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Thermally activated relaxation processes in vitreous silica: An investigation by Brillouin scattering at high pressures

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We have carried out Brillouin-scattering experiments on vitreous silica at temperatures between 50 and 300 K and pressures up to 3 GPa. Application of pressure leads to considerable changes of the acoustic absorption and the velocity of sound. In order to explain our observations, we start from the so-called "tunneling model," which is often used to explain the low-temperature anomalies of amorphous solids. With an extension of this model, we are not only able to describe our experimental results but also the acoustic behavior of vitreous silica at higher temperatures in general. The quantitative fits of the experimental data achieved in this way give a hint as to the nature of the low-energy excitations existing in glasses.

I. INTRODUCTION

In general, glasses exhibit a local atomic order like crystalline materials, whereas a long-range order is missing. In the case of vitreous silica, well-defined SiO_4 tetrahedra are the basic units of the amorphous network. In covalently bonded glasses, long-range order is lost because of the occurrence of relatively small but random variations of the bond angles. For this reason the geometrical configuration of glasses is not as well defined as that of crystals and it is quite plausible that small local rearrangements of single atoms or small clusters of atoms are possible even at temperatures well below the glass-transition temperature. For a phenomenological description of this situation, we may introduce "defect states" that reflect the properties of those specific configurations in the glassy network where motion is possible. The structural units forming the defect states are weakly connected with the otherwise rather rigid network. It is this ease with which small local changes can take place that gives rise to acoustic and thermal properties of glasses which differ considerably from those of their crystalline counterparts.

Let us first consider the behavior of glasses at very low temperatures. At temperatures around or below 1 K, glasses exhibit a variety of properties which are anomalous in comparison with those of their crystalline counterparts.[1-3] The tunneling model[4,5] offers a successful phenomenological description of this behavior. This model is based on the assumption that certain atoms or small groups of atoms can occupy different stable positions, thus forming the defect states mentioned above. In the simplest case such a defect state consists of a "particle" moving in a double-well potential. The transition from one well to the other is expected to occur by quantum-mechanical tunneling. In this case we call the defect states "tunneling systems." Unfortunately, the microscopic nature of these tunneling systems is known neither in general nor in specific cases. The existence of tunneling systems gives rise to unusual thermal, acoustic, and dielectric properties. They lead to a strong enhancement of the specific heat well above the Debye value, particularly at very low temperatures. It should be pointed out that their dynamical properties are governed by their internal motion, i.e., by the tunneling process.

At higher temperatures, however, the tunneling motion loses its importance. Thermal activation enables the particles of the defect states to jump over the barrier in order to go from one stable position to the other. Therefore, with rising temperature a continuous transition from quantum to classical states must occur, although the nature of the defect states is not altered.

Based on the assumption that the same defect states determine the elastic properties of vitreous silica from cryogenic to room temperature, we develop a phenomenological model which leads to a correct description of the acoustic properties in a very wide temperature and frequency range. We start with the tunneling model and extend it by taking the thermally activated motion into account and by making two additional but simple assumptions concerning the relevant distribution functions. This simple "defect model," as we call it here, describes not only the conventional acoustic measurements reported in the literature, but also our Brillouin-scattering experiments carried out at high pressure very well.

The present paper is structured as follows. The description of the experimental procedure in Sec. II is followed by the presentation of our experimental results in Sec. III. The extension of the tunneling model and analytic approximations are discussed in Sec. IV. The results of our numerical calculation and microscopic implications are reported in Secs. V and VI, respectively. The conclusion in Sec. VII contains a brief summary of the pertinent findings of this study.

II. EXPERIMENTAL PROCEDURE

We have performed Brillouin-scattering experiments under hydrostatic pressure up to 3 GPa in the temperature range from 50 K to room temperature. Pressure was generated in a Syassen-Holzapfel cell[6] with two anvils of conical shape made from synthetic sapphire. The height and larger diameter of the anvils were 8 mm, and the smaller diameter at the high-pressure side was 2 mm. The sample volume, sealed by a copper-beryllium gasket, was 200 μm high and had a diameter of 700 μm. A mixture of ethanol and methanol was used as a pressurizing medium.[7] The pressure was determined to an accuracy of 0.03 GPa via the frequency shift of the fluorescence light of a ruby.[8] Our sample of vitreous silica [Suprasil W (Ref. 9)] had a diameter of 500 μm and was 160 μm thick. Because of the large thermal contraction of the alcohol mixture, the pressure in the cell decreased on cooling.

The velocity of sound, v, and the acoustic absorption α of longitudinal phonons were determined by Brillouin scattering. An argon-ion laser working at the wavelength $\lambda_L = 488$ nm was used for illumination. The scattered light was analyzed using an arrangement of a triple-pass plane and a confocal Fabry-Pérot interferometer in tandem.[10] Knowing the refractive index n of the sample, the sound velocity can be deduced directly from the frequency shift $\Delta\nu$ of the scattered light by

$$\Delta\nu = \pm \frac{2nv}{\lambda_L} \sin\left[\frac{\theta}{2}\right] . \tag{1}$$

The scattering angle θ was 178° in our experiment, resulting in a Brillouin frequency $\Delta\nu \simeq 36$ GHz. This shift is determined by the frequency $\omega/2\pi$ of the phonons taking part in the scattering event. The backscattering geometry minimizes the frequency uncertainty due to the finite aperture of the detected light. We have neglected the temperature dependence of the refractive index, but we have taken its increase with pressure of 10^{-2} per GPa into account.[11]

From the measured, linewidth Γ, the lifetime of the scattering phonons and thus the absorption can be deduced using the relation

$$Q^{-1} = \frac{\Gamma}{\Delta\nu} , \tag{2}$$

where Q^{-1} is the internal friction which is related directly to the absorption α and angular frequency ω of the phonons via the relation $Q^{-1} \equiv \alpha v/\omega$. High resolution was achieved using a confocal interferometer with a mirror spacing of 25 mm. The high contrast necessary to suppress the relatively intense Rayleigh line was obtained by a plane Fabry-Pérot interferometer, working in the triple-pass mode.

