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LETTER TO THE EDITOR

The origin of the boson peak in network-forming glasses

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Abstract. An analysis using a simple model is presented with the aim of providing an explanation for the characteristics of low-energy excitations in glasses with directional bonds. The model predicts the appearance of three types of acoustic excitation: weakly, strongly, and mesoscopically localized modes, and, in addition, recovers the excess density of states at low energies. We claim that the latter two excitations constitute the two broad bands observed in Raman spectra, i.e. the lower band (the boson peak) consists of strongly localized modes, and mesoscopically localized modes contribute to the second higher band at around the Debye cut-off frequency ω_D .

Glasses are extremely interesting objects in the physics of condensed matter, with universal properties such as the T -linear specific heat below a few K, the thermal conductivity plateau at around 10 K, and the low-energy broad peak observed in Raman spectra, the so-called boson peak. The T -linear specific heat at low temperatures is described well, but qualitatively, in the framework of the two-level tunnelling model [1, 2]. The origins for the latter two properties, however, remain a question of considerable current interest [3]. It is believed that vibrational states responsible for the boson peak contribute also to the thermal conductivity plateau, because the energy range spanned by the plateau covers that for the boson-peak spectra, indicating that acoustic excitations must cease to propagate when their wavelength λ reaches the nm range [4, 5]. That is, acoustic modes may cross over to strongly localized modes satisfying the Ioffe–Regel condition, $ql_s \approx 1$, where l_s is the scattering length. Recent inelastic neutron and x-ray scattering measurements for vitreous silica ($v\text{-SiO}_2$) [6] support this view, though opposite results and claims based on inelastic x-ray scattering have also been reported [7]. Thus, the origin of the boson peak is still debated—even qualitatively.

This letter provides an analysis using a simple model, on the basis of which we hope to achieve an understanding, from a qualitative point of view, of the unique properties of low-energy vibrational states in glasses with directional bonds. The model proposed here is abstract, but when we discuss the characteristics of low-energy excitations in glasses, its significance will be clear. Firstly, all that is required is to construct a model exhibiting *strongly* localized modes (modes with the localization length $\ell(\omega)$ of the order of the wavelength $\lambda(\omega)$ in the acoustic band). Many structural models for glasses have been proposed [8] since the seminal work by Dyson [9], but there is no satisfactory model giving rise to strongly localized modes *in the acoustic band*, except that of fracton excitations in fractal structures [10, 11]. Our model, described below, predicts the appearance of three types of excitation in the acoustic band: weakly, strongly, and mesoscopically localized modes, and, in addition, recovers the excess density of states at low energies observed in inelastic neutron scattering experiments [5] and derived from specific heat data for glasses

[12]. We claim that the latter two excitations constitute two broad bands at low energies. That is, the lower band consists of strongly localized non-dispersive modes, and these constitute the so-called boson peak. Mesoscopically localized modes are dispersive, and contribute to the second higher band.

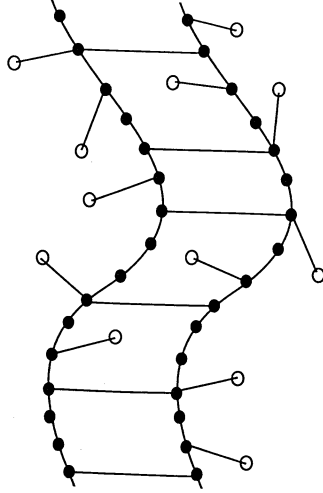


Figure 1. A schematic illustration of the model, where the sizes of the cells are randomly distributed, having six or eight atoms. The number of side atoms is taken to be 40% of the total number of main atoms, and they are randomly attached to the two main chains.

The dimensionality is not an important factor for the origin of boson peaks, since they are observed for polymer glasses (1D), chalcogenide glasses like $\text{Ge}_x\text{Se}_{1-x}$ (2D), and glasses such as $v\text{-SiO}_2$ (3D). Our model for glasses with directional bonds is a quasi-1D one, having two main chains with constant mass M of atoms, and these are connected to their nearest neighbours by linear springs with constant strength K . The central hypothesis of our model is that, in glasses with directional bonds, there should be a certain number of extra vibrational states, which we attach to each of the main chains with the mass M by linear springs with the strength k_i at site i . The mass M and the force constant k_i are related to the characteristic frequency by $\omega_i^2 = k_i/M$, where the parameters ω_i^2 are random quantities and distributed in the range from ω_{\min}^2 to ω_{\max}^2 . This distribution originates from the local distortion and strain in the atomic arrangement in glasses. In other words, the key features of glasses are incorporated in this distribution. Figure 1 is a schematic illustration of our model (the broken-ladder model). We should stress that the mass M does not correspond directly to the mass of one atom, but does to that of a group of atoms, e.g. the mass of monomers in polymers or tetrahedral units in $v\text{-SiO}_2$. Since we focus our attention on the behaviour of the modes with eigenfrequencies below the Debye cut-off frequency ω_D , the above simplification (the centre-of-mass system) does not lose the generality of the model. Again, we should emphasize that the broken bonds (side atoms) in figure 1 do not directly correspond to the true atomic arrangement in glasses. These simply indicate some kind of vibrational state. This should be associated with the vibrational state in the local potential minima with different curvatures ($k_i = M\omega_i^2$) due to the different environments of the various entities. Anderson *et al* [2] suggested for $v\text{-SiO}_2$ that there are of the order of 2^N metastable states denoted by double-well potentials, where N is the number of SiO_4 tetrahedra. They supposed [2] that double-well potentials with *low-enough* barrier heights

