Spectral Shape of Relaxations in Silica Glass

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Precise low-frequency light scattering experiments on silica glass are presented, covering a broad temperature and frequency range (9 GHz $< \nu <$ 2 THz). The spectra show a power-law low-frequency wing of the relaxational part of the spectrum with an exponent α proportional to temperature in the range $30 < T < 200$ K. A comparison of our results with those from acoustic attenuation experiments performed at different frequencies shows that this power-law behavior rather well describes relaxations in silica over 9 orders of magnitude in frequency. These findings can be explained by a model of thermally activated transitions in double well potentials.

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Relaxations are a characteristic feature of glasses. They show up as a broad quasielastic contribution in neutron and light scattering spectra [1–3] and also as a damping of sound waves [4–8] or as a dielectric loss [9]. The acoustic attenuation, or equivalently the internal friction Q^{-1}, of silica glass (a-SiO$_2$) obtained at different frequencies demonstrates the presence of a broad distribution of relaxation rates [4,5]. For temperatures above some 10 K it is assumed that relaxations are due to thermally activated transitions in asymmetric double well potentials (ADWP's) [5,10,11], where the same ADWP's relax via tunneling at low temperatures ($T \lesssim 1$ K) [12]. Within this model it is possible to extract the distribution of barrier heights $g(V)$ from the experimental data [5,7,8,13].

Although relaxations in silica have been extensively studied so far, a spectroscopic work that covers a broad frequency range is still missing. Acoustic and dielectric studies usually measure at a single frequency only, and spectroscopic techniques like neutron and Raman scattering have typically a low-frequency limit around 100 GHz and therefore cover only a small part of the relaxational contribution, in a range where it is difficult to extract the spectral shape of relaxations. Recently, it has become possible to obtain low-frequency light scattering spectra of glasses at temperatures well below T_g, extending the spectral resolution to frequencies below 10 GHz for some polymeric and anorganic glasses [13,14].

We refine this approach in order to study the much lower signal levels available for silica. Our data for the first time show the spectral shape of relaxations in silica glass over a broad temperature and frequency range. This enables us to perform a cross test on models about relaxations in glasses, regarding the frequency and temperature dependence of relaxations. Furthermore, we will compare our data with internal friction data to examine whether both techniques probe the same kind of relaxations.

Depolarized inelastic light scattering spectra of a sample of Suprasil 300 (synthetic silica, Heraeus, <1 ppm of OH$^-$ groups) were obtained using an Ar$^+$ laser (514.5 nm, 400 mW) and a six-pass Sandercock tandem Fabry-Perot interferometer (FPI) [15]. The sample was mounted in a dynamic helium cryostat. The Suprasil windows of the cryostat are antireflection coated, and the cold windows are mounted tensionless in order to avoid tension induced birefringence. Since the signal levels available from the scattering of silica are much lower than for other glasses studied so far [13,14], the optical scheme was improved and optimized for alignment on low intensities [16]. We use a 180° backscattering geometry with a selection of depolarized scattering. Here the laser beam enters a Glan-Taylor polarizer (extinction 10^{-6}) as the extraordinary beam. The polarized component of the light is reflected and focused on the sample. The scattered light is collected by the same lens and passes through the same Glan-Taylor prism, transmitting the depolarized component. The scattered light is collected within an angle of about 4°. Special care was taken to avoid contributions to the signal from the windows of the cryostat and the polarizer [16].

We recorded spectra with the free spectral ranges (FSR's) of 1000 and 150 GHz over two spectral ranges on either side of the elastic line. The experimentally determined finesse of the spectrometer is better than 120 and typically about 140. In order to suppress higher transmission orders of the tandem (multiples of 20 FSR's could give contributions to the signal for a Sandercock tandem FPI [13,17–19]), we use a prism in combination with either of two interference filters of a width of 10 nm and 1150 GHz (FWHM). The contrast of the spectrometer was determined to be better than 10^9 at all frequencies. The absence of possible contributions from either the elastic line or from higher transmission orders was further validated by measurements at a low temperature, $T = 6$ K, where the anti-Stokes side of the spectrum showed no deviations from the dark count level of our detector. Since the vibrational part, which could lead to parasitic contributions, rises slower with temperature than the signal from relaxations, it is clear that signals from higher transmission orders do not disturb our spectra. Further experimental details can be found elsewhere [16].