III. RESULTS

In Fig. 1 we show our measurements of the acoustic absorption under zero pressure in the temperature range between 50 and 300 K. With increasing temperature the absorption rises, passes through a maximum, and decreases again. Despite a scatter of the experimental points, the height $Q^{-1}_{\max}$ and temperature $T_{\max}$ of the absorption maximum can be determined with relatively high accuracy. We deduce from our data $Q^{-1}_{\max} \simeq 5.5 \times 10^{-3}$ and $T_{\max} \simeq 130$ K. Within the accuracy of the measurements, our results are in agreement with those reported in Ref. 12.

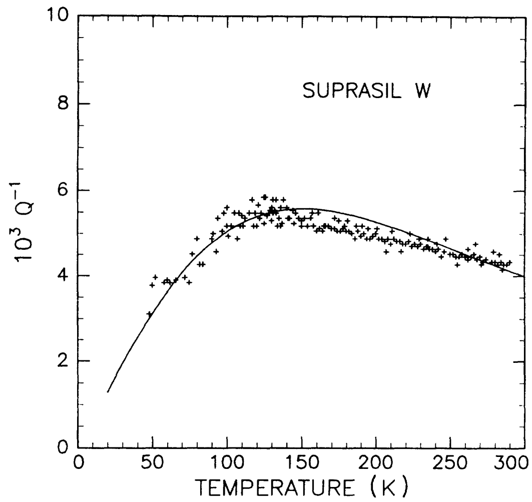

FIG. 1. Internal friction of vitreous silica as a function of temperature measured at 36 GHz by Brillouin scattering. The solid line is our fit to this set of data.

The application of pressure leads to strong and interesting changes of the acoustic properties. The absorption rises in the whole temperature range accessible to our experiment. As shown in Fig. 2 we have measured the pressure dependence of the absorption at room temperature in more detail. At small pressures the internal friction rises approximately quadratically and starts to saturate above 1.5 GPa. A similar behavior has been reported for ultasonic frequencies.[13] In this technique changes of the acoustic impedance of the sample and pressure medium have, however, considerable influence on the apparent attenuation. In Fig. 3 the internal friction is plotted as a function of temperature at different pressures. It rises strongly with pressure at the high-temperature side of the absorption peak. At the same time the position of the maximum shifts toward higher temperatures. In fact, no peak is observed anymore up to

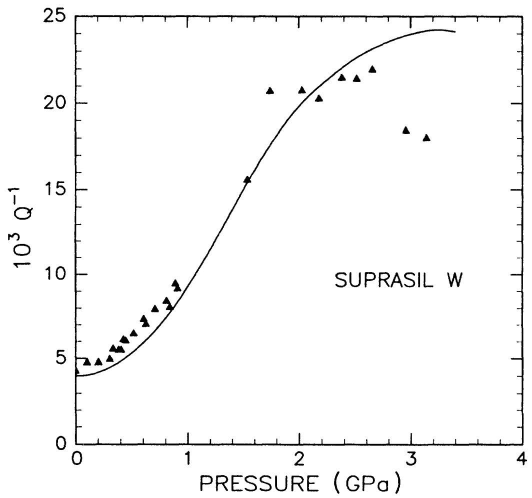

FIG. 2. Internal friction of vitreous silica at room temperature as a function of pressure. The solid line represents the theoretical fit desribed in the text.

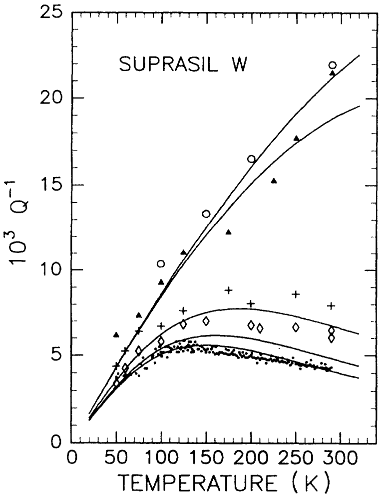

FIG. 3. Internal friction of vitreous silica as a function of temperature measured at different pressures [1 bar (●), 0.45 GPa (◊), 0.71 GPa (+), 1.9 GPA (▲), 2.3 GPa (○)]. The large scatter of the data is caused by the small sample volume in the high-pressure cell. The solid lines are fitting curves discussed in the text.

room temperature if a pressure of 2 GPa is applied. A similar shift of the peak temperature, although at lower pressures, had also been observed in ultrasonic measurements.[14]

In the following two figures, the pressure variation of the sound velocity is shown . At room temperature a strong decrease of the velocity from $v = 5960$ m/s at zero pressure to $v = 5250$ m/s at 2.3 GPa is observed. As can be seen in Fig. 4, above that pressure the velocity slowly rises again in agreement with previous measurements.[13,15] In Fig. 5 the temperature dependence of the velocity is plotted for various pressures. As in previous ultrasonic measurements[16] at zero pressure, the velocity decreases approximately linearly at low temperatures. Around 60 K it passes through a minimum and rises again. The position of this minimum seems to be independent of frequency.[12,17,18] With increasing pressure the velocity is reduced in the whole temperature range and the position of the minimum shifts to higher temperatures. At our highest pressures of about 2 GPa, the velocity decreases within the accuracy of our data linearly with temperature in the whole temperature range. The minimum of the velocity is obviously shifted to temperatures above room temperature. It should be pointed out that below the minimum the temperature variation of the velocity is hardly changed by pressure.

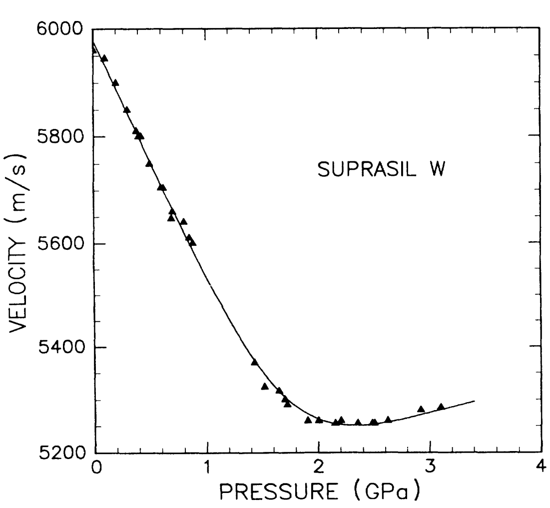

FIG. 4. Pressure dependence of the velocity of sound at room temperature. The velocity passes through a minimum at about 2.3 GPa. The curve is only a guide for the eye.

