cm^{-1}, with $\ell^{-1} = \ell_{TLS}^{-1} + \ell_0^{-1}$. This residual absorption is illustrated by the dashed horizontal line in Fig. 1. Its origin had not been discussed at the time. A third region (III) shows a peak around 120 K.[19] The temperature position of this peak is a function of the measuring frequency ω. It follows a thermally activated process with a mean activation

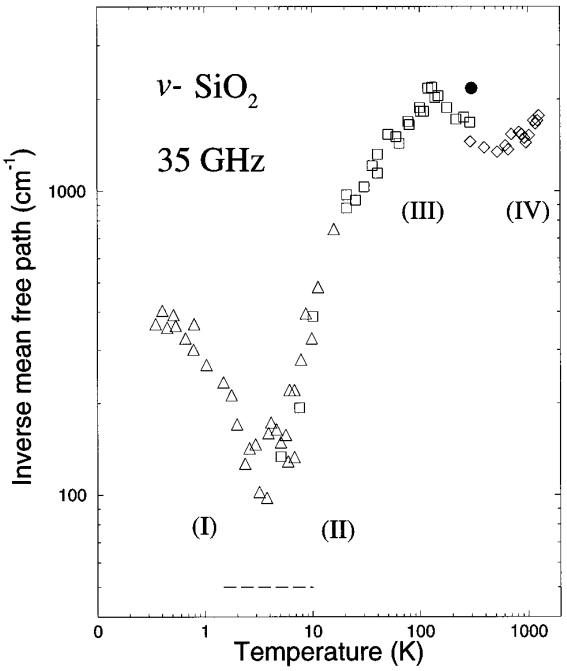

FIG. 1. Inverse mean free path ℓ^{-1} of LA phonons measured in v-SiO_2 with Brillouin scattering: the △ are from Ref. 18, the □ from Ref. 19, and the ◇ from Ref. 20. The ● is a measurement at room T from Ref. 14; that it falls significantly above the other points could be due to an unusual sample quality, but more likely (Ref. 17) to insufficient resolution of the spectrometer. The dashed line at low T corresponds to ℓ_0^{-1}. The four distinct regions (I–IV) are discussed in the text.

energy of ≈570 K. This is the β relaxation. Although its nature is not really known, the phenomenon is well established since it was measured over seven decades in ω.[21] For this process, the linewidth is $\Gamma \propto \omega^2$ at high temperatures, i.e., when ω is small compared to the inverse relaxation time τ^{-1}, while one finds $\Gamma \propto \omega$ near the peak.[19] Finally, in region IV above ≈500 K,[20] the origin of the attenuation, which is likely to be related to phonon anharmonic processes, is still being worked on.[19,12,22] One also finds there $\Gamma \propto \omega^2$ in accordance with a dynamical process involving excitations of very short lifetimes.

The entire curve in Fig. 1 establishes that ℓ^{-1} is a strong function of T. It demonstrates that the attenuation at this frequency must essentially be of *dynamical* origin, contrary to the hypothesis that above 100 K it is associated with *structural* disorder.[14] The general behavior illustrated in Fig. 1 is not specific to v-SiO_2 but has been found in many kinds of glasses, e.g., boron oxide,[23] phosphate glasses,[24] or polymers.[25] In the case of v-SiO_2, the only component that could be attributed to static disorder in measurements at 35 GHz is in fact the constant $\ell_0^{-1}=50$ cm^{-1} which was evidenced around 3 K. It must be noted that this elastic scattering contribution is only 2% of the room-T value which is dominated by fast relaxation, $\Gamma \propto \omega^2$.

