

On the theory of Boson peak in glasses

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A universal mechanism of the Boson peak formation in glasses is proposed. The mechanism is based on the concept of interacting quasi-local oscillators. Even in the case of weak interaction the low-frequency spectrum becomes unstable. Due to anharmonicity the system undergoes a transition into a new stable configuration. As a result, below some characteristic frequency ω_c , proportional to the typical strength of interaction, the renormalized density of states becomes a universal function of ω with a Boson peak feature, i.e. the reduced density of states $g(\omega)/\omega^2$ has a maximum at a frequency $\omega_b \ll \omega_c$. We derive an analytical form of this function.

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The purpose of the present paper is to propose a universal mechanism of Boson peak formation in glasses. The Boson peak (BP) is usually observed in a wide temperature range in the inelastic light and neutron scattering intensities at low frequencies, corresponding to a maximum in the reduced density of vibrational states $g(\omega)/\omega^2$ [1]. The position of this maximum correlates with a low temperature bump in the reduced specific heat $C(T)/T^3$ where T is the temperature.

In spite of numerous efforts, there is no widely accepted theory of the Boson peak phenomenon. An interesting feature is that the BP usually does not show up as a peak in the density of states (DOS) $g(\omega)$ itself but only in the reduced DOS, $g(\omega)/\omega^2$. A crucial question is that whether this peak corresponds to phonon degrees of freedom or to some additional harmonic excitations in glasses, quasi-localized (resonant) modes (QLM). In the first case it would correspond either to an anomalous dispersion of the acoustic phonon excitations that has not been observed in experiment or to some low lying optical modes. Disorder in an amorphous material would destroy the long range coherence of optical modes. This makes a distinction between them and quasi-localised (resonant) modes impossible. Therefore, we base our theory of the Boson peak on harmonic excitations in glasses which coexist and interact with long wavelength acoustic phonons (sound waves).

The QLM (or broken up, low lying optical modes) can be described as harmonic oscillators (HO) that interact with the phonons [2–8]. QLM are also found by numerical simulations, see [9] and references therein. Due to their interaction with phonons they should in-

evitably interact with one another [10, 11]. This interaction can cause a mechanical instability of the system and the Boson peak phenomenon [12].

For illustration, consider a system of two interacting HO with a potential energy

$$U_{\text{har}}(x_1, x_2) = M_1\omega_1^2 x_1^2/2 + M_2\omega_2^2 x_2^2/2 - I_{12}x_1x_2. \quad (1)$$

Here M_i are the masses and ω_i the frequencies of the two oscillators. The interaction strength is given by [11]

$$I_{12} = g_{12}J/r_{12}^3, \quad J \equiv \Lambda^2/\rho v^2 \quad (2)$$

where g_{12} accounts for the relative orientation of the HO, r_{12} is their distance, ρ the mass density of the glass and v a sound velocity. The interaction between the HO is due to the coupling between a single HO and the surrounding elastic medium (the glass). Possible additional short range interactions do not introduce qualitative differences. The HO-phonon coupling has the form [7] $\mathcal{H}_{\text{int}} = \Lambda x \varepsilon$, where Λ is the coupling constant and ε the strain.

Diagonalization of Eq. (1) yields two frequencies

$$\tilde{\omega}_{1,2}^2 = \frac{\omega_1^2 + \omega_2^2}{2} \pm \sqrt{\left(\frac{\omega_1^2 - \omega_2^2}{2}\right)^2 + \frac{I_{12}^2}{M_1 M_2}}. \quad (3)$$

The smaller value, $\tilde{\omega}_2^2$, becomes negative when I_{12} exceeds the threshold (critical) value $I_c \equiv \omega_1\omega_2\sqrt{M_1M_2}$. A negative $\tilde{\omega}_2^2$ indicates an instability of the corresponding eigenstate, *vibrational instability* — the previous minimum at $x_1 = x_2 = 0$ becomes a saddle point of the potential energy $U_{\text{har}}(x_1, x_2)$.

This instability persists also in a system of many interacting HO. However, in a real glass an unstable HO is always stabilized by anharmonic forces into a nearby minimum of the potential energy. The position of this minimum depends on the interaction between HO. The new frequencies, in these new minima, are real and different from the original ones. Thus the vibrational spectrum is reconstructed. This is the mechanism of the Boson peak formation.