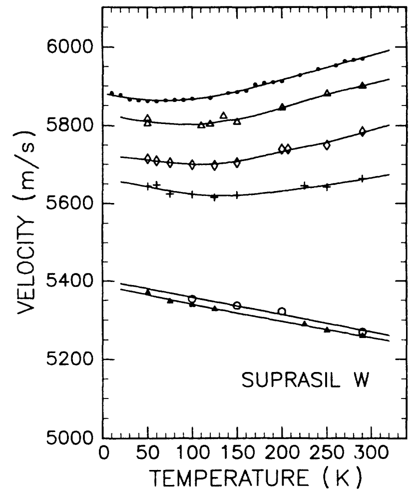

FIG. 5. Temperature dependence of the velocity of sound at different pressures [1 bar (●), 0.2 GPa (△), 0.45 GPa (◊), 0.71 GPa (+), 1.9 GPa (▲), 2.3 GPa (○)]. With increasing pressure the minimum shifts to higher temperatures. The solid lines are only guides for the eye.

Before discussing the tunneling model and its extension, we briefly consider the temperature dependence of the internal friction at low frequency. As an example, we have schematically plotted the results of very recent measurements[18] performed at 11.4 kHz in Fig. 6. At the

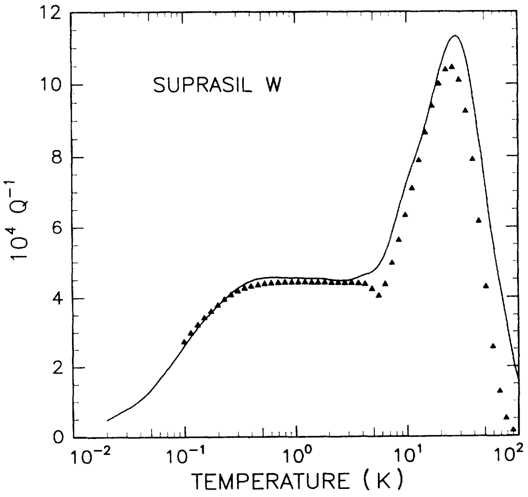

FIG. 6. Temperature dependence of the internal friction of vitreous silica at 11.4 kHz. The solid line represents experimental results from Ref. 18; the triangles show the result of our numerical calculations.

lowest temperatures the absorption rises steeply. At higher temperatures the curve bends over and becomes temperature independent. Therefore, the absorption is very often said to exhibit a "plateau." With increasing frequency the onset of the plateau shifts to higher temperatures. At 20 MHz it is degenerated to a tiny maximum followed by a shallow minimum.[19] The comparison of data, reported in the literature and obtained at different frequencies, leads to the important conclusion that the magnitude of Q^{-1} in the plateau range is slightly frequency dependent. It seems that an increase by a factor of 2 is observed when going from 3 kHz to 50 MHz.[14,20] As we will see, this experimental feature can neither be explained by the standard tunneling model nor by the extension presented in this paper.

Above 4 K a strong rise of the absorption is found. We believe that this is the signature of the onset of thermally activated processes. At still higher temperatures an absorption maximum is observed at a temperature $T_{\max}$ which depends on frequency.

IV. THEORETICAL CONSIDERATIONS AND ANALYTIC APPROXIMATIONS

We start with the description of the standard tunneling model[4,5] and introduce afterward some new features which allow us to explain the acoustic properties of vitreous silica at high temperatures. As mentioned above, the tunneling model is based on the assumption that for a small fraction of atoms or groups of atoms two sites are accessible, separated by an energy barrier of height V. This situation is visualized in Fig. 7. The abscissa describes the position of the "particle" with the mass m or, more generally, reflects its configurational coordinate d. We assumed the two wells to be one dimensional, harmonic, and identical for all systems for simplicity. Starting from the single well, each particle has vibrational states separated by the energy splitting $2E_0$, where E_0 represents the zero-point energy. The difference in the depth of the wells is referred to as the asymmetry energy Δ. If tunneling occurs, the common ground state will not only be split as a result of Δ, but will also experience a tunnel splitting Δ_0. Using the WKB method, this quantity is found to be approximately

$$\Delta_0 \simeq \frac{2E_0}{\pi} e^{-\lambda} , \tag{3}$$

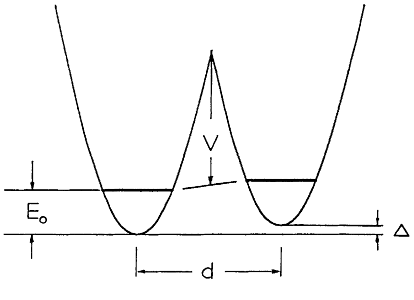

FIG. 7. Double-well potential with barrier height V, asymmetry energy Δ, and distance d in configurational space. E_0 is the ground-state energy of the tunneling particle.

where λ is the tunneling parameter, for which we may write

$$\lambda = \frac{d}{2\hbar}\sqrt{2mV} . \tag{4}$$

The total level splitting of the ground state is given by

$$E = (\Delta^2 + \Delta_0^2)^{1/2} . \tag{5}$$

Because of the random structure, the parameters of the tunneling systems will exhibit a distribution. In the tunneling model it is assumed that Δ and λ are independent of each other and uniformly distributed:

$$P(\Delta,\lambda)d\Delta\, d\lambda = \bar{P}\, d\Delta\, d\lambda . \tag{6}$$

The coupling of the tunneling systems to a strain field e is generally described by a deformation potential γ. In first approximation we write

$$\gamma = \frac{1}{2}\frac{\partial\Delta}{\partial e} . \tag{7}$$

The tensorial nature of the coupling parameter has been neglected for simplicity. Furthermore, it is presumed that the value of γ is not correlated to other parameters and can be approximated by a constant. Of course, strain fields also cause a variation of Δ_0, but it is generally assumed that the corresponding deformation potential is negligibly small compared to that defined above.[21] Our measurements at high pressure support this assumption. This question will be discussed once again at the end of this paper.

