Spatial structure of boson peak vibrations in glasses

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Low-frequency Raman scattering in glasses in the region of the boson peak is described in terms of the vibration spatial correlation functions. It is shown that the frequency dependence of the light to vibration coupling coefficient $C(\omega)$ is determined by the vibration correlation length l_ω and the spatial dimensionality of the vibration eigenmodes. The linear law $C(\omega) \propto \omega$ for the boson peak which is found experimentally in many glasses corresponds in the model to 1D spatial geometry of vibration eigenmodes. The estimated amplitude of the boson peak in the Raman scattering is in good agreement with the experimental data in vitreous silica. [S0163-1829(99)04801-8]

Vibrational excitations in disordered solids have been intensively investigated in past years. Long wavelength vibrations can be well described as delocalized excitations which correspond to the sound waves and have Debye density of states. At higher frequencies, 0.5–3 THz, the density of vibrational states in glasses, when normalized to the Debye one, has a bump, the so-called boson peak (see, e.g., Refs. 1–3) which also survives in the supercooled liquid state and in some cases, like in boron oxide, even above the melting point.[4] The nature of the excess excitations which form the boson peak is still unclear. The characteristic length of these vibrations is of the order of a few nanometers; this is a mesoscopic region between the short and long range order. There are attempts to describe the excess vibrations within phenomenological models like the soft-potential model,[5] fractal model,[6] and models that ascribe the boson peak to vibrations localized on the structure heterogeneities of a nanometer scale[7] or due to homogeneous structure correlations.[8] Recently, stringlike clusters of cooperatively moving particles were found in a model glass forming liquid; this result was obtained by a molecular dynamics simulation of a Lennard-Jones mixture.[9] The typical length of strings is of the order of nanometer. A question arises: can these stringlike fast motions have any relation to the boson peak? In the present paper we will show that a simple interpretation of the experimental data on the low-frequency Raman scattering in the region of the boson peak in glasses implies the one-dimensional spatial structure of the boson peak vibrations and thus indirectly supports a connection between stringlike objects of Ref. 9 and the boson peak. To check the model, the estimated intensity of the Raman scattering at the boson peak maximum is compared with the integrated intensity of the Brillouin line; it is shown that their relative intensity is in reasonable agreement with the known experimental data in vitreous silica.

The inelastic light scattering intensity is determined by the Fourier transform of the correlation function of the dielectric susceptibility fluctuations $\delta\chi_{\alpha\beta}(\mathbf{r},t)$,[10]

$$I(q,\omega) = A \int dt \, d\mathbf{r}_1 d\mathbf{r}_2 \, e^{i\omega t - i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} \langle \delta\chi^+(\mathbf{r}_1,t)\,\delta\chi(\mathbf{r}_2,0)\rangle \tag{1}$$

(A is a constant that depends on the experimental setup; tensor indices are omitted for simplicity since we are not interested here by the polarization dependence of the scattering). Variation of the dielectric susceptibility by the acoustical phonons is proportional to the strain tensor,

$$\delta\chi_{\alpha\beta} \propto P_{\alpha\beta\gamma\delta}(\partial u_\gamma/\partial r_\delta + \partial u_\delta/\partial r_\gamma), \tag{2}$$

where $P_{\alpha\beta\gamma\delta}$ is the tensor of elasto-optic constants and $u_\alpha(\mathbf{r},t)$ are the atomic displacements. Since the boson peak vibrations lie in the acoustical region and have a characteristic length $l \gtrsim 1$ nm we assume that they have the same light to vibration coupling constants as in the case of the acoustical vibrations. As a result, the following expression for the Raman intensity holds:[11,12]

$$I(q,\omega) = A P^2 \int d\mathbf{r} \, e^{i\mathbf{q}\mathbf{r}} \langle \nabla u_\omega^+(\mathbf{r}) \nabla u_\omega(0)\rangle g(\omega). \tag{3}$$

In Eq. (3) $g(\omega)$ is the vibrational density of states and $u_\omega(\mathbf{r})$ is the amplitude of a vibration with a frequency ω. The brackets mean the spatial and statistical averaging. It is convenient to introduce a normalized correlation function $F_\omega(r)$ defined by the equation

$$\langle \nabla u_\omega(\mathbf{r}) \nabla u_\omega(0)\rangle = F_\omega(r)\langle |\nabla u_\omega(0)|^2\rangle. \tag{4}$$