Brillouin results on transverse acoustic (TA) waves, for $\omega_{TA}/2\pi=16$ GHz, were obtained in 90° scattering and are available from 20 to 300 K.[10,19] The attenuation is quantitatively the same as that measured on the LA modes (Fig. 1) when due account is taken of the different frequencies. In the regime $\Gamma \propto \omega^2$ the damping of both LA and TA modes fall on the same ω^2 line at 300 K.[13]

Disorder scattering could only start to dominate at high frequencies, owing to the law $\Gamma \propto \omega^4$. There are various experimental estimates for the strength of this scattering. These were obtained by adjusting theoretical laws for phonon mean free paths to the observed plateau in the thermal conductivity (see, for example, Refs. 26 and 27). Using the parameters of Ref. 27, one finds that the Rayleigh component, ℓ_R^{-1}, should be $\ell_R^{-1} \approx 9\times10^6$ cm^{-1} at 1 THz. Extrapolating the Brillouin value of ℓ^{-1} with a ω^2 law (Fig. 2) one finds at room T and 1 THz a value $\ell^{-1} \approx 1\times10^6$ cm^{-1}. Hence, one in fact expects that disorder scattering should become dominant above ≈300 GHz. This value is close to the lower-frequency limit of current INS and IXS investigations.[13,14] Owing to the high power dependence, $\Gamma \propto \omega^4$, and since $\Gamma > \omega$ makes no sense in this physical situation as noted already by Ioffe and Regel,[28] the value $\Gamma = \omega$ is a limit that should be rapidly reached, at $\omega \geqslant \omega_{co} \approx 1$ THz. The corresponding crossover wave vector is then $q_{co} = \omega_{co}/v_{LA} \approx 1$ nm^{-1}. This wave vector is also rather close to the lower limit practically achievable in current IXS experiments. We believe this is a reason that the interpretation of IXS data taken alone remained ambiguous. Particular care must be taken in selecting an appropriate expression for the dynamical structure factor, $S(q,\omega)$, which can be used to analyze jointly the INS and IXS data.

An expression for $S(q,\omega)$ accounting for a somewhat similar crossover situation was first derived for a percolation model using an effective medium approximation (EMA).[29] It was further developed to describe Brillouin scattering from fractal aerogels.[30,31] The shape of this structure factor, for a large region around ω_{co} and q_{co}, mainly depends on the values of ω/ω_{co} and q/q_{co}. It should be noted that $S(q,\omega)$ *per se* never contains information about propagation vs localization. Correlation functions involving a higher power of the fluctuating variable are needed to that effect.[32] The simplest example is probably the DHO response which describes a localized spring as well as propagating long-wave phonons. The $S(q,\omega)$ of Refs. 29 and 30 makes no exception. This spectral shape is essentially produced by the ''damping crossover,'' irrespective of whether the excitations above ω_{co} become localized or not. According to another EMA study of acoustic excitations in disordered systems, it is likely that v-SiO_2 is too densely packed to allow for true acoustic localization,[33] in which case one should presumably think of the excitations above ω_{co} as *neither localized nor propagating*, as recently suggested in another context.[34] This ''crossover model'' for $S(q,\omega)$ is the one that was used to represent jointly INS and IXS results on v-SiO_2, giving $\omega_{co}/2\pi \simeq 1$ THz.[13] Scattering is indeed observed with neutrons at $\omega > \omega_{co}$ and under conditions where momentum conservation rules cannot be obeyed, producing the boson peak.[13] This confirms that momentum is not any more a good quantum number for the corresponding excitations, in agreement with the notion that they have ceased to propagate, at least in the usual sense. That this $S(q,\omega)$ agrees with IXS results is also shown in Ref. 15 for the better spectra reported in Ref. 14.