The strain field of a sound wave causes a modulation of Δ and hence an oscillation of the level splitting E. If the temperature is kept constant, the population of the two levels must follow the perturbation, resulting in a relaxation process[22] and leading to an internal friction

$$Q^{-1} = \frac{\gamma^2}{\rho v^2}\int_0^\infty\int_0^\infty dE\, d\tau\, P(E,\tau)\left[\frac{\Delta}{E}\right]^2\frac{1}{k_BT} \times \operatorname{sech}^2\left[\frac{E}{2k_BT}\right]\frac{\omega\tau}{1+\omega^2\tau^2} , \tag{8}$$

where ρ is the density and τ the relaxation time of the defect states. $P(E,\tau)$ stands for the distribution of level splittings and relaxation times. It also reflects the distribution of the parameters of the defect states. The corresponding expression for the variation of the sound velocity reads

$$\frac{\delta v}{v} = -\frac{\gamma^2}{2\rho v^2}\int_0^\infty\int_0^\infty dE\, d\tau\, P(E,\tau)\left[\frac{\Delta}{E}\right]^2\frac{1}{k_BT} \times \operatorname{sech}^2\left[\frac{E}{2k_BT}\right]\frac{1}{1+\omega^2\tau^2} . \tag{9}$$

The relaxation time τ depends on the mechanism of relaxation. In most cases the relation between the asymmetry energy Δ and τ is known, so that Δ can be expressed by E and τ.

At very low temperatures relaxation takes place with the rate

$$\tau_d^{-1} = A\Delta_0^2 E \coth\left[\frac{E}{2k_BT}\right] , \tag{10}$$

via the one-phonon or direct process. Here A is a constant reflecting the coupling between the phonon bath and tunneling systems.[22] The dominance of this relaxation mechanism has been well established in many experiments carried out with glasses. At higher temperatures, i.e., above a few kelvin, multiphonon processes become increasingly important. In this case the rate is still proportional to Δ_0^2, but the temperature dependence becomes much more pronounced. In a rather simplified way these processes can be taken into account by introducing a two-phonon process which is often referred to as a "Raman process."[23] Because we are not interested in the transition from the direct to the activated relaxation, this process will not be considered further.

Since our experiments have been carried out at higher temperatures, we only have a glimpse at the predictions of the tunneling model with respect to the low-temperature properties. We start with Eq. (8) and put in the distribution function for the parameters of the tunneling systems and the expression for the relaxation time. In the limiting case of very low temperatures, one finds $Q^{-1} \propto T^3/\omega$, in agreement with experiments.[3] At higher temperatures the absorption is expected to level off, as seen in Fig. 6, and the simple relationship

$$Q^{-1} = \frac{\pi}{2} C \tag{11}$$

is found from Eq. (8). In this plateau region the internal friction is expected to be frequency and temperature independent and to be only determined by the constant $C = \bar{P}\gamma^2/\rho v^2$. In fact, the same relation should hold as well if Raman processes dominate or, more generally, if the relevant relaxation rate is proportional to Δ_0^2. From the measurements[18] mentioned above, the numerical value $C = 2.8 \times 10^{-4}$ has been deduced from the plateau. We will use this value in our further discussion and do not consider this quantity as a fitting parameter.

The variation of the sound velocity at very low temperatures is determined by two processes, the relaxation and resonant processes. The resonant process causes a logarithmic increase of the sound velocity with temperature.[24] Without going into detail we want to mention that measurements of this effect also give a direct measure of the constant C. The values found in such measurements are consistent with that mentioned above.

At higher temperatures, roughly speaking above 5 K, the potential barrier can be surmounted by thermally activated processes. For a given defect state, the rate τ_a^{-1} of this process increases exponentially with temperature. If the depth of the two wells differs by the amount Δ, one obtains

$$\begin{aligned} \tau_a^{-1} &= 2\nu_0 \cosh\left[\frac{\Delta}{2k_BT}\right] e^{-F/k_BT} \\ &= 2\nu_0 \cosh\left[\frac{\Delta}{2k_BT}\right] e^{S/k_B} e^{-V/k_BT} \\ &= \tau_0^{-1} \cosh\left[\frac{\Delta}{2k_BT}\right] e^{-V/k_BT} , \end{aligned} \tag{12}$$

where ν_0 is the vibrational frequency of the particle in a single well, i.e., $E_0 = h\nu_0/2$. We have used the free energy $F = V - TS$ (Ref. 25) instead of the standard expression for the Arrhenius-type relaxation, where only the barrier height V is taken into account. In the case of two-state systems, we expect that $S/k_B = \ln 2$, and hence $\tau_0^{-1} = 4\nu_0$, but we will see in Sec. V that $\tau_0^{-1} = 8\nu_0$ could be more appropriate to describe our results.

The integration of Eqs. (8) and (9) can only be carried out numerically. In order to gain some insight into the frequency and temperature variation of the elastic properties and into the numerical values of the important parameters, we will make some simplifying approximations, so that the integration can be done analytically. We compare the expressions obtained in this way with experimental results reported in the literature.