$F_\omega(r)$ satisfies the normalization condition $F_\omega(r) \approx 1$ at $r \to a$, where a is the average interatomic distance. From Eqs. (3) and (4) it is clear that the spatial Fourier transform of this correlation function, $F_\omega(q) = \int d\mathbf{r} \, e^{i\mathbf{q}\mathbf{r}} F_\omega(r)$, determines the Raman scattering intensity:

$$I(q,\omega) = A P^2 F_\omega(q)\langle |\nabla u_\omega(0)|^2\rangle g(\omega). \tag{5}$$

For example, a reasonable choice of $F_\omega(r)$ is an exponential correlation function that may have a power-law prefactor, $F_\omega(r) = (a/r)^\alpha \exp(-r/l_\omega)$. Here l_ω is a correlation length which for the boson peak vibrations presumably is of the medium range order. Such correlation function has two factors. The first one describes the exponential decrease due to localization and the second one is a power law prefactor which reflects a specific geometry (e.g., fractal) of the vibration eigenmodes. This prefactor corresponds to decreasing of the vibrational correlations in 3D space inside the localiza-

tion region of the vibration (i.e., at $r < l_\omega$); it can appear, for example, if the effective dimension of the vibration is less than 3.

For the purpose of the present paper we do not need to know the exact form of the spatial correlation function of vibrations $F_\omega(r)$. All we need is to suppose that at distances higher than some characteristic length l_ω the correlation function decays faster than a power law. Thus we write $F_\omega(r)$ in a general form

$$F_\omega(r) = (a/r)^\alpha f(r/l_\omega),\qquad(6)$$

where the function $f(r/l_\omega)$ describes the particular law of the spatial decay of the vibrational correlations due to disorder.

The typical value of the momentum transfer in light scattering experiments is $q \sim 10^{-2}$ nm^{-1}; with the characteristic length l_ω of the boson peak vibrations of the order of a nanometer one has $q l_\omega \ll 1$. As a result, in the first approximation one can neglect the q dependence in Eq. (5). Using Eq. (6) it is easy to find that the Fourier transform of $F_\omega(r)$ at $q = 0$ is equal to

$$F_\omega(q=0) = 4\pi b a^\alpha l_\omega^{3-\alpha} + O(q^2 l_\omega^2),\qquad(7)$$

where the constant b is of the order of 1; it is determined by a particular form of the function f,

$$b = \int_0^\infty x^{2-\alpha} f(x)\,dx.\qquad(8)$$

To find the Raman intensity (5) we use Eq. (7), a rough estimate $\nabla u_\omega \sim u_\omega/l_\omega$, and we take into account that the mean energy of an oscillator in the classical limit is equal to T, so

$$\langle |u_\omega(0)|^2 \rangle \approx T/\rho\omega^2,\qquad(9)$$

where ρ is the mass density. This gives for the Raman intensity the following result:

$$I(\omega) = \frac{4\pi A P^2 b a^\alpha l_\omega^{1-\alpha} g(\omega) T}{\rho\omega^2}.\qquad(10)$$

The light-to-vibration coupling constant $C(\omega)$ is defined by Shucker and Gammon[13] for the Stokes Raman scattering in glasses as

$$I(\omega) = C(\omega)g(\omega)(n(\omega)+1)/\omega \approx C(\omega)g(\omega)T/\omega^2 \qquad(11)$$

where $n(\omega)$ is the Bose factor that at room temperature can be approximated by T/ω. Comparing Eqs. (10) and (11) one has

$$C(\omega) = (4\pi A P^2 b a^\alpha l_\omega^{1-\alpha}/\rho) \propto l_\omega^{1-\alpha}.\qquad(12)$$

