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ABSTRACT

Neutron scattering experiments have been performed to study the structure and dynamics of three preparations of silica: a dense glass (fused quartz), a flame-hydrolyzed aggregate (Cab-O-Sil, grade M5) and a polymeric aerogel. The experiments were performed on the three materials at temperatures selected from 300, 77 and 4.2 K. Neutron inelastic scattering was measured at \( Q = 2.5, 2.9 \) and \( 4.0 \text{ Å}^{-1} \).

The elastic scattering indicates a systematic decrease in positional correlations on progressing from fused quartz through Cab-O-Sil to aerogel. The inelastic scattering was analyzed with the Buchenau model \([1]\) to obtain the sample, \( Q \) and temperature dependences of the density of states, \( g(\nu) \). In the aerogel \( g(\nu) \) increases with temperature at frequencies greater than \( 1.5 \text{ THz} \) and is enhanced at \( Q = 2.5 \text{ Å}^{-1} \). Thus a complete explanation of the inelastic scattering from aerogels must account for multiphonon processes, local antiphase motions and anharmonic effects.

INTRODUCTION

Silica may be prepared through a number of fabrication routes to produce a rich variety of structural forms. These include polycrystalline aggregates of quartz, high density glass and low density networks created by flame hydrolysis or hypercritical drying of gels. The unique structures and dynamics of the low density materials lead to applications in radiation detectors, high efficiency transparent insulators, and high surface area catalyst substrates.

In glassy forms of silica the fundamental structural unit is an \( \text{SiO}_4 \) tetrahedron. The local environment of each tetrahedron varies due to the statistical nature of configurations in the vitreous state. Buchenau et al. investigated the neutron inelastic scattering from vitreous silica \([2,3]\). These authors analyzed the mixed coherent and incoherent scattering from silica by an intuitively appealing expression,

\[
d^2\sigma/d\Omega d\nu \propto Q^2 S(Q,0) n(\nu) g(\nu)/\nu
\]

where \( \nu \) is the vibrational frequency, \( g(\nu) \) is the density of states, \( S(Q,0) \) is the elastic scattering intensity and \( n(\nu) \) is the thermal population factor, \( 1 + [\exp(\hbar \nu/kT)-1]^{-1} \). The expression is expected to be valid for vibrational modes which are harmonic, have a wavenumber much less than \( Q \) and consist of in-phase motions of neighbouring atoms as occurs in sound waves and librational motions.
The present experiment is a comparison of neutron elastic and inelastic scattering from three samples of silica: fused quartz, Cab-O-Sil (grade M5) and a polymeric aerogel. Measurements at three convenient temperatures, 300 K, 77 K and 4.2 K and at Q values 2.5, 2.9 and 4.0 Å⁻¹ were made to search for anomalous variations in the density of vibrational states in the range 0.3 to 6.0 THz. These experimental conditions most readily yield structural and dynamical information which is dominated by interactions on molecular length scales and therefore complement recent neutron scattering experiments that attempt to investigate large scale "fractal" structures and dynamics of silica aggregates [4–8].

EXPERIMENTS

The fused quartz specimen was in the form of a tube of diameter 25 mm, wall thickness 1 mm and height 60 mm. The Cab-O-Sil (M5) specimen was prepared as a slurry in D₂O which was subsequently dried in vacuum at 120 C. This treatment compacts the sample by a factor of about three and is designed to exchange surface hydrogen with much less strongly scattering deuterium. The aim was to collect neutron scattering information from silica and not from the surface water and bound hydroxyl groups that are present in untreated specimens. The sample was contained in an aluminum can of diameter 62 mm, height 60 mm and wall thickness 0.2 mm. The polymeric aerogel sample was prepared by a two-stage protocol [9] in which tetraethoxysilane was first hydrolyzed in acid solution and then condensed under basic conditions. It was contained in a can similar to that of the Cab-O-Sil but having a diameter of 25 mm. A cycle of evacuation at 120 C and flushing with D₂O vapour was repeated three times to minimize the signal from surface water and hydroxyl groups. All sample cans were backfilled with helium to facilitate thermal equilibration.

The neutron scattering experiments were conducted on the N5 triple axis spectrometer at the NRU reactor of Chalk River Nuclear Laboratories. Soller slits set the beam divergence to 0.6°. The monochromator and analyzer were silicon crystals oriented to scatter from (111) planes. For most measurements the spectrometer was operated in constant Q mode with fixed scattered energy 3.52 THz and a graphite filter in the scattered beam. Thus the beam was free of second and third order contamination. For small angle elastic scattering the collimation was reduced to 0.2°, the graphite filter was replaced by a beryllium filter before the monochromator and the neutron wavelength was fixed at 4.09 Å. The beam was 50 mm wide and illuminated a large volume of sample but scattering from the analyzer suppressed the fast neutron contribution to the beam width and we could reach a Q of 0.02 Å⁻¹.

For a sample at a given temperature we first measured the elastic scattering, S(Q,0), to obtain structural information and the normalizing factor required in equation (1). Then we measured S(Q,ν), the variation of intensity with frequency, on the neutron energy loss side at a selection of Q values including 4.0, 2.9 and 2.5 Å⁻¹. Temperatures were set by filling the cryostat with liquid helium (4.2 K) or liquid nitrogen (77 K) or by leaving it empty (300 K).
Small angle scattering from the Cab-O-Sil sample was consistent with smooth surfaced primary particles of diameter 130 Å. The particle cores are thought to have an equilibrium glass intermolecular structure but a less well defined structure at the surface with randomly distributed OH- or O- terminations of SiO₄ tetrahedra [10]. Small angle scattering from the aerogel indicates mass fractal structure over a limited range of length scales. For 0.03 ≤ Q ≤ 0.1 Å⁻¹ the slope of a log-log plot of intensity versus Q is -2.40 ± 0.03, consistent with other experiments [11] and with predictions for reaction limited cluster-cluster aggregation followed by partial collapse on drying. The transition from the fractal region to the Porod limit is incomplete so one concludes there are no smooth primary particles or that the structure is fractal down to molecular length scales.