In the relaxation phenomena the main contribution stems from asymmetric systems since the factor $(\Delta/E)^2$ appears in the relevant equations. Therefore, we may replace in our estimates Δ by E without making a large error. Furthermore, only system with an energy splitting comparable to k_BT are important, so that E can be substituted by k_BT. Under these assumptions analytic expressions can be obtained since the double integrals (8) and (9) can be split up into the product of two simple integrals. For the relaxation rate in the case of thermally activated relaxation, we may use the simplified relation

$$\tau_a^{-1} \simeq \tau_0^{-1} e^{-(V/k_BT)} . \tag{13}$$

As shown in Fig. 6, a strong rise of the absorption is found above 5 K, which we attribute to the thermally activated process. If this process dominates, the relaxation rate is mainly determined by the activation energy. In order to calculate the internal friction and velocity change, the distribution function $P(E,\tau)$ has to be known, which can be deduced from $P(\Delta, V)$. Although different distribution functions have been proposed in the literature,[26] we see no obvious reason why the uniformity of the distribution of Δ should be restricted to small values. Since the amorphous structure is frozen in at the glass transition temperature T_g, we expect that a more or less flat distribution of the asymmetry energy extends up to k_BT_g. As far as the barrier height of the defect states is concerned, we presume a strict correlation with their tunneling parameter. If the double-well potentials consist of two well-defined harmonic potentials, the barrier height will be proportional to the square of the separation d, i.e, $V \propto d^2$. Assuming the mass of the tunneling particles to be constant, we immediately find from Eq. (4) the relation

$$\lambda = \frac{V}{E_0} \ . \tag{14}$$

This is a very coarse simplification and can only be considered as a first approximation. Furthermore, this relation is only valid for large tunneling parameters and has to be slightly modified for the general case [see Eq. (20)]. Thus we may assume in our further discussion that $P(\Delta, V) = \bar{P}/E_0$ is also uniform. Putting $\Delta \simeq E \simeq k_B T$, as discussed above, we can calculate the acoustic loss and find a linear increase with temperature:

$$Q^{-1} = \frac{\pi C k_B T}{E_0} \ . \tag{15}$$

We have applied this relation to various experimental data[14,27–31] in order to estimate the constant Ck_B/E_0 and found values in the range of $(1.5–2.8)\times 10^{-5}$ K^{-1}. It is not surprising that a large scatter of the data exists, since they are an outcome of experiments carried out with different samples and have been obtained by different techniques. Using the value $C = 2.8\times 10^{-4}$ from low-temperature experiments mentioned above, we may estimate the value of E_0. The surprisingly small value $E_0/k_B \simeq 15K$ is extracted.

The zero-point energy can also be estimated in a totally different way. It can be found from the temperature T^*, which reflects the transition from the plateau to the linear rise of the absorption. In low-frequency measurements, i.e., around 10 kHz, the transition is observed at about $T^* = 5$ K. At higher frequencies the transition, though less pronounced, occurs at roughly the same temperature. From Eqs. (11) and (15) we deduce $E_0 \simeq 2k_B T^*$, yielding the extremely low value of $E_0/k_B = 10$ K. This means that the relaxing systems are either rather heavy or exhibit extremely small force constants.

In a similar manner the qualitative behavior of the velocity can be derived. For moderately low temperatures, i.e., around 1 K, we find that the tunneling-induced relaxation processes cause a logarithmic decrease of the velocity.[23] The slope of the decrease depends on the kind of relaxation process. Therefore, the slope changes as soon as the transition from direct to multiphonon processes occurs.[20,23] Independent of the relaxation mechanism, the frequency variation at fixed temperatures is expected to be logarithmic. We will not look into the matter since we are mainly interested in the behavior of vitreous silica at higher temperatures where the velocity changes are caused by thermally activated processes. If the same approximations are applied to the internal friction, one can solve the equation for the velocity change analytically in the limiting case $\omega\tau_0 \ll 1$ and obtain

$$\frac{\delta v}{v} = \frac{C k_B T}{E_0} \ln(\omega\tau_0) \ . \tag{16}$$

As already shown by several authors and in agreement with our data in Fig. 5, the velocity of sound varies, in fact, approximately linearly with temperature between 5 and 25 K. From the data available in the literature, it can be additionally extracted that this variation is roughly proportional to the logarithm of the applied frequency. The compiled data of different authors[12,16,17,28,32–35] are shown in Fig. 8 and are rather well described by Eq. (16). From these data we extract $Ck_B/E_0 \simeq 2\times 10^{-5}$ K^{-1} and $\tau_0 \simeq 10^{-13}$ s.

Above 60 K the velocity increases again. This cannot be explained by the defect model. It seems to be a specialty of glasses with an "open" structure similar to that of vitreous silica.[36] Several explanations have been brought forward, but we do not enter in this discussion because it is beyond the scope of this paper.

According to Eq. (15) we expect the internal friction to rise linearly with temperature. In order to obtain a maximum in the absorption, an upper limit $V_{\max}$ of the distribution function for the barrier heights must exist. To estimate this cutoff in $P(\Delta, V)$, we use the fact that the main contribution to the absorption comes from systems fulfilling the condition $\omega\tau = 1$. With Eq. (13) we expect the maximum to occur at the temperature $T_{\max}$ given by

$$k_B T_{\max} = -\frac{V_{\max}}{\ln(\omega\tau_0)} \ . \tag{17}$$

Using the value $\tau_0 = 10^{-13}$ s estimated from the change of the velocity of sound and the maxima in the internal friction shown in Figs. 1 and 6, we get $V_{\max}/k_B \simeq 500$ K. Bearing in mind that the maximum is caused by the cutoff in the distribution function, we expect from Eq. (15) that $Q_{\max}^{-1} \propto T_{\max}$. In Fig. 9 we have compiled the available data[12,14,17–20,27–33,35–38] and obtained such a correlation over a frequency variation of eight orders of magnitude. Combining Eqs. (15) and (17), we find $Q_{\max}^{-1} \propto -1/\ln(\omega\tau_0)$, again in agreement with the experimental observation.

Before presenting our numerical calculations, we briefly consider the relevant barrier heights at a given

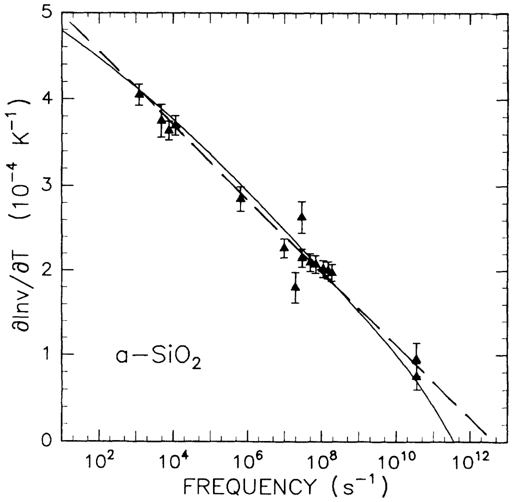

FIG. 8. Slope $\partial \ln v/\partial T$ of the linear temperature variation of the velocity of sound (measured between 5 and 15 K) vs frequency. Roughly speaking a logarithmic variation with frequency is observed and indicated by a dashed line. The data points are taken from Refs. 12, 16, 18, 28, and 32–35. Our fit is shown by the solid line.