The upper part in Fig. 1 displays the intensity of the depolarized backscattering spectra of silica. At high

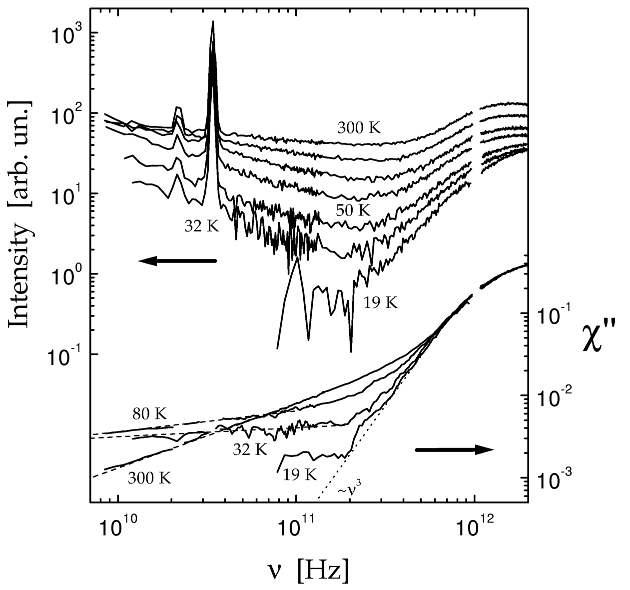

FIG. 1. Light scattering spectra of silica: Intensity spectra for the temperatures 300, 200, 125, 80, 50, 32, and 19 K (from top to bottom, left scale) and the resulting susceptibility spectra $\chi''(\nu)$ for the temperatures 300, 80, 32, and 19 K (bottom, right scale, smoothing over five points) are shown. The dashed lines correspond to power-law fits of the low-frequency part of the susceptibility spectra.

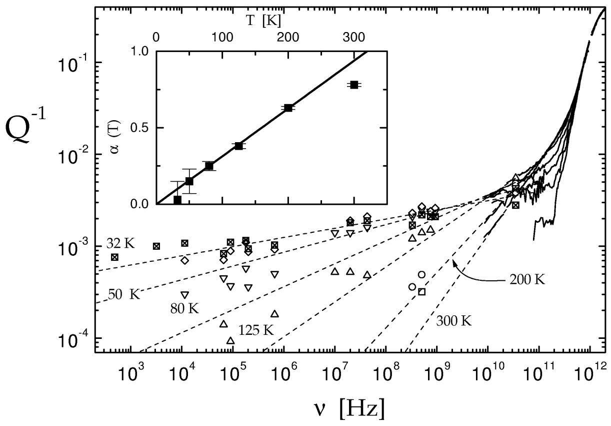

FIG. 2. Light scattering susceptibility (solid lines) normalized to internal friction obtained from the Brillouin lines at 35 GHz [20]. Dashed lines are power-law fits to the light scattering data. Symbols show internal friction at the same temperatures (references in the caption of Fig. 3) (□: 300 K, ○: 200 K, △: 125 K, ▽: 80 K, ◇: 50 K, and ⊠: 32 K). The inset shows the exponent $\alpha(T)$ of the low-frequency wing of the light scattering susceptibility. The solid line corresponds to a proportionality fit up to 200 K and yields $\alpha = T/319$ K.

frequencies the boson peak is observed. The signal passes through a minimum and shows features of a central peak. At frequencies of 35 and 20 GHz two narrow peaks are observed that correspond to the longitudinal and transversal Brillouin lines and are due to a leakage from imperfect polarization and to the finite aperture, respectively. Apart from the Brillouin lines, the central peak shows a power-law frequency dependence, and its shape considerably changes with temperature.

The susceptibility representation, $\chi''(\nu) = I/[n(\nu) + 1]$ of the Stokes side, excludes the trivial temperature dependence due to the Bose factor $n(\nu)$. The susceptibility data in Fig. 1 have been smoothed by adjacent averaging over five points. The presence of two contributions to the low-frequency light scattering in glasses can be distinguished by the different temperature dependence: the vibrational contribution dominates at high frequencies and scales with the Bose factor (i.e., the susceptibility is temperature independent), whereas the relaxational spectrum that dominates at lower frequencies strongly changes with temperature. As can be seen by the crossing of the spectra at different temperatures, this is not simply due to an increase of the susceptibility with temperature as would be expected in the case of higher-order scattering processes. For all temperatures, the low-frequency wing of our spectra shows a power-law behavior. The temperature dependence of the exponent, $\alpha(T)$, is shown in the inset in Fig. 2: α is proportional to temperatures up to 200 K, with $\alpha = T/319$ K.

