

Interaction of quasilocal harmonic modes and boson peak in glasses

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The direct proportionality relation between the boson peak maximum in glasses ω_b and the Ioffe-Regel crossover frequency for phonons ω_d is established. For several investigated materials $\omega_b = (1.5 \pm 0.1)\omega_d$. At frequency ω_d the mean free path of the phonons l becomes equal to their wavelength because of strong resonant scattering on quasilocal harmonic oscillators. We prove that the established correlation between ω_b and ω_d holds in the general case and is a direct consequence of bilinear coupling of quasilocal oscillators with the strain field.

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The properties of harmonic vibrational excitations in disordered media and glasses is now a very active topic of scientific research (see Ref. 1, and references therein). Contrary to the well established behavior of electrons in disordered conductors there is no consensus at all regarding the harmonic vibrations in ordinary glasses. The most common and challenging of their signatures is the so-called boson peak observed in numerous experiments in low-frequency Raman and inelastic neutron scattering. The physical origin of the peak is, however, still a matter of great debates. The common view is that the solution of this problem is a cornerstone for our veritable understanding of glassy vibrational dynamics.

The main discussion in the literature now involves the question of whether the harmonic vibrations responsible for the boson peak are propagating plane waves (phononlike)² or localized because of disorder.³ The third possibility, which we share in this paper, is that they are neither propagating waves nor localized but have a diffusive nature.⁴ They consist of appropriate superposition of quasilocal vibrations in soft single-well potentials existing in glasses.⁵

For the solution of this crucial question, quite powerful and expensive experimental techniques are now in use. First there are the Raman experiments themselves. But since visible light due to energy and momentum conservation laws does not interact with sound plane wave excitations,⁶ one has to use two other possibilities, namely, inelastic x-ray and neutron scattering.

The main difficulty in the inelastic x-ray scattering experiments is the very high incident photon energy (≈ 20 KeV), and its relatively small change, of the order of 10^{-7} . As a result, the ‘‘x-ray boson peak’’ is superimposed on the steep wings of strong elastic line in the forward direction. Therefore, a serious problem arises: to correctly resolve it and answer the crucial question whether it changes with the momentum transfer.

This difficulty explains why recently two independent groups using the same experimental setup but different fitting procedures have arrived to completely opposite conclusions about the propagating character of the excitations in vitreous SiO_2 at the boson peak range.^{2,3} The situation with inelastic neutron Brillouin scattering (for *small* momentum transfer) is not much better. Here we should stress to avoid

confusion that in neutron scattering up to now well pronounced boson peak results were obtained for large momentum transfer.

To solve this problem, from our point of view, it is necessary to separate the Brillouin (phonon) lines of the boson peak (as in the usual light scattering experiments). Then increasing the momentum transfer \mathbf{q} one can observe how the Brillouin line shifts and broadens approaching the boson peak from the low frequency side. This scenario implies the existence in the q range $0.1-1 \text{ nm}^{-1}$ of *two peaks*, one from damped phonons (Brillouin line) and another the boson peak itself. However, such experiments will hardly appear in a nearest future.

Therefore at this stage of our knowledge, any theoretical insight into the problem would help a lot to establish the true picture of the harmonic vibrations in glasses. The main idea is that the boson peak, being a universal glassy property, should be related with other universal properties of glasses.

In Refs. 7,8,5 the idea was put forward that the boson peak originates not from phonons but from *quasilocal harmonic oscillators* and corresponds to the Ioffe-Regel crossover frequency for phonons ω_d . As it was conjectured in Ref. 5, above, ω_d phonons *cease to exist* as well defined plane wave excitations. Later this idea was adopted (supported) in many papers,^{3,9} though taken alone without any theory, it, of course, could not explain why this correlation actually occurs.