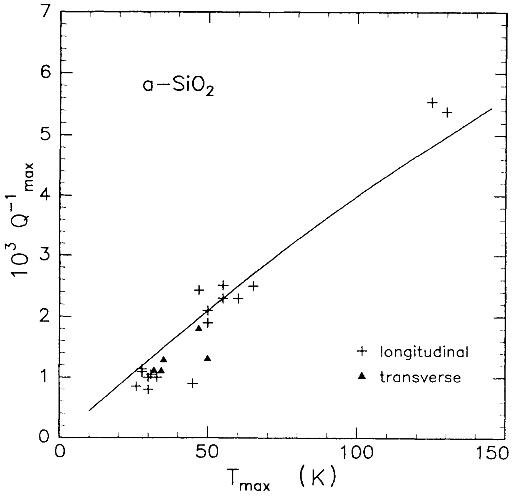

FIG. 9. Internal friction $Q^{-1}_{\max}$ of vitreous silica at the maximum as a function of the temperature $T_{\max}$ at which the maximum is observed. The data are taken from different authors and experiments at frequencies between 400 Hz and 36 GHz (Refs. 12, 14, 17–20, 27–31, and 35–38). The solid line represents our fitting curve described in the text.

temperature. In other words, we ask the question, which part of the distribution function $P(\Delta, V)$ can be investigated in acoustic measurements? For this purpose we consider those systems that fulfill the condition $\omega\tau=1$ and have an energy splitting of $E \simeq k_B T$. For the direct process we deduce

$$\ln\omega \simeq \ln T - \frac{2V}{E_0} + \ln\frac{4Ak_BE_0^2}{\pi^2} , \tag{18}$$

and for the thermally activated one

$$\ln\omega \simeq -\frac{V}{k_BT} - \ln\tau_0 . \tag{19}$$

The important point is that at a fixed frequency the barrier height V of the dominant defect states is related only to the logarithm of the temperature in the case where relaxation occurs via the direct and, without proof, for the Raman process. Therefore, experiments at low temperatures are only sensitive to a narrow range of the distribution function with small values of V. However, a linear relationship between temperature and barrier height is found for the thermally activated regime. Therefore, measurements in this temperature range seems to be a suitable tool to scan the distribution function in its full extent.

V. NUMERICAL RESULTS

We will discuss the result of our numerical calculations in two steps. The first step is to consider the behavior of vitreous silica under zero pressure. Instead of the analytical approximations made in Sec. IV, we given the full results of our numerical fits. The second step will be to discuss the influence of pressure onto the acoustic properties.

Applying the WKB method to the calculation of the tunnel splitting, we find, for two one-dimensional, harmonic potentials,

$$\Delta_0 = \frac{2E_0}{\pi}\left[\left[\frac{V}{E_0}+1\right]^{1/2} + \left[\frac{V}{E_0}\right]^{1/2}\right] \times \exp\left[-\left[\frac{V^2}{E_0^2}+\frac{V}{E_0}\right]^{1/2}\right] . \tag{20}$$

We have used this expression in our numerical calculations, although Eq. (3) would have led to nearly the same results. Furthermore, we assume that the various relaxation processes are independent of each other. This allows us to add the relaxation rates given by Eqs. (10) and (12).

To carry out the numerical integration of Eqs. (8) and (9), we have to choose a suitable distribution function for the asymmetry energy Δ and barrier height V. As mentioned in Sec. IV, we use a constant distribution for the asymmetry energy. As far as the distribution function of V is concerned, an upper limit has to exist. As a reasonable guess,[39] we assume a Gaussian-like distribution with a width σ_0:

$$P(\Delta, V) = \frac{\bar{P}}{E_0}\exp(-V^2/2\sigma_0^2) . \tag{21}$$

This Gaussian-like distribution is not normalized. It is approximately constant in the range of small barrier heights and thus leads back to Eq. (6), where the original assumption of the tunneling model is formulated. Only a weak variation is allowed for the explanation of the absorption in the plateau region and the linear temperature variation of the velocity at temperatures around 10 K. At higher barrier heights, however, the distribution has to decrease sufficiently fast to cause the required rapid reduction of the absorption above the maximum temperature. Carrying out the numerical fits under these assumptions leads, in fact, to good agreement with the experimental data in the temperature range above 10 K, i.e., in the temperature range where thermally activated processes predominate. It should be pointed out that similar fits have been carried out by several authors[26,35,40] using a distribution function which decays exponentially with the barrier height. According to our calculations, the agreement with the experiment is less satisfactory with respect to the description of the velocity changes.

Furthermore, we want to make a few remarks on the description of the low-temperature acoustic properties. The numerical calculation of the absorption at frequencies up to about 100 MHz yield a shallow minimum just before the activated process takes over. This shallow minimum has in fact been observed experimentally in many experiments.[14,18–20] The reason for this behavior lies in the fact the number of systems contributing to the relaxation process differs in the tunneling and thermally activated regimes. The real problem in fitting the acoustic properties at low temperatures by the tunneling or defect model lies in the observation that in the MHz range[14,19] the absorption at liquid-helium temperature is considerably higher than expected from the tunneling or defect model. Within the framework of the model presented here, only a very weak frequency dependence should exist. In the tunneling regime a dependence such as this can only occur if the distribution function $P(\Delta, V)$ exhibits a strong increase of the number of systems with very small barrier heights. The explanation of this effect is, however, still open.

We have carried out numerical fits for different frequencies, temperatures, and pressures. Before we compare them with experimental data, we want to state that five parameters enter the relevant equations. However, already two of them, namely, C and A, are determined by low-temperature measurements. Therefore, we use the values $C=2.8\times10^{-4}$ and $k_B^3 A=1\times10^8$ $\mathrm{K}^{-3}\mathrm{s}^{-1}$ without further discussion. Thus only the three free parameters, namely, the zero-point energy E_0, the width of the distribution function σ_0, and the entropy S, are left and are extracted from our fitting procedure.