Let us see if this frequency and temperature dependence of relaxations can be described within our present understanding of glasses. In 1955 Anderson and Bömmel attributed relaxations in silica to thermally activated processes with a broad distribution of relaxation times [4]. Theodorakopoulos and Jäckle calculated the light scattering due to structurally relaxing two-state defects and have shown its relation to the acoustic attenuation [10]. This approach was refined by Gilroy and Phillips [11]. The ADWP's responsible for the thermally activated transitions are assumed to be the same that at lower temperatures ($T \lesssim 1$ K) relax via tunneling and are responsible for the low temperature anomalies of glasses, i.e., the parameters for the potential wells are taken from the tunneling model [12]. Following the assumption that the distribution of asymmetry parameters Δ is flat, the light scattering susceptibility $\chi''(\nu)$ and the internal friction Q^{-1} depend only on the distribution of barrier heights $g(V)$ [7,8,10,11]:

$$\chi''(\nu) \propto Q^{-1} \propto \int_0^\infty \frac{2\pi\nu\tau}{1 + (2\pi\nu\tau)^2}\, g(V)\, dV\,. \qquad (1)$$

Here the relaxation time $\tau = \tau_0 \exp(V/k_B T)$, where τ_0 is the fastest relaxation time that occurs. Assuming an exponential distribution of barrier heights, $g(V) = V_0^{-1} \exp(-V/V_0)$, the model predicts for the low-frequency wing of the relaxation spectrum, $\nu \ll (2\pi\tau_0)^{-1}$, a power-law susceptibility spectrum with an exponent proportional to temperature [11]: $\alpha = k_B T/V_0$. The inset in Fig. 2 shows that the exponents of our silica data agree with the model for temperatures below 200 K and we obtain $V_0/k_B = 319$ K. At 300 K the observed exponent is less than expected from the model. Since the exponent of the susceptibility cannot become higher than 1 for relaxation processes and is already close to 1 at room temperature, the deviation at 300 K comes as no surprise. Indeed at higher temperatures up to T_g it is found that the exponent remains constant at 1 [26]. The simple assumption of thermally activated relaxations over barriers with an exponential distribution of barrier heights can therefore well account for the observed temperature dependence of the spectral shape of the low-frequency light scattering data of silica.

Within the model of Theodorakopoulos and Jäckle the distribution of activation energies is reflected in the light scattering susceptibility just in the same manner as in the internal friction [i.e., $\chi''(\nu) \propto Q^{-1}$; cf. Eq. (1)] [10,11]. Taking the internal friction at a frequency that is also accessible to light scattering spectroscopy, the proportionality constant can be eliminated in order to directly compare the results of both techniques. In Fig. 2 we plot the susceptibility data of Fig. 1 scaled to the internal friction measured at 35 GHz [20]; a single factor is used for all spectra, showing that the temperature dependence of $\chi''(\nu)$ around 35 GHz is the same as that of the internal friction. Acoustic data from different experiments have a scatter of about a factor of 2, and within a factor of 2 follow the extrapolations of the light scattering data. It appears that relaxations indeed show up in the same manner for both techniques and that with good approximation the spectral shape of relaxations in silica shows a power-law behavior with an exponent $\alpha = T/319$ K over the whole available frequency range 500 Hz $< \nu <$ 500 GHz.

This can be further demonstrated by comparing the distributions $g(V)$ of the barrier heights obtained from the different experiments. Equation (1) can be further simplified, assuming a broad distribution of barrier heights $g(V)$. In this case the susceptibility spectrum $\chi''(\nu)$ and the internal friction $Q^{-1}(T)$ for $2\pi\nu\tau_0 \ll 1$ directly reflect the distribution of correlation times and thus the distribution $g(V)$ [8]:

$$\chi'' \propto Q^{-1} \propto T g(V), \quad \text{where } V = k_B T \ln(1/2\pi\nu\tau_0)\,. \tag{2}$$

Assuming that $g(V)$ is temperature independent and that thermally activated transitions determine the light scattering spectra and the internal friction at temperatures above some 10 K, this distribution of barrier heights can be directly extracted from the data by rescaling the axes with T. Explicitly, we multiply the $\log(\nu)$ axis by T and divide the Q^{-1} and χ'' axes by T.

Then a master curve for $g(V)$ should result for the rescaled $\chi''(\nu)$ spectra and for the acoustic data $Q^{-1}(T)$ for the different frequencies. Since the amplitude of the light scattering data has already been fixed with respect to the acoustic data, the only parameter for the rescaling is $\nu_0 = (2\pi\tau_0)^{-1}$. Unlike the acoustic experiments our spectra cover this cutoff frequency at the transition from the power-law relaxational contribution to the vibrations in the range of the boson peak (cf. Fig. 1). From the light scattering spectra we obtain $\nu_0 = 800$ GHz (i.e., $\tau_0 = 0.2$ ps), which is in good agreement with previous results taken from acoustic data [5,10], and we use this value for the rescaling of all the data. For the rescaling of the light scattering data we use the frequency range where the power law holds and where the contribution from vibrations to the spectra is negligible. In principle, the distribution $g(V)$ can be obtained from a single experiment at one frequency (cf., e.g., [7,8]). The light scattering experiment, however, probes the temperature and frequency dependence of the susceptibility simultaneously, allowing a cross test of the model [13].