Let us consider a system of randomly distributed, interacting HO with an initial DOS, $g_0(\omega)$, where $g_0(\omega)$ is a monotonously increasing function of ω in the frequency range from 0 to ω_0 (it is normalized to 1). For the harmonic part of the interaction we take the generalization of Eq. (1) and add an anharmonic term to stabilize the system

$$U_{\text{anhar}} = (A/4) \sum_i x_i^4. \quad (4)$$

We will consider the interaction I_{ij} between the oscillators to be a *small parameter* of our theory. Namely, we assume that the typical random interaction I between neighboring HO is much smaller than the typical values of the product $M\omega_0^2$. As $|I| \ll M\omega_0^2$ the frequencies of the order of ω_0 will be practically unaffected by the interaction whereas HO with frequencies

$$\omega < \omega_c \simeq |I|/M\omega_0 \ll \omega_0 \quad (5)$$

will be displaced to new minima.

Since the concentration of unstable HO is much smaller than the one of the stable ones a low frequency oscillator is usually surrounded by high frequency ones. Therefore we can split our problem into two parts. First we consider a cluster containing a low frequency oscillator with frequency $\omega_1 \lesssim \omega_c$ which is surrounded by a large number N of HO with much higher frequencies $\omega_j \sim \omega_0$. To determine the eigenfrequencies of the interacting oscillators belonging to the cluster one should solve the secular equation of the order of $N + 1$ in ω^2 . However, the variations of the high eigenfrequencies should be small and can be discarded as they are proportional to the small parameter $I/M\omega_0^2$. As a result, one gets for the smallest eigenfrequency a linear equation. It can easily be solved, and one can show that such cluster becomes unstable under the condition

$$M_1\omega_1^2 < k \quad \text{where} \quad k \equiv \sum_j \frac{I_{1j}^2}{M_j\omega_j^2}. \quad (6)$$

For the unstable situation one has to take the anharmonicity, Eq. (4), into account. The new low frequency of the coupled oscillators is then given by

$$\tilde{\omega}_1^2 = \begin{cases} \frac{1}{M_1}(M_1\omega_1^2 - k), & k < M_1\omega_1^2 \\ \frac{2}{M_1}(k - M_1\omega_1^2), & k > M_1\omega_1^2 \end{cases}. \quad (7)$$

It is remarkable that the anharmonicity which has been used in deriving the second Eq. (7) does in the end not enter this equation, as well as our final result, Eq. (20).

Thus the derivation of the new (reconstructed) DOS amounts to a calculation of the distribution of k , $\rho(k)$. Inserting Eqs. (2) and (6) into the definition of $\rho(k)$ gives

$$\rho(k) = \left\langle \delta \left(k - \frac{J^2}{M} \sum_j \frac{g_{1j}^2}{r_{1j}^6 \omega_j^2} \right) \right\rangle. \quad (8)$$

Here the angular brackets denote the averaging over the positions of the N high frequency HO, their frequencies and orientations. For simplicity we take equal masses $M_j = M$ and for g_{ij} a uniform distribution in the interval $[-1/2, 1/2]$.

Using the Holtmark method [13] one gets

$$\rho(k) = \frac{1}{\sqrt{2\pi}} \frac{B}{k^{3/2}} \exp \left(-\frac{B^2}{2k} \right) \quad (9)$$

where

$$B = \frac{1}{3}(2\pi)^{3/2} \frac{Jn}{\sqrt{M}} \left\langle \frac{1}{\omega} \right\rangle_0 \equiv \omega_c \sqrt{M}. \quad (10)$$

Here n is the concentration of HO and $\langle 1/\omega \rangle_0$ is the ω^{-1} moment of the initial DOS $g_0(\omega)$. This formula is the definition of the characteristic frequency ω_c introduced by order of magnitude in Eq. (5). $Jn \simeq I$ is the typical interaction between the nearest neighbours and $\langle 1/\omega \rangle_0 \simeq 1/\omega_0$. We assume that the average $\langle 1/\omega \rangle_0$ is finite, i.e. at small ω the initial DOS $g_0(\omega) \propto \omega^n$ with $n > 0$.