Let us start the discussion with the fit of the temperature variation of the sound velocity in the temperature range between 5 and 25 K. If the distribution function $P(\Delta, V)$ were constant, the temperature variation of the velocity would be strictly linear as indicated by Eq. (16). Because of the decrease of the number of systems with higher energy barriers, the velocity change levels off at higher temperatures. In the experiment, however, not only a leveling off, but also a minimum is observed. As pointed out, our model does not account for the increase of the velocity at higher temperatures. Considering the decrease, we find, in fact, a linear variation with temperature, and excellent agreement is obtained with respect to the frequency variation of the slope $\partial \ln v/\partial T$ as shown in Fig. 8 by the solid line. In the fitting procedure the value $E_0/k_B=12$ K for the zero-point energy has been used. The position of the fitting curve shown in Fig. 8 is only moderately sensitive to the exact value of τ_0. Because of the scatter of the experimental points, the value of τ_0 can only be determined with a limited accuracy. Consistent with the fit of the internal friction discussed below, we have chosen $\tau_0=5\times10^{-13}$ s, implying that the entropy S has to be different from the one expected for a two-state system. This value is also not far from our estimates in Sec. IV made under several restrictions. A closer inspection of the fitting curve shows that the frequency variation is not strictly logarithmic. The reason for this is twofold. At low frequencies the deviation from the constant distribution $P(\Delta, V)$ becomes noticeable; at high frequencies the assumption $\omega\tau_0 \ll 1$ is no longer valid. The curve shown in Fig. 8 demonstrates that we are able to predict the temperature variation of the sound velocity correctly at temperatures between 10 and 25 K in a frequency range which covers nearly eight orders of magnitude.

After having fixed the parameter E_0 by the velocity change, only σ_0 and S are free parameters for the fit of the internal friction. At first glance it seems to be relatively simply to obtain the correct position $T_{\max}$ of the absorption maximum because $T_{\max}$ can be adjusted by the cutoff of the distribution function $P(\Delta, V)$, i.e., by the width σ_0 of the Gaussian distribution. The difficulty lies, however, in the wide frequency range where such measurements have been carried out and which we want to describe. According to Eq. (17), the position of the maximum is also influenced by the value of τ_0. Our calculations agree quite well with our experimental results and with low-frequency measurements reported in the literature when $\sigma_0/k_B=445$ K and $S/k_B=\ln 4$. The latter value is surprising since we had expected to find the value ln2 for the entropy because we were considering two-state defects. We will comment on the particular aspect at the end of this section. The relation between the height $Q_{\max}^{-1}$ and position $T_{\max}$ of the absorption peak is plotted in Fig. 9. The deviation from strict linearity is caused by the nonuniformity of $P(\Delta, V)$.

In addition, we are now able to describe the temperature variation of the absorption. In Figs. 1 and 6 examples are shown for 11.4 kHz and 36 GHz. We want to point out that no new parameter has been introduced to fit the magnitude of the internal friction. Minor discrepancies are not surprising if we take into account that our model is extremely simple. We shall discuss some possible improvements at the end of this section.

How can we explain the experimental features observed under pressure within the framework of our model? The strong pressure dependence of the absorption indicates that pressure has considerable influence on the distribution of the barrier heights. In a first approximation we assume that $\bar{P}$ and E_0 remain constant under pressure and only the width of the distribution function $P(\Delta, V)$ is changed. In this case the low-temperature acoustic properties are expected to be hardly affected by pressure, which is also in agreement with former experiments by ultrasonic techniques.[14] We introduce a quadratic relation between width σ and pressure p for reasons we will discuss below and write

$$\sigma(p)=\sigma_0+ap^2\ , \tag{22}$$

where a is a constant. First of all, this relation for the width allows us to describe the rise of the internal friction and its leveling off at higher pressures at room temperature. In Fig. 2 the numerical fit with the value $a/k_B=240\ \mathrm{K(GPa)}^{-2}$ is shown together with the experimental data. At small pressures the absorption rises because more and more systems are generated which are able to contribute to the absorption. As soon as the width of the distribution function becomes so wide that the barrier height of those systems, giving the dominant contribution to the internal friction or the velocity change, is smaller than σ, the absorption increases less rapidly with pressure. In other words, as long as the absorption is measured at the high-temperature side of the peak, a strong pressure increase is observed. If the measurement is carried out at the low-temperature side, the pressure dependence will level off.

The pressure dependence of the width of $P(\Delta, V)$ introduced by Eq. (22) also leads to the correct prediction of the temperature variation of the internal friction at different pressures. The proposed broadening of the distribution under pressure causes only a moderate increase of the absorption at low temperatures. It leads, however, to a shift of the peak to higher temperatures and to a drastic increase of the absorption at room temperature. In Fig. 3 the calculated behavior of the absorption is shown together with the experimental results. The agreement is satisfactory, taking the large scatter of the experimental data in high-pressure measurement into account.

At first glance, absorption and velocity under pressure seem to behave completely different. Whereas the absorption is strongly influenced by pressure, hardly any change is seen in the linear decrease of the velocity at low temperature. But this different behavior is only found at low temperature where the absorption depends quite weakly on pressure as well. This can be understood if the height of the distribution function $\bar{P}$ and deformation potential are more or less constant.[41] Thus the only variation to be regarded in the coupling factor $C=\bar{P}\gamma^2/\rho v^2$ is the decrease of the velocity shown in Fig. 4. An open question is the reason for the shift of the velocity minimum. It is partially caused by the increase of σ with pressure, but in addition the slope of the high-temperature rise is reduced. Obviously, the mechanism causing the velocity rise at higher temperatures is also strongly influenced by the application of pressure.

In summary, the assumptions of a Gaussian-like distribution of the barrier heights and of an increase of its width with pressure lead to a good description of the experimental situation. This means that the application of pressure increases the activation energy of the double-well potentials and at the same time generates new systems. How can this be understood on a microscopic basis?

