# Correlated Motions in Glasses Studied by Coherent Inelastic Neutron Scattering

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Coherent inelastic neutron scattering provides detailed information about the correlated atomic displacements in the vibrational modes of a glass. As an example, we show the wave-vector dependence of the scattering function of vitreous $SiO_2$ corresponding to different peaks in the one-phonon density of states. Pending the availability of results from computer simulations, we give a qualitative comparison with the Sen-Thorpe model.

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The intermediate-range order in insulating and semiconducting glasses is a subject of current interest and controversy.[1,2] In addition to the use of structural probes like diffraction and extended x-ray absorption fine structure, dynamical information obtained from inelastic neutron scattering and Raman and ir spectroscopy is being used to test the validity of different models.[3] These spectroscopies measure essentially a one-phonon density of states, modulated by a matrix element which, except in the case of certain modes of special symmetry,[1,2] is assumed to have a regular variation over the frequency range investigated.

Since the density of states is essentially a statistical quantity, representing the relative number of vibrational modes in a particular frequency region irrespective of the types of motion involved, the information obtained in this way is quite limited and often inadequate to provide precise identification of particular modes. For example, the high-frequency doublet in $SiO_2$ at $\hbar\omega = 130$–$150$ meV (1 meV $\simeq 8$ cm$^{-1}$) has been interpreted as either an optical mode split by the macroscopic electric field[3,4] or as "bulk" and "surface" Si-O stretching modes associated with clusters in the glass.[2]

The purpose of this Letter is to show that accurate coherent inelastic neutron-scattering (CINS) measurements provide information about the correlated atomic displacements in modes at a given frequency and hence offer the opportunity to make precise tests of different models for the intermediate range structure and dynamics. CINS measures the scattering function in terms of the wave-vector transfer $\mathbf{Q}$ and the energy transfer $E$ which in the conventional harmonic phonon expansion can be written

$$S(\mathbf{Q},E) = S^{(0)} + S^{(1)} + S^{(m)}. \tag{1}$$

The first term in Eq. (1) represents the elastic scattering:

$$S^{(0)}(\mathbf{Q},E) = S_{\rm el}(\mathbf{Q})\delta(E) = \frac{1}{N}\sum_{ij}\frac{b_i b_j}{\langle b^2\rangle}\exp[-(W_i+W_j)]\exp[i\mathbf{Q}\cdot(\mathbf{R}_i-\mathbf{R}_j)], \tag{2}$$

where $W_i$ is proportional to the mean-square displacement $\langle u_i^2\rangle$ about the equilibrium site $\mathbf{R}_i$, and $b_i$ is the scattering length of atom $i$. The second term represents the one-phonon scattering which on the neutron-energy-loss side is given by

$$S^{(1)}(\mathbf{Q},E) = \frac{1}{2N}\sum_{ij}\frac{b_i b_j}{\langle b^2\rangle}\exp[-(W_i+W_j)]\exp[i\mathbf{Q}\cdot(\mathbf{R}_i-\mathbf{R}_j)] \times \sum_{\lambda}\hbar\frac{(\mathbf{Q}\cdot\mathbf{e}_i^{\lambda})(\mathbf{Q}\cdot\mathbf{e}_j^{\lambda})}{(M_iM_j)^{1/2}\omega_{\lambda}}\langle n_{\lambda}+1\rangle\delta(E-\hbar\omega_{\lambda}), \tag{3}$$

where $\mathbf{e}_i^{\lambda}$, $\omega_j$, and $\langle n_{\lambda}\rangle = [\exp(\hbar\omega_{\lambda}/kT)-1]^{-1}$ are the displacement vector, frequency, and population factor of the normal mode $\lambda$ in the network. The third term represents multiphonon scattering which involves double and higher multiple sums over normal modes and generally introduces a relatively smooth background under the one-phonon scattering.

In the past, CINS measurements in glasses have generally been analyzed under the *incoherent approximation,* which assumes that when $S(\mathbf{Q},E)$ is averaged over an extended range of $|\mathbf{Q}|$ the correlation between motions of distinct atoms dies out and the factor $(\mathbf{Q}\cdot\mathbf{e}_i^{\lambda})(\mathbf{Q}\cdot e_j^{\lambda})$ may be replaced by $\frac{1}{3}Q^2(e_i^{\lambda})^2\delta_{ij}$. In this case Eq. (3) takes the much simpler form

$$S_{\rm inc}^{(1)} = \sum_i\frac{b_i^2}{\langle b^2\rangle}\exp(-2W_i)\frac{Q^2}{2M_i}\frac{g_i(E/\hbar)}{E}\langle n+1\rangle, \tag{4}$$

where $g_i(\omega)$ is the displacement-weighted density of states for atoms of type $i$.