Figure 3 shows the result of this rescaling procedure. The light scattering data from the different temperatures show an excellent agreement and the exponential distribution as discussed above. Within the scatter of the acoustic data of about a factor of 2, we obtain a master curve for all the available data ($10 < T < 200$ K). The rescaling of the abscissa involves both the temperature and the frequency of the data. Therefore at a fixed barrier height of say $V/k_B = 200$ K, we compare data that have been obtained at a temperature of 200 K and a frequency of about 200 GHz with those obtained at a temperature of 10 K and a frequency of 500 Hz. Considering this range, it is indeed surprising that the scaling works so well. The rescaled acoustic data cover the range both above and below the temperature of the loss peak found in silica at temperatures between some 25 and 130 K [5,6]. (In Fig. 2 the presence

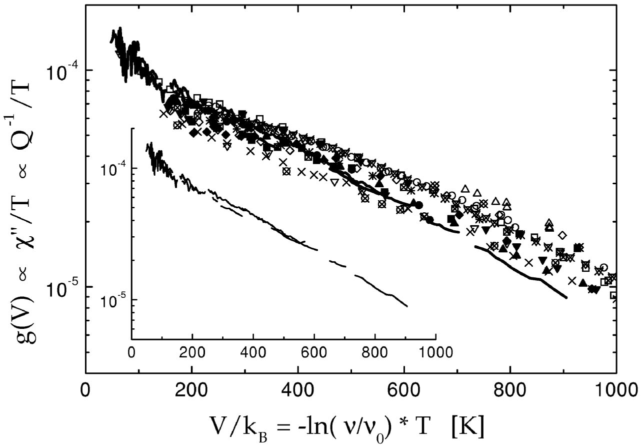

FIG. 3. Distribution of barrier heights $g(V)$ as obtained from the different techniques at different temperatures and frequencies by rescaling the data. Solid lines: light scattering; symbols: internal friction (solid squares: 35 GHz [20], solid circles: 930 MHz [21], solid up triangles: 748 MHz [21], solid down triangles: 507 MHz [21], solid diamonds: 330 MHz [21], open squares: 43 MHz [22], open circles: 20 MHz [4], open up triangles: 10 MHz [23], crosses: 660 kHz [11], open down triangles: 201 kHz [23], open diamonds: 180 kHz [7], crossed squares: 90 kHz [24], crossed circles: 66 kHz [23], crossed down triangles: 11.4 kHz [6], crossed circles: 3170 Hz [25], stars: 484 Hz [25]). The inset shows the rescaling of the light scattering data alone ($T = 200$, 125, 80, 50, and 32 K).

of this peak is not seen at low frequencies, because the lowest temperature plotted is 32 K.) Taking acoustic data alone, it was found that a modified Gaussian distribution describes the data better than the exponential distribution obtained from our light scattering data [7]. This is demonstrated by the fact that some of the acoustic data show a slight curvature on the semilogarithmic plot in Fig. 3, which is absent for the rescaled light scattering data [27]. However, the simple model with only two parameters, τ_0 and V_0, rather well describes relaxations in silica over a broad temperature and frequency range.

In conclusion, we extend existing light scattering data on silica by about 1 order of magnitude to lower frequencies, covering a broad range in temperature down to some 20 K. Our data for the first time reveal the spectral shape of relaxations over more than one decade in frequency, where relaxations clearly dominate over the vibrational contribution to the spectrum. The relaxations show a power-law spectral shape at low frequencies with an exponent α proportional to temperature. Our data are in good quantitative agreement with a model attributing relaxations in glasses to thermally activated transitions with an exponential distribution of barrier heights $g(V)$. We further compare the light scattering susceptibility $\chi''(\nu)$ with the internal friction Q^{-1} and find that within a factor of 2 the power-law behavior extends down to frequencies of some 500 Hz. Therefore, for temperatures above ~ 10 K, relaxations in silica can be described by two single parameters, $\nu_0 = 800$ GHz and $V_0/k_B = 319$ K, for all frequencies extending up to the onset of the boson peak. Although it is known that this model in its simplest form presented here does not work for all glasses [13,14], we believe that our demonstration, that the model works remarkably well for silica, a paradigmatic glass, should be considered in any refinement of models describing relaxations in glasses.

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