This equation gives the frequency dependence of the coupling coefficient. It is commonly believed that in glasses at the frequencies of the boson peak and higher ones the vibrations fulfill the Ioffe-Regel criterion,[14] i.e., they have only one characteristic length that determines both the vibration length λ and the correlation length l_ω, (Refs. 15–17)

$$\lambda \sim l_\omega \propto v/\omega.\qquad(13)$$

According to Eq. (12) it means that in this frequency range

$$C(\omega) \propto \omega^{\alpha-1}.\qquad(14)$$

The frequency dependence of $C(\omega)$ in the region of the boson peak in glasses is known from the comparison of the Raman spectra with the neutron ones[18–20] and with specific heat data.[21] It was found that typically

$$C(\omega) \propto \omega.\qquad(15)$$

This corresponds to $\alpha=2$ in the correlation function (6). Thus, if vibrations are on the Ioffe-Regel limit then according to Eq. (6) the correlation function decreases as r^{-2} inside the localization region, e.g., as the surface of a sphere that surrounds the localization region.

Such type of the spatial correlation decay is demonstrated by the vibrations of one-dimensional (1D) objects embedded in three-dimensional space. Indeed, if the vibrations have 1D spatial structure then the correlation function $F_\omega(r)$ at a distance r is proportional to the probability that a 1D line intersects the surface of a sphere of the radius r in some fixed vicinity S_0 of this point. This probability is equal to $S_0/4\pi r^2$ and corresponds to $\alpha=2$ in the correlation function (6). S_0 has the sense of the cross section of the 1D objects. Let us note that the similar relation describes the correlations in the fractal structures,[6,22]

$$F(r) \propto r^{d_f-3} \exp(-r/\xi),\qquad(16)$$

where d_f is the fractal dimension that characterizes the internal geometry of the object and ξ is the correlation length. Preexponential factor r^{-2} corresponds to $d_f=1$. Within the frames of the present model it means that vibrations constituting the boson peak in Raman spectra are effectively one dimensional. There are also other arguments in favor of this conclusion.[23,24]

Recently, stringlike cooperative motions have been found in a model glass-forming liquid.[9] A molecular dynamics simulation revealed stringlike motions with a typical size of these 1D objects of some nanometers; the total fraction of the particles contributing to these motions is 5–6%. This well corresponds to the known properties of the boson peak vibrations: their characteristic length is of the order of some nanometers and the fractional integrated density of states is $\sim 10\%$ in a strong glass-former–vitreous silica. Since the system investigated in Ref. 9 is a fragile glass former, the boson peak vibrations should have a smaller fraction of the total density of states than in silica,[25] so 5–6% is a reasonable value for such a fragile glass former.

The result of the present model for the intensity of the boson peak in Raman scattering can be checked by a comparison of the predicted intensity, Eq. (10), with that of the Brillouin lines. Experimentally this ratio was measured in silica glass, Refs. 12 and 26. The expressions for Brillouin scattering are well known (see, e.g., Refs. 27 and 28). In 90° geometry of experiment the intensity of depolarized Brillouin light scattering $I_{VH}^{Br}(\omega)$ is the following:

$$I_{VH}^{Br}(\omega) = A\,\frac{\pi\omega P_{44}^2(n(\omega)+1)}{\rho v_t^2}\,\delta(\omega-\omega_t),\qquad(17)$$

where P_{44} is the respective component of the tensor of elasto-optic constants, v_t is the transversal sound velocity, ω_t is the frequency of the transversal Brillouin line, and A is the

same constant as for the Raman scattering in Eq. (10). The expression (10) now has to be generalized in order to take into account the polarization indices. Neglecting the fluctuations of the elasto-optic constants, it is easy to show[12] that in the same 90° geometry of the experiment the intensity of depolarized Raman scattering $I_{VH}(\omega)$ is determined by the equation

$$I_{VH}(\omega) = 4\pi A P_{44}^2 \int d^3\mathbf{r} \langle \nabla u_\omega(\mathbf{r}) \nabla u_\omega(0) \rangle. \qquad (18)$$

To obtain this equation it was supposed that in a rough approximation all terms of the tensor $\nabla_i u_k(\mathbf{r}, t)$ have in average the same amplitude independently of the directions i and k and different components of $\nabla_i u_k$ do not correlate. Using the estimation (10) of the similar expression (3) one obtains

$$I_{VH}(\omega) = 8\pi^2 A P_{44}^2 b a^2 l_\omega^{-1} g(\omega) \frac{n(\omega)+1}{\rho\omega}. \qquad (19)$$