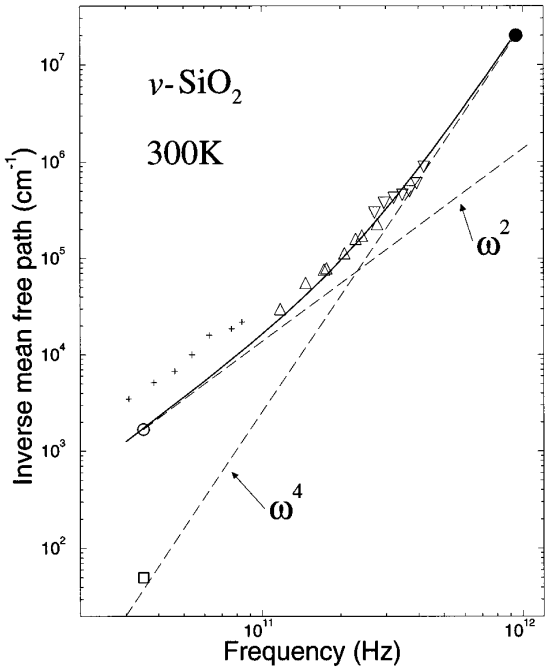

FIG. 2. Summary of the available information on the mean free path of LA phonons at room T in v-SiO_2: the ● is the Ioffe-Regel crossover frequency, corresponding to the upper limit of the Rayleigh scattering regime, taken from Ref. 13; the Rayleigh contribution is shown by the dashed line $\propto\omega^4$ which passes near the residual contribution ℓ_0^{-1} (□), taken from Ref. 18; the ○ is the Brillouin result from the same reference, with a line $\propto\omega^2$ representing the relaxational contribution; the solid line is the sum of these two processes; the other symbols are measurements taken from Ref. 11 as discussed in the text.

Following the above ideas, Fig. 2 summarizes the high-frequency spectroscopic data on v-SiO_2 for LA phonons at 300 K. The crossover frequency $\omega_{co}/2\pi=950$ GHz is taken from Ref. 13. The value $\ell_{co}^{-1}=2\omega_{co}/v_{LA}$ is shown at ω_{co} (●). A line $\ell_R^{-1}\propto\omega^4$ is drawn through this point. Remarkably, it passes very close to and slightly below the background contribution $\ell_0^{-1}=50\ \mathrm{cm}^{-1}$ at 35 GHz, which is the upper limit for the static structural contribution at that frequency. On the other hand, the Brillouin point at 35 GHz, taken from Fig. 1 at 300 K, is shown with a line $\ell^{-1}\propto\omega^2$ passing through it and representing the fast relaxation regime. The sum of the two straight lines is the solid curve which represents the expected mean-free-path dependence on frequency for the combined processes. Finally, we complete the figure with data obtained using a picosecond pulse-echo technique.[11] The points shown are those at 300 K from Fig. 7 of Ref. 11. They correspond to three distinct chemical-vapor-deposition-prepared v-SiO_2 thin films of different thicknesses. The points from 100 GHz to 440 GHz fall on the predicted curve within their accuracy. As already noted in Ref. 11, the frequency dependence of ℓ^{-1} is faster than ω^2 in this region. Figure 2 now suggests that this corresponds to the crossover between $\ell^{-1}\propto\omega^2$ and $\ell^{-1}\propto\omega^4$, which is located at $\omega/2\pi\simeq210$ GHz in our figure. The pulse-echo points at lower frequencies (+) lie above the Brillouin value. They were obtained on a relatively thick film. In that case, as already explained in Ref. 11, static fluctuations of the film thickness can lead to a spread of the acoustic path which might translate into an apparent additional loss.

