Structural Relaxation in Vitreous Silica

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The temperature dependence of the inelastic neutron-scattering intensity from vitreous silica has been studied between 50 and 300 K down to frequencies of 150 GHz. Above 500 GHz one finds essentially harmonic behavior. Low-frequency anharmonic behavior can be described by a relaxational model using parameters determined from ultrasonic measurements. The dynamic structure factor shows that relaxation involves coupled rotational jumps of SiO₄ tetrahedra, with a jump width of the atoms smaller than 0.8 Å. These results support the hypothesis of a common origin of low-temperature glass anomalies.

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Although low-frequency excitations in glasses have been studied extensively over the last few years¹⁻³ their nature remains a puzzle. In addition to sound waves, common to both glasses and crystals, glasses appear to contain three different kinds of "excess" excitations. First, infrared,⁴ Raman,⁵ thermal,^{1,3} and inelasticneutron³ studies show a density of harmonic modes in the range 200 GHz to 1 THz over and above the soundwave (Debye) contribution. Both heat-capacity and quantitative inelastic-neutron measurements³ in vitreous silica, for example, give a density of states up to 8 times larger than the Debye value calculated from the measured sound velocities (up to 500 GHz). The neutron experiment also identifies the local motion involved in these excess modes as harmonic libration of coupled SiO₄ tetrahedra.

Second, both Raman^{5,6} and, less clearly, infrared⁴ measurements below room temperature show a relaxational or quasielastic contribution to the excitation spectrum, reminiscent of states seen in acoustic studies^{1,2} of thermally activated relaxation processes in a range of glasses. However, attempts to link optical and acoustic measurements by the description of relaxation with a model based on *symmetric* double-well potentials^{5,7} have not been successful in matching both the temperature and frequency dependences of the quasielastic contributions.

The third group of additional excitations comprises the tunneling or two-level states^{1,8} studied in a wide range of glasses between 10 mK and 1 K. Results of thermal, acoustic, and electrical measurements have been successfully interpreted and related by theory although in most cases the microscopic nature of tunneling states is as yet

unknown.

The lack of any microscopic picture of low-frequency excitations has meant that no convincing synthesis of these three classes of phenomena has been possible, and each has usually been studied separately. In this Letter we report a study of quasielastic neutron scattering in vitreous silica which allows us to develop a picture of the microscopic motion involved in relaxation similar to that carried through previously³ for excess harmonic modes. Analysis of the results using a distribution of *asymmetric* double-well potentials allows a consistent interpretation of all relaxation phenomena.

The measurements were done on two cold-neutron time-of-flight spectrometers, the IN6 at the Institut Laue-Langevin at Grenoble and the SV5 at the reactor DIDO at Jülich. The IN6 with its intensity and good resolution was used to study the temperature dependence of the inelastic scattering. Since the IN6 measurements were restricted in momentum transfer O to values below 2.6 Å $^{-1}$, the measurements at room temperature were extended to 4.2 Å⁻¹ on the SV5 at Jülich adapted to measure relatively high Q values with good resolution (FWHM 0.2 meV = 50 GHz). The difficulty of these measurements is the determination of a small inelasticscattering contribution very close to the elastic line where counting rates are 2 to 3 orders of magnitude higher. Therefore one has to subtract both the emptycontainer background and the tail of the elastic line determined separately in a long vanadium run. On the SV5 these two contributions together were twice as high as the signal itself, so that long measuring times (20 d) were required.

The static structure factor is plotted as a function of Q



FIG. 1. Momentum-transfer dependence of neutron-scattering intensities: (a) elastic, (b) inelastic at 220 GHz (from 150 to 290 GHz), and (c) at 1 THz (from 0.7 to 1.3 THz). The line in (b) is a fit to the points in (c).

in Fig. 1(a) to show the excellent agreement between measurements made on the two spectrometers. A combination of IN6 and SV5 measurements of the dynamic structure factor, calibrated against the elastic intensity to give absolute values, is shown in Figs. 1(b) and 1(c) at 220 GHz and 1 THz, respectively. Within experimental error the dynamical structure factor is the same for all frequencies, so that the measured intensity can be characterized by a single parameter ΔI which is taken as the difference between counting rates at 2.6 and 0.6 Å⁻¹ at a given temperature and frequency, effectively subtracting the *Q*-independent multiple-scattering background from the data.