The explanation of such a correlation based on the theory of soft atomic potentials in glasses¹⁰ was proposed in Ref. 5. The main idea is that at this frequency the *dipole-dipole interaction* between quasilocal harmonic oscillators renormalizes their density of states (DOS) from the bare value $g(\omega) \propto \omega^4$ (for independent oscillators) to $g(\omega) \propto \omega$ (for coupled oscillators) behavior. As a result, a boson peak appears in $g(\omega)/\omega^2$ at a frequency $\approx \omega_d$. The reason for the DOS transformation is a *strong level repulsion* in the course of the interaction of oscillators. Above ω_d the oscillators become *delocalized*.¹¹

This correlation was checked indirectly for $\text{As}_x\text{Se}_{1-x}$ glasses⁸ and excellent agreement was found between the position of the bump in the reduced specific heat $C(T)/T^3$ (prototype of the boson peak), and the energy $E_d = \hbar \omega_d$ for different x compositions. The direct evidence should of course include the comparison of the boson peak and the Ioffe-

Regel crossover frequency which is explicitly calculated from the mean free path of phonons l . In its turn l can be easily evaluated from the fit of the thermal conductivity data which are available for many glasses. The purpose of our paper is to make just such a comparison.

In this paper, on the basis of experimental data analysis for different glasses, we have established a direct proportionality relation between the position of the boson peak and the Ioffe-Regel crossover frequency ω_d . At this frequency, the phonon mean free path with respect to the resonant scattering on quasilocal harmonic oscillators becomes equal to the wave length. To proceed further, we should briefly review the main theoretical and experimental results in this field.

It is well known that for many low-temperature properties of glasses two-level systems (TLS's) and phonons are responsible.¹² However, at higher frequencies it is well established that there is an excess of *additional* low frequency harmonic modes which dominate the specific heat above a few K.^{13,14} They also strongly reduce the phonon mean free path producing the plateau in the thermal conductivity of glasses.¹⁵

In Ref. 7 it was argued that these excess modes are quasilocal soft harmonic oscillators (HO) coexisting with TLS's (and phonons) with density of states increasing as $g(\omega) \propto \omega^4$ at moderate frequencies ($W/\hbar < \omega \leq \omega_d$, see below). As a result of raising the temperature, the linear temperature behavior of the specific heat (TLS's contribution) changes to $C(T) \propto T^5$ dependence. Such crossover results in a minimum in $C(T)/T^3$, at some $T_{\min} \approx 0.5-3$ K.^{7,16}

The quasilocal vibrations open also a new effective channel for the phonon scattering. Their steeply rising DOS, $g(\omega)$, leads to the same frequency dependence of the inverse mean free path for phonons because of resonant scattering on these oscillators¹⁵

$$l_{\text{res, HO}}^{-1} = \frac{\pi}{6\sqrt{2}} \frac{C\omega}{v} \left(\frac{\hbar\omega}{W} \right)^3 \propto \omega^4. \quad (1)$$

This dependence looks similar to elastic Rayleigh scattering from glass inhomogeneities though the physical mechanism is drastically different. Even very optimistic estimates show that Rayleigh contribution is at least 4 times smaller than follows from experimental data on thermal conductivity.¹⁷ On the other hand, the resonant scattering mechanism (1) with C taken from low temperature sound velocity measurements gives correct values of the thermal conductivity plateau without additional fitting parameters (see below). Therefore, we believe that in ordinary glasses the Rayleigh scattering is small in comparison with this contribution.

Except for the sound velocity v there are only two parameters in Eq. (1). The first one is a characteristic energy W which is related with the position of the minimum in $C(T)/T^3$, $W \approx 2kT_{\min}$.^{7,16} The second is a coupling constant C which describes the relative change of v with temperature due to resonance scattering of phonons on TLS's¹²

$$(\Delta v/v)_{\text{res, TLS}} = C \ln(T/T_0). \quad (2)$$

Both experimental values of C and T_{\min} are well known for many glasses. It gave the unique possibility, without any

TABLE I. Boson peak frequency ω_b , coupling constant of longitudinal phonons with TLS's C_l , and T_{\min} for several glasses.