Let us denote by $x(\omega)$ the ratio of the depolarized Raman intensity within one instrumental width γ to the integrated intensity of the depolarized Brillouin line,

$$x(\omega) = \frac{I_{VH}(\omega)\gamma}{\int I_{VH}^{Br}(\omega) d\omega}. \qquad (20)$$

From Eqs. (17), (19), and (20) one can find for $x(\omega)$ the following expression:

$$x(\omega) = 8\pi b a^2 l_\omega^{-1} v_t^2 \gamma g(\omega)/\omega^2. \qquad (21)$$

For what follows, it is convenient to characterize the density of the vibrational states $g(\omega)$ in the region of the boson peak by its ratio $s(\omega)$ to the Debye density of states $g_D(\omega)$:

$$g(\omega) = s(\omega) g_D(\omega), \qquad (22)$$

where

$$g_D(\omega) = 3\omega^2/2\pi^2 v^3, \qquad (23)$$

and v is the averaged sound velocity defined by the equation $3/v^3 = 1/v_l^3 + 2/v_t^3$. As a result one has

$$x(\omega) = \frac{12}{\pi} \frac{a}{l_\omega} \frac{v_t^2}{v^2} \frac{\gamma}{v/a} b s(\omega). \qquad (24)$$

In Ref. 26 it was found experimentally that the depolarized Raman intensity in vitreous silica at $\omega = 6$ cm^{-1} (within one instrumental width of 1.9 cm^{-1}) is equal to $(4.3 \pm 1) \times 10^{-3}$

times the integrated intensity of one depolarized Brillouin line at $T = 295$ K. From the spectra presented in Ref. 26 it is easy to see that at the maximum of the boson peak ($\omega_0 = 55$ cm^{-1}) the depolarized Raman intensity is higher by a factor of 2.8 than at $\omega = 6$ cm^{-1}, so $x(\omega_0) = 1.2 \times 10^{-2}$. The experimental data on the low-energy vibrational density of states in vitreous silica is given in Ref. 2. From Fig. 1 of this paper one can find that the ratio of the actual density of vibrational states to the Debye one, $s(\omega = 55$ cm$^{-1})$, is equal to ~ 4.3. With these values of x, $s(\omega_0)$, and $v_t = 3.9$ km/s, $v_l = 5.9$ km/s,[26] $\gamma = 1.9$ cm^{-1},[26] $a = 1.6$ Å, from Eq. (24) one can obtain

$$l_{\omega_0}/a \sim 3b. \qquad (25)$$

Normally, the parameter b, defined by Eq. (8), is of the order of unity. For example, for an exponential spatial decay of the vibration correlation function, $f(r/l_\omega) = \exp(-r/l_\omega)$, according to Eq. (8) with $\alpha = 2$ one has $b = 1$. Thus, by the order of magnitude Eq. (25) predicts a reasonable value of the vibration correlation length near the maximum of the boson peak. This is another argument in favor of the presented model.

In conclusion, it is shown that the spectrum of the Raman scattering in glasses in the frequency range of the boson peak depends on the internal spatial geometry of the vibration eigenfunctions. A model is proposed that connects the light to vibration coupling coefficient $C(\omega)$ with the vibration correlation function. It is found that the latter has different dependence on the vibration correlation length l_ω for different spatial dimensionalities of the vibration eigenmodes. The frequency dependence of $C(\omega)$ was determined as a function of the dimensionality at the frequencies equal to or higher than that of the boson peak maximum using the assumption that the Ioffe-Regel criterion of localization is fulfilled in this spectral range. It is shown that within the frames of the model the linear frequency dependence of $C(\omega)$ corresponds to the one-dimensional vibrational eigenmodes. A possible connection of the boson peak with the nanoscale stringlike fast motions in a supercooled liquid found recently in a computer simulation[9] is discussed. Taking the vibration correlation function as that for 1D vibrations embedded in 3D space an estimation of the boson peak intensity in the depolarized Raman scattering is obtained. The ratio of this intensity to the integral intensity of the transversal Brillouin line is in reasonable agreement with the experimental data.

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