It is now of interest to attempt a calculation of $\kappa(T)$ using the direct spectroscopic information on $\ell^{-1}(\omega,T)$. This approach is opposite to the former ones indicated above which adjusted the parameters of theoretical expressions to the experimental $\kappa(T)$.[26,27] First one should notice that the plateau in $\kappa(T)$ occurs around 10 K,[1,26] which corresponds to dominant phonons between 0.5 and 1 THz. Up to $\approx$15 K, the damping of these phonons produced by the β relaxation is totally negligible. Hence, at and below the plateau one can use $\ell^{-1}=\ell_{TLS}^{-1}+\ell_R^{-1}$, where ℓ_{TLS}^{-1} produces the low-T region of $\kappa(T)$, while ℓ_R^{-1} controls the plateau. Using the standard Debye expression, as written, e.g., in Ref. 26, and the ℓ^{-1} values corresponding to Figs. 1 and 2, one finds that the calculated $\kappa(T)$ corresponds well to the experimental one below $\approx$5 K, while it is somewhat too small in the plateau region. However, such a calculation is really too simple, as $\kappa(T)$ is strongly dominated by TA phonons,[35] while in Fig. 2 the value ℓ_R^{-1} is the $\ell_{R,LA}^{-1}$ appropriate to LA phonons. One knows that for point defects $\ell_R^{-1}\propto1/\lambda^4$, and theory predicts roughly the same scattering strength for LA and TA modes of the same λ.[36] Under the assumption that this also applies to v-SiO_2,[37] one finds then $\ell_{R,TA}^{-1}\simeq(v_{LA}/v_{TA})^4\ell_{R,LA}^{-1}\simeq6\ell_{R,LA}^{-1}$. Introducing the two different mean free paths in the Debye model, the calculated $\kappa(T)$ starts falling below the measurement already around 1 K, and in the plateau region it is almost an order of magnitude too small. However, the density of states calculated with the Debye model is also much too small, by roughly the same amount, and it neither accounts for the observed specific heat at the same temperatures,[38] nor for the more direct INS data.[4] Hence, if one were to use the real density of states in the $\kappa(T)$ calculation, good agreement with experiment would be achieved. This indicates that the excess density of states *contributes like acoustic modes* to the observed heat transport in the plateau region. The existence of an excess at frequencies slightly below ω_{co} also agrees with EMA calculations.[33] This confirms the approach used in Ref. 13 where the inelastic spectrum was treated as entirely acoustic. In the alternate picture which assumes that the structural contribution is $\ell^{-1}\propto\omega^2$ instead of $\propto\omega^4$,[14] one finds *no plateau* in $\kappa(T)$, and the actual conductivity is also much too small at small T as the inverse mean free path does not drop sufficiently fast with ω.

In conclusion, spectroscopic and thermal evidence now converge to establish the essential role played by Rayleigh scattering of the phonons. The region where this law dominates at room T in v-SiO_2 is small, about half an order of magnitude in ω. It is, however, *essential*, as it is that law that leads to the strong damping crossover at $\omega_{co}/2\pi\approx1$ THz. This allows, at higher ω, scattering processes in which momentum conservation is not required, which thus explains the boson peak around 1 THz. A spectral function which includes the boson peak is able to account for the data taken both in INS and IXS.[13,15]