and short distances for the tunnelling contribute to the T -linear specific heat below a few K; the number of such potentials is estimated from the specific heat data [1] to be approximately 1/250 (0.4%) of the total number of potentials for the SiO_2 group. The number of double-well potentials with *high* barrier heights, not relevant to the tunnelling, is of the order of N (the number of harmonic potentials). Provided that the extra vibrational state introduced in the present letter corresponds to these entities, it is reasonable that we require the number of extra vibrational states (side atoms) to be about 40% of the total number of tetrahedra. We do not take into account the contribution from double-well potentials with *low* barrier heights relevant to the tunnelling, because the number of these is not large, as mentioned above; that is, the effect of anharmonic potentials is neglected.

The Hamiltonian for our model is given by

$$H = \sum_i \left[\frac{P_i^2}{2M} + \frac{p_i^2}{2M} + \frac{K}{2}(U_i - U_{i-1})^2 + \frac{k_i}{2}(u_i - U_i)^2 \right] \quad (1)$$

where U_i and u_i are the generalized coordinates, representing displacements of atoms (in the centre-of-mass system) or changes of angular variables. The corresponding momenta are described by P_i and p_i , respectively. Capital letters denote quantities relating to main chains and lower-case letters those for side 'atoms'. Note that, *when localized*, vibrations lose their pure longitudinal or transverse character, and direct coupling to density fluctuations with neutrons or x-rays probes the one-component projection of the vibrations. Thus, the scalar approximation given in equation (1) is useful in for discussing the characteristic behaviours of the dynamic structure factor $S(q, \omega)$.

The dynamical structure factor $S(q, \omega)$ is expressed in terms of the Fourier transform

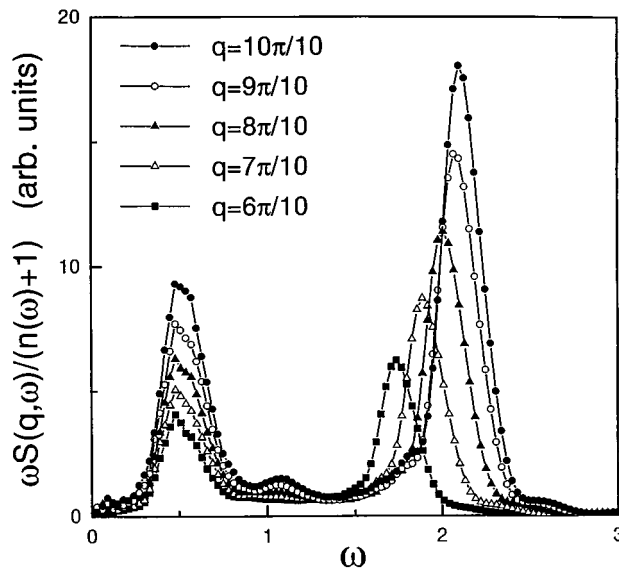


Figure 2. The ω -dependences of $S(q, \omega)$ for the model of figure 1 with the total site number $N = 12000$. The force constants k_i —that is, the curvatures of the potential minima—are uniformly distributed from $k_i(\text{min}) = 1/4$ to $k_i(\text{max}) = 1$. The system of units $M = K = a = 1$ is used.

of the correlation function of density fluctuations as

$$S(q, \omega) = \frac{1}{2\pi} \int dt e^{-i\omega t} \langle \delta\rho_{-q}(0) \delta\rho_q(t) \rangle$$

where $\delta\rho_q(t)$ is the q -component of the density fluctuation. The angular brackets $\langle \dots \rangle$ represent thermal averaging. Decomposing $U_i(t)$ (and $u_i(t)$) defined in equation (1) into normal modes, one obtains

$$\delta\rho_q(t) = -ie^{i\omega_\lambda t} \sum_i q e_i(\lambda) e^{-iqr_i} + O(U^2).$$