 ΔI is plotted in Figs. 2(a) and 2(b) for two frequencies against the product of the Bose factor f_B (essentially proportional to temperature in this regime) and the Debye-Waller factor e^{-2W} derived from the temperature dependence of the elastic intensity at 2.6 Å⁻¹. At 700 GHz the intensity varies linearly with temperature, as expected for harmonic vibrations, and is in quantitative agreement with the density of states derived from the heat capacity.³ In contrast, at 220 GHz the intensity varies approximately quadratically below 150 K, and at



FIG. 2. Temperature dependence of inelastic neutronscattering intensities at (a) 700 GHz, and (b) 220 GHz (see text). The dashed line in (b) denotes the harmonic contribution. (c) The temperature dependence of the Raman scattering at 5 cm⁻¹ (upper curve) and 10 cm⁻¹ (300 GHz), together with a fit derived from ultrasonic data (see text).

room temperature is larger by a factor of 3 than that calculated for harmonic vibrations with use of the density of states derived from the heat capacity.³ At low temperatures ΔI approaches the expected harmonic value. The excess intensity, the difference between the solid and dashed curves in Fig. 2(b), decreases with increasing measuring frequency, and is undetectable above 600 GHz at room temperature or below.

Quantitative analysis is based on a classical treatment of the asymmetric double-well potential, shown in Fig. 3. The coherent neutron cross section is given by

$$\frac{d^2\sigma}{d\Omega\,d\omega} = \frac{k_f}{k_i} \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{ij} b_i b_j \langle e^{i\mathbf{Q}\cdot\mathbf{r}_j(t)} e^{-i\mathbf{Q}\cdot\mathbf{r}_i(0)} \rangle dt,\tag{1}$$

where \mathbf{k}_i and \mathbf{k}_f are the initial and final neutron wave vectors, $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$, b_j is the coherent scattering length of atom j, and $\mathbf{r}_j(t)$ is the position vector of atom j at time t. The sum is over all pairs ij and the brackets denote a thermal aver-

age. In the model, an atom j can jump between positions $\mathbf{R}_j + \mathbf{d}_{j/2}$ and $\mathbf{R}_j - \mathbf{d}_{j/2}$, where \mathbf{R}_j is the average position vector and \mathbf{d}_j the jump vector. The thermal average in Eq. (1) can be calculated from the dynamics of the double well. After our summing over atom pairs, Fourier transforming in time, and integrating over double-well potentials, the inelastic (quasielastic) cross section is given by

$$\frac{d^2\sigma}{d\,\Omega\,d\omega} = \frac{1}{\pi} \frac{k_f}{k_i} \int \int \frac{\tau}{1+\omega^2 \tau^2} \operatorname{sech}^2 \left[\frac{\Delta}{2k_{\mathrm{B}}T} \right] I^{(1)}(Q) g(\Delta,\tau) d\Delta d\tau, \tag{2}$$

where the relaxation rate τ^{-1} is given by the sum of the jump rates Γ_1 and Γ_2 (Fig. 3), $g(\Delta, \tau)$ is the distribution function per unit volume for asymmetry Δ and relaxation time τ normalized to the total number of relaxation states, and

$$I^{(1)}(Q) = \left| \sum_{j} b_{j} e^{-W_{j}} e^{i\mathbf{Q}\cdot\mathbf{R}_{j}} \sin(\mathbf{Q}\cdot\mathbf{d}_{j}/2) \right|^{2}, \qquad (3)$$

where e^{-W_j} is the Debye-Waller factor for atom j and the sum is over all atoms in the relaxing entity. One important feature arising from the sech² factor in Eq. (2) is that the quasielastic scattering increases in magnitude with increasing temperature, in agreement with experiment but not predicted by the symmetric-well model, where the Lorentzian emerges with its full weight from the elastic line as temperature increases. A related point has been made in connection with modeling of the temperature dependence of the acoustic attenuation.^{9,10}

Equation (2) is identical in form to the equivalent cal-

culation for Raman scattering^{5,7} except for the replacement of $I^{(1)}(Q)$ by a factor proportional to the polarizability. Both Raman and neutron quasielastic-scattering intensities should therefore have the same frequency and temperature dependences if both arise from relaxation. This is an example of a more general result that follows from the interpretation of both Raman⁵ and inelastic neutron scattering¹¹ as space and time Fourier transforms of correlation functions which in the limit of low Qare equivalent when both arise from the same physical process. The similarity between the temperature and frequency dependence of quasielastic Raman and neutron intensities, shown in Figs. 2(b) and 2(c), therefore provides strong *experimental* evidence for a common origin.