If, on the other hand, the full expression Eq. (3) is retained, it is clear that $S^{(1)}$ in fact contains information about the correlations between motions of different atoms precisely through the factors $(\mathbf{Q}\cdot\mathbf{e}_i^{\lambda})\times(\mathbf{Q}\cdot\mathbf{e}_j^{\lambda})$ which are averaged out in the incoherent approximation.

As an example, we present data on $S(Q,E)$ for vitreous $SiO_2$ taken at the Intense Pulsed Neutron Source. These form part of a systematic series of measurements which have been carried out in the last two years on $AB_2$ glasses, including $SiO_2$, $GeO_2$, $BeF_2$, and $SiSe_2$. Since a glass has no long-range order, we expect averages over the whole system to be a function of scalar $Q$ only, although $\mathbf{Q}$ must still be taken as a vector inside the summation sign in Eq. (3); explicit forms are given by Carpenter and Pelizzari.[5] The $SiO_2$ measurements were made on the LRMECS chopper spectrometer[6] at a temperature of 33 K using a fixed incident energy of 218 meV. This relatively large energy made it possible to cover the full range of one-phonon vibrations (maximum $\hbar\omega \sim 165$ meV) with a substantial range in $Q$, about 6–13 $\text{Å}^{-1}$ at 165 meV and even larger for smaller $\omega$. The energy and wave-vector–transfer resolution were approximately 15 meV and 0.5 $\text{Å}^{-1}$. Full details of data analysis, including corrections for sample-holder scattering, detector efficiency, self-shielding in the sample, and multiple scattering, will be described in a later paper.

Figure 1 shows a two-dimensional plot of the inelastic part of $S(Q,E)$, plotted for $E > 20$ meV to avoid any contamination by the resolution-broadened elastic scattering. From this overall picture it is immediately obvious that, in addition to peaks in the $E$ distribution due to certain modes with energies $E = \hbar\omega$ that are particularly numerous, there are pronounced oscillations as a function of $Q$ which represent correlations in the motions and positions of nearby atoms.

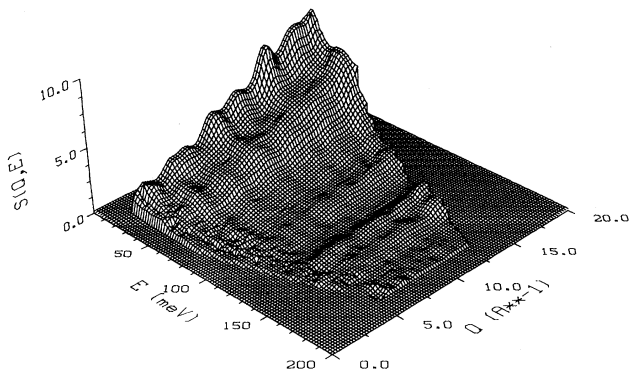


FIG. 1. Scattering function of $a$-$SiO_2$ at 33 K.

Figure 2 represents the one-phonon density of states obtained from Eq. (4) by averaging over the $Q$ range 6.0 to 13.0 $\text{Å}^{-1}$. The multiphonon scattering $S^{(m)}$ has been subtracted in this figure by procedures described elsewhere.[4] By comparison with optical data[3] and ball-and-spring models[7] of the glass, the peaks at $\sim 50$, $\sim 100$, and 130–150 meV can be ascribed to rocking, bending, and stretching motions, respectively, of the Si–O–Si bonds. The behavior for $E < 15$ meV is only approximate in view of the subtraction of resolution-broadened elastic scattering from the data in the region. Figure 4 is consistent with earlier beryllium-filter data[8] but more accurate because of the greater range in $Q$, especially at higher energies, and the lower statistical errors.

The main interest, however, lies not in the density of states [Eq. (4)] but in the detailed $Q$ dependence described by Eq. (3). For a given mode, this can be considered as the Fourier transform of the density-density correlation function for that particular mode.[5] As an example we show in Fig. 3 the $Q$ variation of the inelastic part of $S(Q,E)$ for modes corresponding to 49.2, 98.5, and 145.7 meV. These are representative of the rocking, bending, and stretching peaks in the density of states; the specific energies arise because they correspond to particular time channels in each detector group (flight paths are identical for each detector).