Glass	T_{\min} (K)	ω_b (cm^{-1})	C_l (10^{-4})
SiO ₂	2.1 ^a	52 ^b	3.1 ^c
As ₂ S ₃	0.8 ^d	26 ^e	1.6 ^{c,f}
B ₂ O ₃	1 ^a	28 ^g	2.4 ^h
Se	0.6 ^a	18 ⁱ	1.2 ^c
PS	0.9 ^j	17 ^k	3.6 ^c
GeO ₂	1.75; 2 ^l	45 ^b	2.5 ^m
LaSF-7	2.5 (?)	80 ⁿ	1.2 ^c
LiCl·7H ₂ O	3.3 ^a	60 ^o	7.2 ^c

^aReference 19.

^bReference 20.

^cReference 21.

^dReference 22.

^eReference 23.

^fReference 24.

^gReference 25.

^hReference 26.

ⁱReference 27.

^jReference 28.

^kReference 29.

^lReference 30.

^mReference 31.

ⁿReference 32.

^oReference 33.

fitting parameters using Eq. (1), to successfully reproduce the correct value of the thermal conductivity plateau for vitreous SiO₂ and Se (Ref. 15) and for some other glasses as well.¹⁸ From this point of view one can consider Eq. (1) to be in good agreement with the thermal conductivity data.

Using Eq. (1) one can easily obtain the expression for the Ioffe-Regel crossover frequency ω_d ^{8,5}

$$\hbar\omega_d = 0.75WC^{-1/3}. \quad (3)$$

For example for v -SiO₂, $C_l = 3.1 \times 10^{-4}$, $W/k = 4.2$ K, and $\hbar\omega_d/k \approx 47$ K.

Now we can proceed to the main aim of our paper and check whether there exists a correlation between the boson peak frequency ω_b and ω_d determined by Eq. (3). For that purpose, we collected all the necessary experimental parameters T_{\min} , C_l , and ω_b for several glasses in Table I. The two different values of T_{\min} for a -GeO₂ correspond to two different samples investigated in Ref. 30. The value of T_{\min} for LaSF-7 glass is a reasonable guess value (we did not find it in the literature).

Now using the relation $W = 2kT_{\min}$ and Eq. (3) we can calculate ω_d for longitudinal phonons and compare it with ω_b . The result of this comparison is shown on Fig. 1. One can see from the figure that all the data lies near a straight line which has a slope equal to 1.53. This means that within the experimental accuracy there is a direct proportionality relation between the boson peak maximum ω_b and the Ioffe-Regel crossover frequency for phonons ω_d .

In what follows we are going to prove that this correlation results in fact from the *bilinear coupling* between quasilocal oscillators and the deformation field ε

$$\mathcal{H}_{\text{int}} = \Lambda x \varepsilon \quad (4)$$

proposed in Ref. 15. In this sense it can be regarded as a rather general rule.

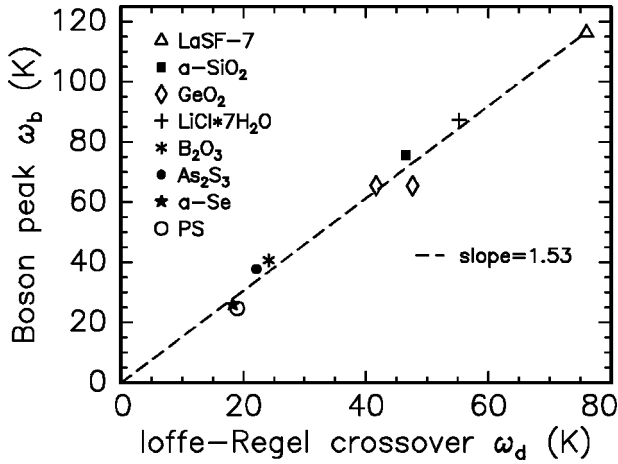


FIG. 1. Position of the boson peak ω_b versus the Ioffe-Regel crossover frequency ω_d for several glasses.