Here $\{e_i(\lambda)\}$ is the eigenvector belonging to the eigenfrequency ω_λ . Substitution of this expression into the definition of $S(q, \omega)$ yields

$$S(q, \omega) = \frac{(n+1)}{\omega N} \sum_\lambda \delta(\omega - \omega_\lambda) \left| \sum_i q e_i(\lambda) e^{-iqr_i} \right|^2 \quad (2)$$

where n is the Bose–Einstein distribution function and N the total number of atoms. We use the forced-oscillator method (FOM) [13, 14] to calculate $S(q, \omega)$. The method, developed for calculating densities of states (DOS) and eigenvectors, is based on the principle that a linear mechanical system when driven by a periodic external force of frequency Ω will respond with a large amplitude in those eigenmodes. By taking the external force in the equation of motion derived from equation (1) as $q \exp(i\Omega t - iqr)$, we can efficiently calculate $S(q, \omega)$ for very large systems by means of the FOM [15]. The calculated results for $S(q, \omega)$ are given in figure 2 for the specific parameters $M = 1$, and $K = 1$, where periodic boundary conditions are taken for $N = 12\,000$. The lower and upper limits for the distribution of the frequency ω_i are taken to be $k_i(\min) = 1/4$ and $k_i(\max) = 1$. The force constant $K (=1)$ should correspond to the (largest) stretching force constant (K_r in Keating’s notation) and the force constant k_i should be smaller than the strength of K . It is not easy to meaningfully estimate the value of k_i . However, for instance, the relevant force constant aside from K_r for glasses with directional bonds is the bending one, K_θ , whose strength is in general about a half of that of K_r . Thus, the above choice of the parameters k_i seems to be reasonable.

An important conclusion drawn from figure 2 is that two bands clearly appear in the spectra. The lower peaks, which broaden with increasing q , are almost independent of the momentum transfer q (non-dispersive). The higher band appears close to the Debye cut-off frequency ω_D . The higher band depends strongly on the momentum transfer q , indicating that the modes contributing are dispersive. This two-band feature at low energies is plainly observed for network-forming glasses.

In order to establish the characteristics of modes contributing to these two bands, the density of states (DOS) $D(\omega)$ and the localization lengths $\ell(\omega)$ have been calculated by means of the FOM and are shown in figure 3 [13, 14]. The definition of the localization length is

$$\ell(\omega_\lambda) = \left(\sum_i |e_i(\lambda)|^2 \right)^2 / \sum_i |e_i(\lambda)|^4.$$

One can appreciate from figure 3 that a hump in the DOS appears at around $\omega \approx 0.5$, whose energy range is the same as that of the lower peak of the calculated function $S(q, \omega)$. This excess density of states in figure 3 should correspond to the hump in the quantity $D(\omega)/\omega^{d-1}$ (since we can take $d = 1$ in the present case) which has been demonstrated to appear for inelastic neutron scattering experiments [5] and derived from the specific heat data of glasses [12]. The calculated results for the localization lengths $\ell(\omega)$ in units of

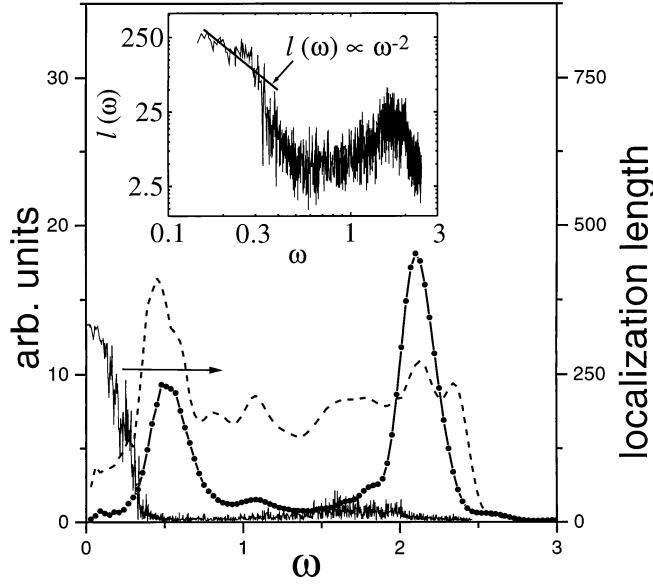


Figure 3. The density of states $D(\omega)$ and the ω -dependence of localization lengths $\ell(\omega_\lambda)$. Note that $D(\omega)$ given by the dashed line for our quasi-1D model corresponds to the quantity $D(\omega)/\omega^{d-1}$ for the d -dimensional systems introduced in reference [4]. The calculated results for $S(q, \omega)$ for $q = \pi$ are given by the solid line. The system of units is the same as that used in figure 2. The inset shows that the localization lengths are proportional to ω^{-2} below about $\omega \approx 0.3$.