For $SiO_2$, pending the completion of detailed computer simulations,[9] the simple picture of Sen and Thorpe[10] is intuitively appealing and easily accessible to calculations of $S^{(1)}(Q,E)$. In this model, two delta-function modes appear by virtue of the assumptions of (a) nearest-neighbor central forces only and (b) perfect $SiO_4$ tetrahedra. Figure 4 shows the behavior of $S^{(1)}(Q,E)$ for these two modes, which represent the upper limits of the bond-bending ($\omega_3$) and bond-stretching ($\omega_4$) distributions. With the parameters of Galeener, Leadbetter, and Stringfellow,[3] these modes have frequencies $\hbar\omega_3 = 99.6$ meV and $\hbar\omega_4 = 146.1$ meV, and so they can be compared with

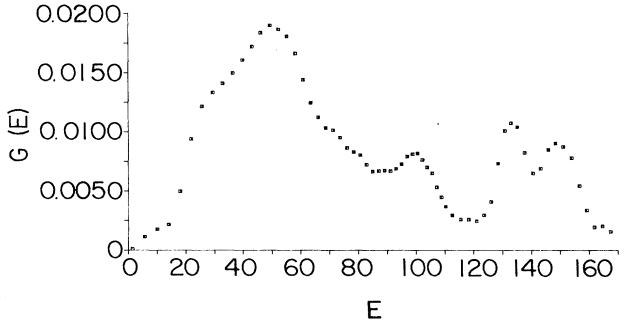


FIG. 2. One-phonon density of states $g_i(E/\hbar)$ for $a$-$SiO_2$.

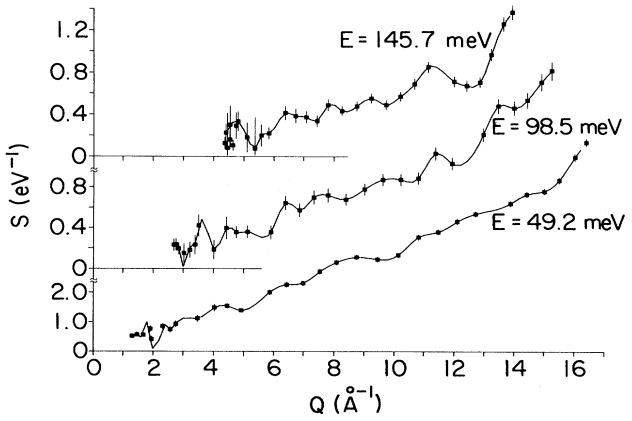


FIG. 3. $Q$ variation of $S(Q,E)$ for $a$-$SiO_2$ at $E=49.2$, 98.5, and 145.7 meV. The solid curves represent cubic spline fits through the data, taking account of the statistical errors indicated by the bars on each data point.

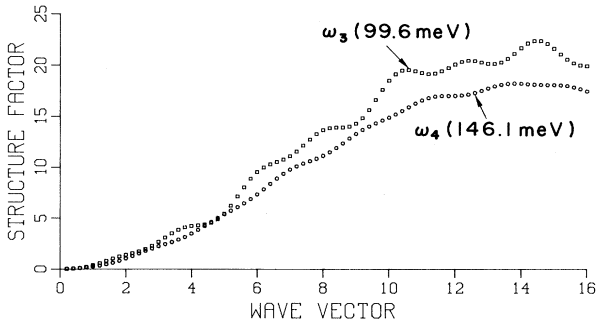


FIG. 4. $S^{(1)}(Q,E)$ for the $\omega_3$ and $\omega_4$ modes of the Sen-Thorpe model (Ref. 10).

the experimentally observed modes at 98.5 and 145.7 meV in Fig. 3. Clearly, Fig. 4 does not reproduce the detailed behavior of Fig. 3. First, the oscillations are more pronounced in the higher-energy mode in the experiment, whereas in the model the lower-energy $\omega_3$ mode has a larger amplitude of oscillation: The oxygen atom is nearly stationary in this mode and therefore the interference between motions of second-nearest-neighbor silicon atoms (with a period of $2\pi|\mathbf{R}_{Si(1)}-\mathbf{R}_{Si(2)}|=2.15$ Å$^{-1}$) is more visible. Second, the periods of the oscillations are shorter in the experimental structure factors, in the range 1.6 to 1.8 Å$^{-1}$, suggesting correlations that extend beyond second neighbors.

Clearly, the neutron data contain sufficient information to support a more detailed picture of the glass dynamics than that provided by this simple model. We believe that direct comparisons between these data and the equivalent quantities from realistic computer simulations will provide definitive assigments to the features in the density of states and the associated intermediate-range order. Moreover, systematic CINS measurements on glasses, for example on the series $SiO_2$, $SiS_2$, $SiSe_2$, $SiTe_2$, should illustrate the changes in this intermediate-range structure with composition.

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