Relaxation contributions to ultrasonic and infrared absorption, analyzed for the same model, give results which contain an additional factor of $\omega^2 T$ in the classical limit⁵, so that the ultrasonic absorption, for example, is given by¹⁰

$$\alpha = \frac{\gamma^2}{\rho v^3 k_{\rm B} T} \int \int \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \operatorname{sech}^2 \left[\frac{\Delta}{2k_{\rm B} T} \right] g(\Delta, \tau) d\Delta d\tau, \tag{4}$$

where γ is the acoustic coupling constant, ρ is the density, and v is the velocity of sound.

The relationship between $d^2\sigma/d\Omega d\omega$ and α implicit in Eqs. (2) and (4) cannot be tested directly because acoustic and neutron experiments are made in nonoverlapping frequency ranges. However, by our choosing a distribution of



configurational coordinate

FIG. 3. Asymmetric double-minimum potential. Inset: Model of coupled rotational motion of five tetrahedra as a possible configuration coordinate.

barriers (together with a uniform distribution for Δ) to fit α , the ultrasonic data^{10,12} can be scaled in frequency for comparison with neutron and Raman data. The distribution of relaxation times is obtained by use of the classical formula for an asymmetric double well,

$$\tau = \tau_0 \operatorname{sech}\left(\frac{\Delta}{2k_{\mathrm{B}}T}\right) \exp\left(\frac{V}{k_{\mathrm{B}}T}\right),\,$$

where τ_0 is given by ultrasonic data^{2,10} as approximately 10^{-13} s. The calculated curves are shown as the solid lines in Figs. 2(b) and 2(c), respectively, showing that the asymmetric-well model for structural relaxation gives an accurate description of acoustic, Raman,⁹ and neutron data with a common distribution function $g(\Delta, \tau)$. (The available far-infrared data are not sufficiently complete for detailed analysis, although in contrast to the symmetric case the asymmetric model gives the observed temperature dependence.⁴)

The total number of relaxation states can be obtained if $I^{(1)}(Q)$ in Eq. (3) can be evaluated quantitatively. Because $I^{(1)}(Q)$ is the same at 220 GHz as at 1 THz, where harmonic modes dominate, the dynamic structure factor can be calculated with the same five-tetrahedra unit, shown in the inset in Fig. 3, that was used in a previous publication³ to calculate the dynamic structure factor of harmonic modes. Only if the jump distance dof the central oxygen atoms is less than about 0.8 Å⁻¹ are the two structure factors identical over the complete range of Q probed in this experiment. We therefore conclude that relaxation involves coupled SiO₄ tetrahedra jumping through a distance of approximately 0.5 Å, a value consistent with computer simulations of SiO₂ networks.¹²

With use of this value of d, the observed neutron intensity gives a number density of 6×10^{26} m⁻³ (about 0.01 state per atom) if the asymmetry is taken to be evenly distributed up to half the barrier height with barrier distribution derived from the ultrasonic loss data² with an average barrier of 570 K and a width of 410 K. In fact the fit is insensitive to the precise form of barrier distribution, and the solid curve giving an identical fit to the Raman data was calculated using a distribution with no low barrier cutoff.¹⁰ With this number density the ultrasonic data at 26 GHz give a coupling constant of 1 eV, within a factor of 2 of that measured for tunneling states,^{1,2} the only available estimate for the strength of the phonon coupling to two-well potentials.

In summary, all four probes of structural relaxation (quasielastic neutron and Raman scattering, and acoustic and infrared absorptions) can be consistently and convincingly explained in vitreous silica on the basis of classical activated relaxation processes. The neutron data give direct experimental evidence that relaxation can be described as rotation of coupled SiO₄ tetrahedra through distances of about 0.5 Å, motion similar to that involved in low-frequency harmonic vibrations and found in calculations of low-frequency modes of SiO₂ clusters.¹² These results lend support to a common interpretation of all three groups of low-frequency excitations found in glasses,¹³ although the link between relaxation

and tunneling states is not yet finally established. Finally, it should be pointed out that SiO_2 is an ideal material for this study of relaxation processes because the basic tetrahedron structural unit preserves its integrity in the glass with a characteristic structure factor, and also because relaxation associated with the glass transition temperature occurs at much higher temperatures than the quasielastic scattering studied here. Similar clear-cut results are unlikely to be found in other glasses.

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