The DOS is reconstructed to $\tilde{g}(\omega) = \tilde{G}(\omega^2)/2\omega$ where

$$\begin{aligned} \tilde{G}(\omega^2) &= \langle \delta(\omega^2 - \tilde{\omega}_1^2) \rangle_{k, \omega_1} \equiv \\ &\equiv \int_0^\infty dk \rho(k) \int_0^\infty d\omega_1^2 G_0(\omega_1^2) \delta(\omega^2 - \tilde{\omega}_1^2) \end{aligned} \quad (11)$$

and $G_0(\omega_1^2) \equiv g_0(\omega_1)/2\omega_1$. Using Eq. (7) and integrating Eq. (5) we obtain

$$\begin{aligned} \tilde{G}(\omega^2) &= \frac{1}{2} \int_0^\infty dk \rho \left(k + \frac{1}{2}M\omega^2 \right) G_0 \left(\frac{k}{M} \right) + \\ &+ \int_0^\infty dk \rho(k) G_0 \left(\omega^2 + \frac{k}{M} \right). \end{aligned} \quad (12)$$

As one can see, for $\omega \ll \omega_c$ $\tilde{G}(\omega^2) = \text{const}$, so that $\tilde{g}(\omega) \propto \omega$, i.e. the reconstructed DOS appears to be a linear function of ω . For high frequencies the first term in Eq. (12) can be discarded and the original DOS is reproduced, $\tilde{G}(\omega^2) = \tilde{G}_0(\omega^2)$ for $\omega \gg \omega_c$.

If the low-frequency HO with their reconstructed linear DOS were isolated, the problem would be solved. There is, however, a further interaction between these HO which we will take into account in the second step of our procedure. The low frequency HO, displaced from their equilibrium positions, create random static forces f . The force f_i acting on the i th oscillator from the j th one is

$$f_i = I_{ij} x_{j0}. \quad (13)$$

In the presence of anharmonicity this again reconstructs the low frequency part of the spectrum (cf with [6]). Consider an anharmonic potential variation under the action of a random static force f , so that $U(x) = Ax^4/4 + M\omega_1^2 x^2/2 - fx$, with ω_1 the oscillator frequency in the harmonic approximation. Under the action of f the equilibrium position shifts from $x = 0$ to x_0 satisfying the equilibrium equation

$$Ax_0^3 + M\omega_1^2 x_0 - f = 0. \quad (14)$$

In the new equilibrium position the oscillator, in the harmonic approximation, acquires the eigenfrequency

$$\omega_{\text{new}}^2 = \omega_1^2 + 3Ax_0^2/M. \quad (15)$$

If $\tilde{g}_1(\omega_1)$ is the distribution function of frequencies ω_1 and $P(f)$ is the distribution of random forces, then one gets the new equilibrium DOS

$$g(\omega) = \int_0^\infty \tilde{g}_1(\omega_1) d\omega_1 \int_{-\infty}^\infty df P(f) \delta(\omega - \omega_{\text{new}}). \quad (16)$$

As the forces between the HO are proportional to r_{ij}^{-3} they have a Lorentzian distribution:

$$P(f) = \frac{1}{\pi} \frac{\delta f}{f^2 + (\delta f)^2}. \quad (17)$$

Assuming $\omega \ll \omega_c$ and integrating Eq. (16) with $\tilde{g}_1(\omega_1) = C\omega_1$ we get

$$\frac{g(\omega)}{\omega^2} = \frac{6C}{\pi\omega^*} \left(\frac{\omega}{\omega^*}\right)^2 \int_0^1 \frac{dt}{1 + (\omega/\omega^*)^6 t^2 (3 - 2t^2)} \quad (18)$$

with

$$\omega^* = \sqrt{3A}^{1/6} (\delta f)^{1/3} / \sqrt{M}. \quad (19)$$

Finally

$$\frac{g(\omega)}{\omega^2} = \frac{3C}{\pi\omega^*} \left(\frac{\omega}{\omega^*}\right)^4 [z_1^2(\omega) + z_2^2(\omega)]^{-1} \times \left[\frac{1}{2z_1(\omega)} \ln \frac{z_1(\omega) + 1}{z_1(\omega) - 1} + \frac{1}{z_2(\omega)} \arctg \frac{1}{z_2(\omega)} \right] \quad (20)$$