Figure 1 presents a comparison of \( S(Q, 0) \) for the three

![Normalized Intensity Graph](image_url)

Figure 1.

Elastic scattering in different forms of silica. The intensity scale is in arbitrary units, but data sets have been normalized by equation (2).
samples at all temperatures investigated. The intensities have been internormalized to within 5% by the requirement

$$\nu = \sum_{\nu=0}^{\nu_{max}} S(Q,\nu) \Delta \nu = \text{Constant}$$

at $Q = 4.0 \text{ \AA}^{-1}$ which is near a node in the oscillatory structure of silica glass. The upper bound $\nu_{max}$ is 6 THz, sufficiently high that the integral yields the same value for a given sample at all three temperatures. There is a decrease in amplitude of the oscillations in $S(Q,0)$ and an increase in the $Q$ range of the small angle scattering tail on traversing the series fused quartz through Cab-O-Sil to aerogel. In aerogel the decrease in elastic scattering intensity by a factor of five at $Q = 4.0 \text{ \AA}^{-1}$ between 4.2 K and 300 K indicates a much stronger temperature dependence than in fused quartz where only minor differences are observed at the two temperature extremes.

Figure 2 presents a comparison of the inelastic neutron scattering from the three materials. The data have been corrected by eq. 1 to obtain an effective density of states or DOS, $g(\nu)$. This spectrum has not been corrected for multiphonon or multiple scattering effects. For fused quartz at 300 K we find excellent agreement with data analyzed similarly by Buchenau et al [2]. At 300 K the inelastic scattering in Cab-O-Sil beyond 2 THz is about twice as intense as in the fused quartz while in aerogel the factor is about twenty. Below 1.5 THz the DOS seems nearly to be independent of temperature but at larger frequencies in the aerogel there is a systematic rise with each temperature. Figure 3 shows the $Q$ dependence of the DOS in the aerogel at 300 K. The spectra are practically identical at 2.9 and 4.0 $\text{\AA}^{-1}$ but at 2.5 $\text{\AA}^{-1}$, near a minimum in the structure factor, there is an enhancement by a factor of 2 near 1 THz and by 30% beyond 2 THz.

DISCUSSION

On the length scales of molecules and SiO$_4$ tetrahedra the three materials are distinguished by the breadth of configuration space available to the fundamental structural units. To gain a detailed understanding of the structures and dynamics of amorphous materials one generally needs to perform computer simulations with reliable intermolecular potentials. Without such assistance a physical picture can still be formed. In the condensed glass the range of molecular orientations and separations is limited by packing constraints and the potential surface experienced by a given molecule or tetrahedron has well defined minima. The observed loss of 20% in the amplitude of oscillations in the elastic scattering between Cab-O-Sil and fused quartz may be explained as a volume fraction of silica in a high degree of disorder. One envisions an outer shell of molecules within about 7 $\text{\AA}$ of the surface of the 130 $\text{\AA}$ particles in Cab-O-Sil. These molecules have reduced packing constraints and randomly terminated silicon bonds, experience broad, ill-defined minima in the intermolecular potential and hence exhibit configurational disorder. A broadened potential surface permits wider vibrational amplitudes and correspondingly stronger damping of the elastic scattering with increased temperature as observed in $S(Q,0)$ at larger $Q$. It
Effective density of states in silica samples as labelled in each frame. The intensity scale is in units of THz\(^{-1}\). The continuous line is a spline fit to data from ref. 2. Data at two temperatures for Cab-O-Sil were not obtained at Q = 2.9 Å\(^{-1}\) but the results at 4.0 Å\(^{-1}\) may be compared to the aerogel which yields the same intensities at either value of Q. Note that for aerogel the intensity scale is greater by a factor of ten.

Figure 3

Effective density of states in aerogel at 300 K and three Q values.
also increases the density of vibrational modes at lower frequencies as we observe in the inelastic scattering.

The very low amplitude of oscillations and strong temperature dependence in $S(Q,0)$ for the aerogel is reminiscent of the structures observed in dense molecular gases except that the positions of the peaks are not strongly temperature dependent. Thus there are wide positional fluctuations about fixed equilibrium positions in the aerogel. Below 1 THz the overlap of results suggests a constant velocity of sound but the increase of intensity with temperature at frequencies greater than 1.5 THz shows that the vibrational spectrum is changing. This might be explained as multiphonon scattering [8] which enhances scattered intensity at larger frequencies and has little influence at lower frequencies, as observed. However multiphonon enhancements increase with $Q$ while the reverse is observed in our data. While eq. 1 assumes only in-phase vibrations of neighbouring molecules, antiphase oscillations are quite conceivable in the highly branched aerogel. The unusual $Q$ and $T$ dependences of the aerogel DOS may also arise because low packing constraints permit molecules to sample anharmonic features of the potential energy surface and eq. 1 assumes only harmonic excitations.

CONCLUSION

Fused quartz, Cab-O-Sil and aerogel form a series of materials with increasing fractions of molecules in configurational disorder and having wide amplitudes of thermal vibration. The density of states in the aerogel cannot be obtained directly by analysis of the scattering data through eq. 1.

REFERENCES