the inter-atomic spacing ($a = 1$) are shown as a function of ω in figure 3, by the narrow line. The solid line represents the result for $S(q = \pi/a, \omega)$. It is recognized that the modes for $\omega_{\min} < \omega < \omega_{\max}$ are strongly localized, while the modes in the lower-frequency regime ($\omega < \omega_{\min}$) are weakly localized. These weakly localized modes have the frequency dependence $\ell(\omega) \propto \omega^{-2}$ as shown in the inset of figure 3; this frequency dependence is the same as that of Anderson's weak localization for a simple mass-disordered 1D system. Next, we present in figure 4 typical mode patterns, to clarify the different characteristics for the above frequency regions. Figure 4(a) shows the eigenmode with $\omega_\lambda = 0.199\,038 < \omega_{\min}$, in which the displacements of the main and the side atoms have almost the same amplitudes and vibrate in phase, i.e. the main atom and its side 'atom' vibrate without stretching or shrinking of the bond. These features are the same as in the case of a purely 1D chain with side atoms [14], for which the appearance of strongly localized modes has been clearly demonstrated. In contrast with these weakly localized eigenmodes, there appear strongly localized eigenmodes in the frequency region $\omega_{\min} < \omega_\lambda = 0.599\,734 < \omega_{\max}$ as shown in figure 4(b). It should be noted that main and side 'atoms' vibrate in anti-phase (i.e. are optically active). The strong-localization region $\omega_{\min} < \omega < \omega_{\max}$ originates from the resonance between the main chains and side 'atoms'. Figure 4(c) shows the eigenmode with $\omega_\lambda = 1.911\,54$ belonging to the higher band in figure 2. The mode pattern possesses quite different characteristics from those given in figures 4(a) and 4(b), indicating that only the atoms in the main chains vibrate substantially, and side 'atoms' do not follow the vibrations of the main chains. In addition, these modes are dispersive and are mesoscopically localized.

We should note that Benassi *et al* [7] have recently reported inelastic x-ray

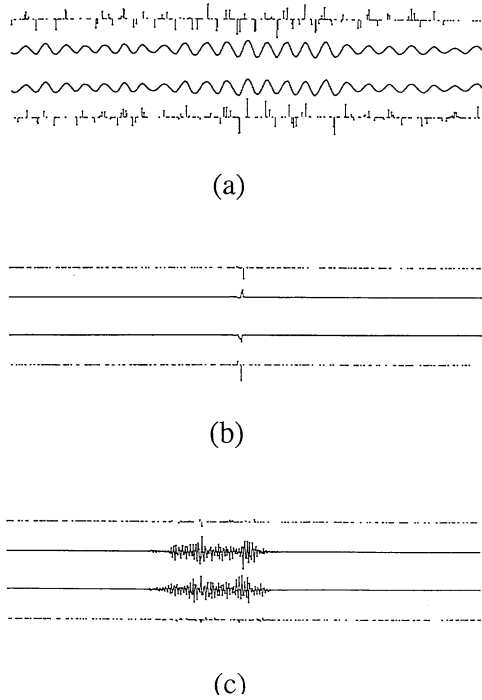


Figure 4. Three types of mode pattern: (a) weakly, (b) strongly, and (c) intermediately localized modes. The upper and lower plots show the displacements of side atoms. The displacements of the main chains are given by the central two curves in each panel. (a) The eigenmode with the eigenfrequency $\omega = 0.199\,038$. (b) The eigenmode with $\omega = 0.599\,734$. (c) The eigenmode with $\omega = 1.911\,54$.

scattering results for $v\text{-SiO}_2$, claiming the existence of *dispersive* modes above the energy corresponding to the boson peak. It seems not sufficient to analyse the data *above* the boson-peak energy assuming only the existence of *strongly* localized modes [6] or *dispersive* (propagating) modes [7] *in the acoustic branch*. We have demonstrated in figures 3 and 4 the coexistence of non-dispersive (strongly localized) and dispersive (mesoscopically localized) modes in the acoustic branch. An analysis of the scattering data in line with the present result—namely, incorporating three different types of mode in the *acoustic* band—should be carried out.

The model proposed here is abstract, but the present work elucidates, for the first time, the crucial difference between strong and mesoscopically localized modes in the acoustic band in glasses. In this respect, our simple model will provide a useful way of thinking about the characteristics of low-energy excitations in glasses with directional bonds.

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