[1] R.C. Zeller and R.O. Pohl, Phys. Rev. B **4**, 2029 (1971).
[2] See, e.g., *Amorphous Solids: Low Temperature Properties*, edited by W.A. Phillips (Springer-Verlag, Berlin, 1981).
[3] U. Buchenau, Z. Phys. B **58**, 181 (1985).
[4] U. Buchenau, M. Prager, N. Nucker, A.J. Dianoux, N. Ahmad, and W.A. Phillips, Phys. Rev. B **34**, 5665 (1986).
[5] S.R. Elliott, Europhys. Lett. **19**, 201 (1992), and references therein.
[6] J. Jäckle, in Ref. 2, p.135.
[7] V.K. Malinovsky, V.N. Novikov, P.P. Parshin, A.P. Sokolov, and M.G. Zemlyanov, Europhys. Lett. **11**, 43 (1990).
[8] P.G. Klemens, Proc. R. Soc. London, Ser. A **208**, 108 (1951).
[9] J.E. Graebner, B. Golding, and L.C. Allen, Phys. Rev. B **34**, 5696 (1986).
[10] R. Vacher and J. Pelous, Phys. Lett. **53A**, 233 (1975).
[11] T.C. Zhu, H.J. Maris, and J. Tauc, Phys. Rev. B **44**, 4281 (1991).
[12] C.J. Morath and H.J. Maris, Phys. Rev. B **54**, 203 (1996).
[13] M. Foret, E. Courtens, R. Vacher, and J.-B. Suck, Phys. Rev. Lett. **77**, 3831 (1996).
[14] P. Benassi, M. Kirsch, C. Masciovecchio, V. Mazzacurati, G. Monaco, G. Ruocco, F. Sette, and R. Verbeni, Phys. Rev. Lett. **77**, 3835 (1996).
[15] M. Foret, E. Courtens, R. Vacher, and J.-B. Such, Phys. Rev. Lett. (to be published).
[16] F. Terki, C. Levelut, J.L. Prat, M. Boissier, and J. Pelous, Phys. Rev. B **53**, 2411 (1996).
[17] For example, between very high purity fused silica and silica obtained from the very different sol-gel process, the velocity of longitudinal acoustic waves varies by less than $\approx$1%, and the attenuation at 35 GHz by $\sim$10%.
[18] R. Vacher, H. Sussner, and S. Hunklinger, Phys. Rev. B **21**, 5850 (1980).
[19] R. Vacher, J. Pelous, F. Plicque, and A. Zarembowitch, J. Non-Cryst. Solids **45**, 397 (1981).
[20] J. Pelous and R. Vacher, Solid State Commun. **18**, 657 (1976).
[21] S. Hunklinger and W. Arnold, in *Physical Acoustics*, edited by W.P. Mason and R.N. Thurston (Academic Press, New York, 1976), Vol. XII, p. 155.
[22] C.J. Morath, G. Tas, T.C.-D. Zhu, and H.J. Maris, Physica B **219&220**, 296 (1996).
[23] J. Pelous, Phys. Lett. **74A**, 275 (1979).
[24] J. Pelous, R. Vacher, and J. Phalippou, J. Non-Cryst. Solids **30**, 385 (1979).
[25] M. Schmidt, R. Vacher, J. Pelous, and S. Hunklinger, J. Phys. (France) Colloq. **43**, C9-501 (1982).
[26] A.K. Raychaudhuri, Phys. Rev. B **39**, 1927 (1989).
[27] J. Jäckle, in *The Physics of Non-Crystalline Solids*, edited by G.H. Frischat (Trans Tech Publications, Aedermannsdorf, Switzerland, 1977), p. 568.
[28] A.F. Ioffe and A.R. Regel, Prog. Semicond. **4**, 237 (1960).
[29] G. Polatsek and O. Entin-Wohlman, Phys. Rev. B **37**, 7726 (1988).
[30] E. Courtens, R. Vacher, J. Pelous, and T. Woignier, Europhys. Lett. **6**, 245 (1988).
[31] For a recent review, see E. Courtens and R. Vacher, in *Amorphous Insulators and Semiconductors*, edited by M.F. Thorpe and M.I. Mitkova, NATO ASI Series (Kluwer Academic, Dordrecht, 1997), pp. 255–288.
[32] D.J. Thouless, Phys. Rep., Phys. Lett. **13C**, 94 (1974).
[33] W. Schirmacher and M. Wagener, Solid State Commun. **86**, 597 (1993).
[34] J. Fabian and P.B. Allen, Phys. Rev. Lett. **77**, 3839 (1996).
[35] P.G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 7, pp. 1–98.
[36] P.G. Klemens, Proc. Phys. Soc. London, Sec. A **68**, 1113 (1955).
[37] As a counter example, $\ell_{R,TA} \approx \ell_{R,LA}$ was reported for samples of sintered glass beads, by H.P. Schriemer, N.G. Pachet, and J.H. Page, Waves Random Media **6**, 361 (1996). The authors were themselves surprised by this result. It certainly points to the need for further experiments on the linewidth of TA phonons in $v\text{-}SiO_2$.
[38] R.O. Pohl, in *Amorphous Solids: Low Temperature Properties* (Ref. 2), p. 27.