VI. MICROSCOPIC IMPLICATIONS

Vitreous silica is built from SiO_4 tetrahedra with a silicon atom at their center. The tetrahedra are sharing the oxygen atom at each corner with another tetrahedron. The linkage at the corner is rather weak and represents the softest spring of the system. It has been proposed that the low-lying excitations in vitreous SiO_2 originate from the coupled rotation of these tetrahedra.[42] This idea has recently been supported by measurements of inelastic neutron scattering.[43] In a regular array of SiO_4 tetrahedra, such a rotational motion is harmonic in a first approximation and extends over the whole solid. It is assumed that in vitreous silica this vibration is spatially localized, although some neighboring tetrahedra are involved in this motion.[44] In addition, one can imagine that because of the irregularity of the environment of a vibrating tetrahedron, this unit can have two positions of equilibrium, leading back to the picture of double-well potentials. The entropy $S/k_B=\ln 4$ extracted from our fitting procedure indicates that the moving particles, i.e., very likely the rotating SiO_4 tetrahedra, have in average four stable positions of equilibrium. This result does not seem to be unreasonable since a rotation around different axes is possible. At very low temperature, however, the approach of double-well potentials is appropriate since tunneling will occur only between the lowest states.

But this is not the only possible explanation for the high value of the entropy deduced in our fit. Another, even more likely explanation could be the following. In general, the potential will not be strictly harmonic until the intersection of the two curves results in a sharp peak, but will exhibit a round maximum. In this case Eq. (14) does not hold anymore. If we replace Eq. (14), for example, by $\lambda=2V/E_0$, put $S/k_B=\ln 2$, and carry out the fitting procedures once again, we end up with practically the same results. Thus we cannot distinguish between these two possible interpretations without knowing more about the microscopic nature of the defect states. It has already been stressed in the literature[21] that a particular relation for the tunnel splitting cannot be justified unless the microscopic symmetry of the potential is known.

The application of pressure does not change the shape of the SiO_4 tetrahedra because they are rather rigid units. According to NMR investigation, pressure causes a slight reduction of the average bond angle at the oxygen atom.[45,46] Although a quantitative description of the pressure dependence of the width of $P(\Delta,V)$ based on a microscopic model seems to be rather difficult, it could be a key to a more profound understanding of the microscopic nature of the defect states. Qualitatively, the following arguments might hold. With decreasing bond angle the rotational motion becomes increasingly hindered and the positions of equilibrium are more and more pronounced, resulting in an increase of the average barrier heights. Because of the ordinary compressibility of glasses, the distance between adjacent silicon atoms will be reduced proportional to the applied pressure. Since the bond length of covalent bonds is practically constant, the angle of rotation necessary for SiO_4 to go from one potential well to the other should increase proportional to pressure. Furthermore, the barrier height depends quadratically on the configurational coordinate. Consequently, it seems to be quite natural that the barrier height increases proportional to p^2. At the same time tetrahedra, having only one well-defined site at zero pressure, are now driven into positions which exhibit more potential minima. In this way new defect states are formed which have small barriers and the distribution function becomes generally wider. However, we are not able to explain why $\bar{P}$ should be almost independent of pressure. Of course, even under high pressure, it will only be a small fraction of the existing SiO_4 tetrahedra which act as defect states.

Finally, we want to mention that the quadratic pressure dependence of the barrier height has also consequences for the deformation potential. In Eq. (7) we have neglected the contribution of $\partial\Delta_0/\partial e$ to the deformation potential γ. Using the Eqs. (3), (14), and (22), it can be easily shown that this contribution is expected to be proportional to p and the change of Δ_0, caused by a weak strain field, can therefore be neglected. In other words, the shape and size of the double-well states is only slightly changed if the pressure applied is small. In contrast, Δ is caused by the asymmetry of the environment. Consequently, $\partial\Delta/\partial e$ is pressure independent in first approximation.

Clearly, some important improvements of our simple model should be made. First of all, the expression for the relaxation we used in the whole temperature range can only be correct under certain circumstances. It is obvious that Eq. (12) used for thermally activated processes is not valid in the simple form if $k_BT>2E_0$. Such inaccuracies should have a minor influence on our numerical results because they are covered by the integrations over two distribution functions. However, the distribution function $P(\Delta, V)$ extracted from our fitting procedure might only be qualitatively correct for the same reason. In addition, we cannot exclude that it is temperature dependent itself. Discrepancies between experimental data and theoretical description become especially noticeable between 5 and 10 K at low frequencies. In this temperature range the transition from one- to multiphonon relaxation takes place and our simple treatment is not appropriate. Better agreement can also be obtained if we allow for a distribution of the zero-point energy E_0. Such a distribution seems to be a natural consequence of the random structure. In order to minimize the number of free parameters we did not pursue this idea. Furthermore, the calculated absorption drops off too rapidly at the high-temperature side of the absorption peak. Apparently, the tail of the distribution of $P(\Delta, V)$ should be flatter than given by a Gaussian. Again, we did not consider this aspect in more detail.

Finally, we want to point out that the defect model developed in our theoretical description is too simple to be able to account quantitatively for all observations. The "soft-configuration model" could probably give a more adequate description.[47,48] Unfortunately, it has not been worked out sufficiently to be applicable to the fitting of our experimental observation.

VII. SUMMARY

We have investigated the acoustic properties of vitreous silica by Brillouin-scattering experiments in the temperature range from 50 to 300 K. Under high pressure strong changes in the elastic behavior are observed which can be understood by the defect model developed in this paper. Starting from the tunneling model, which is generally used to describe the low-temperature properties of amorphous solids, we have extended its range of validity to higher temperatures. We assume that the defect states in glasses gradually transform from tunneling systems to classical defect states. Whereas relaxation via tunneling processes dominate below 5 K, thermally activated processes take over above that temperature. Our experimental results, as well as the acoustic measurements reported in the literature, can be quantitatively explained by the assumption that defect states have an extremely low zero-point energy and by a distribution function of their barrier height following approximately a Gaussian. With increasing pressure this distribution function becomes wider, indicating that the activation energies are growing and new defect states are generated. We believe that the acoustic properties of other glasses as well can be treated in a similar way. Thus it seems that our results are a further step on the way to understand the unusual dynamical behavior of glasses generally.

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