where

$$z_{1,2}(\omega) = \frac{1}{2} \sqrt{\sqrt{9 + 8(\omega^*/\omega)^6} \pm 3}.$$

The function $g(\omega)/\omega^2$ is plotted in Fig.1. It depends

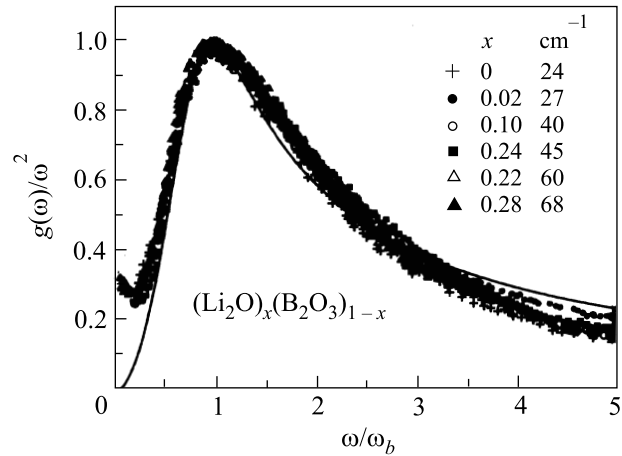


Fig.1. The Boson peak in reduced units: Eq. (20) (solid line) and Raman data for lithium borate glasses [14]. The positions of the BP (for different compositions x) are given the legend

on a single parameter, ω^* . The maximum of $g(\omega)/\omega^2$, i.e. the Boson peak, is at $\omega_b \approx 1.1\omega^*$. For large frequencies, $\omega \gg \omega_b$, $g(\omega) \propto \omega$ while for small frequencies, $\omega \ll \omega_b$, $g(\omega) \propto \omega^4$. Also shown is a comparison of our theoretical curve with Raman scattering data for lithium borate glasses [14] of different compositions. These results are in a rather good agreement with the experimental data and support the idea of a universal form of the Boson peak [15].

The Boson peak frequency, $\omega_b \approx 1.1\omega^*$, is determined by the characteristic value of the random force δf , Eq. (19) acting on a HO with the characteristic frequency ω_c . According to Eq. (13), it is due to the interaction between HO with frequencies of order of ω_c , i.e. $|I_{ij}^{(c)}| \simeq Jn_c$, $J \simeq M\omega_c/g_0(\omega_0)$ where $n_c \simeq g_0(\omega_c)\omega_c$ is the concentration of these HO. The characteristic displacement of an HO from the equilibrium position is $x_0 \simeq \omega_c \sqrt{M/A}$. As a result, we get the estimate

$$\omega_b \simeq \omega_c [g_0(\omega_c)/g_0(\omega_0)]^{1/3}, \quad \omega_b \ll \omega_c. \quad (21)$$

We tested these ideas by numerical simulations. N oscillators with frequencies $0 < \omega_i < 1$ were placed on a

simple cubic lattice with lattice constant $a = 1$ and periodic boundary conditions. For random orientations of the oscillators, g_{ij} , Eq. (2), we took random numbers in the interval $[-0.5, 0.5]$. The anharmonicity parameter, A , and the masses of the oscillators, M_i were set equal to 1. The initial DOS for the noninteracting HO was taken as $g_0(\omega) \propto \omega^n$, with $n = 1, 2, 3$. We minimized the potential energy, and calculated the DOS in the harmonic approximation (around this minimum) for different interaction strengths, J . This procedure was repeated up for 10000 representations. To check for size dependence we did the calculations for different N . Except the case $J = 0.07$, the results did not change between $N = 2097$ and $N = 4096$. The results also did not change by introduction of the cubic anharmonicity.

Fig.2 shows $g(\omega)$ for $g_0(\omega) \propto \omega^2$ and $J = 0.1$ in

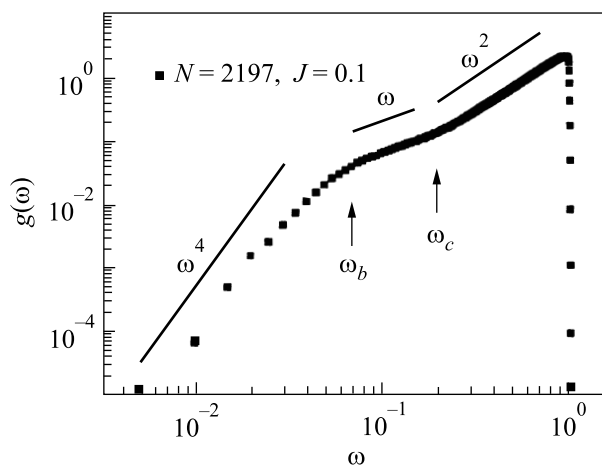


Fig.2. Simulated density of states ($g_0(\omega) \propto \omega^2$, $N = 2097$) in a log-log representation. The arrows indicate two characteristic frequencies ω_b and ω_c

a log-log representation. The predicted cross-overs in the ω -dependence of the DOS are clearly observed at two characteristic frequencies ω_c and ω_b . From the calculated eigenvectors we find that, as expected, near and above ω_b the eigenmodes are complicated superpositions of many HO whereas at the lowest frequencies the HO are weakly coupled.

The dependence of the reconstructed DOS $g(\omega)/\omega^2$ on the interaction strength J is illustrated in Fig.3. One can see the general increase of ω_b and related decrease of the Boson peak intensity with increasing J . This result agrees with recent experiments [16] and molecular dynamic simulations [17]. Our simulations cover one decade in Boson peak frequencies. The insert shows that, in full agreement with our predictions (see Eq. (5) and Eq. (4)), the crossover frequencies change with interaction J as $\omega_c \propto J$ and $\omega_b \propto J^{1+n/3}$.

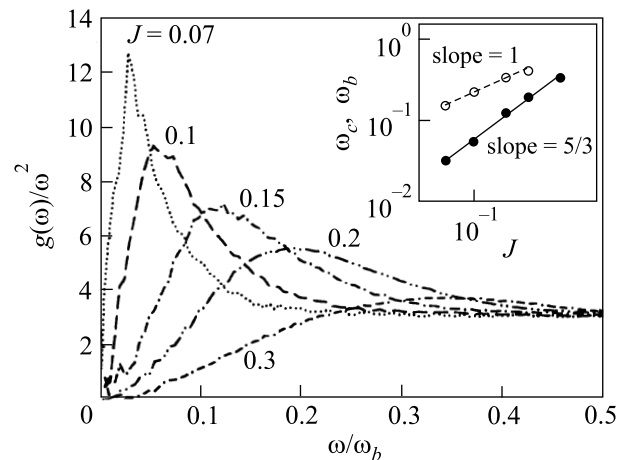


Fig.3. Simulated $g(\omega)/\omega^2$ for different interaction strengths with $g_0(\omega) \propto \omega^2$, $N = 2097$ and $N = 4096$ ($J = 0.07$). The insert shows the scaling of the crossover frequencies ω_c (o) and ω_b (•) with the interaction strength J

In this letter we dealt with the case of weak interaction between HO. If the interaction is increased the characteristic frequencies ω_b and ω_c grow and the gap between them narrows and finally disappears. Then our Boson peak in $g(\omega)/\omega^2$ superimposes the “boundary peak” in $g_0(\omega)$ at the edge of the original vibrational spectrum. The Boson peak can no longer be distinguished from the boundary peak in $g(\omega)$ or from a possible equivalent maximum in $g_0(\omega)$. A similar case with strong coupling between oscillators was investigated in Ref. [10] by means of molecular dynamic simulations and in Ref. [18] using the replica method.

In conclusion, we present a universal picture of the Boson peak formation in glasses where stabilization of the system of weakly coupled harmonic modes by anharmonicity is essential. The principal new result of our approach, compared to previous work, is that the Boson peak emerges naturally on the unstructured flat low frequency part of the initial spectrum $g_0(\omega)/\omega^2$ where no peaks in the DOS existed before. For small interactions the Boson peak frequency is much smaller than the Debye frequency value. It shifts with interaction strength, I , which explains the large variety of Boson peak magnitudes found in experiment.

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