With the use of Eq. (4) one can easily show that the elastic interaction between two oscillators has a dipole-dipole character

$$V_{\text{int}} \approx \frac{\Lambda^2}{\rho v^2 r_{ij}^3} x_i x_j \quad (5)$$

with ρ being the mass density of the glass. Suppose that the DOS of noninteracting oscillators is $g(\omega)$. Then making use of Eq. (4) and the golden rule one can calculate in the usual way the phonon mean free path due to the resonance scattering on these oscillators

$$l_{\text{res.HO}}^{-1} = \frac{\pi \Lambda^2}{2M \rho v^3} g(\omega), \quad (6)$$

where M is an oscillator mass. It is important that this scattering has the same frequency dependence as the bare density $g(\omega)$. The Ioffe-Regel crossover frequency ω_d can be estimated from the equation

$$\left. \frac{g(\omega)}{\omega} \right|_{\omega_d} \approx \frac{M \rho v^2}{\Lambda^2}. \quad (7)$$

In order to determine a position of the boson peak, we should consider the interaction between resonant oscillators. The concentration of such oscillators with frequencies ω lying in a small interval $\delta\omega$ around ω is given by the product $g(\omega)\delta\omega$. Therefore, the nondiagonal transition matrix element of the coupling between the two oscillators (5) is equal to

$$\Delta J \equiv \langle n_{i+1}, n_j | V_{\text{int}} | n_i, n_{j+1} \rangle \approx \frac{\hbar \Lambda^2 g(\omega)}{2M \rho v^2 \omega} \delta\omega. \quad (8)$$

The physical meaning of this quantity is that it gives a characteristic value for a level repulsion of two resonant oscillators because of their interaction.

If $\Delta J < \hbar \delta\omega$ the level repulsion is weak and the interaction does not change $g(\omega)$. If $\Delta J > \hbar \delta\omega$ the level repulsion is strong and renormalizes the original density.⁵ The new

DOS can be found dividing the oscillator concentration in the interval by the characteristic value of their level repulsion

$$\tilde{g}(\omega) \approx \frac{g(\omega)\delta\omega}{\Delta J/\hbar} \approx \frac{M \rho v^2}{\Lambda^2} \omega. \quad (9)$$

We see that the result is a *linear* function of ω which depends only on material parameters of the glass but does not depend on the bare density $g(\omega)$.

In the case when the reduced bare DOS $g(\omega)/\omega^2$ increases with ω we will have a boson peak at some crossover frequency from weak to strong coupling. This frequency is determined by the equation $\Delta J = \hbar \delta\omega$. One can easily see that this equation coincides with Eq. (7) for ω_d . This explains why ω_d correlates with the position of the boson peak in glasses.

The resulting linear ω dependence of vibrational DOS above the boson peak is a very important and general feature of a system of interacting harmonic oscillators with bilinear dipole-dipole coupling (5). It is a direct consequence of linear ω dependence of $|x_{n,n\pm 1}|^{-2} = 2M\omega/\hbar$ and therefore can be regarded as universal. It holds for any bare $g(\omega)$ of quasilocal harmonic modes which rises with frequency faster than ω^2 . It was observed in experiments on inelastic neutron scattering for amorphous polymers,³⁴ α -SiO₂,³⁵ and α -GeSe₂.³⁶

The picture described above implies delocalization of the harmonic excitations above the boson peak though they are not supposed to be plane waves. This is also consistent with existing numerical results. The fact that the Ioffe-Regel criterion does not mean localization for vibrational excitations in disordered system was acknowledged in the computer analysis of the percolation network.³⁷ It was found that vibrational modes above the Ioffe-Regel crossover give substantial contribution to the heat transfer and have some diffusive nature.

Similar results were obtained in Ref. 38 for α -SiO₂ where all modes with $\hbar\omega$ between 5-110 meV were found to be delocalized (just to the right of the boson peak). For amorphous silicon it was found³⁹ that only 3% of vibrational modes (above 70 meV) are localized and do not participate in the heat transfer. The remaining 97% of the modes are delocalized and the majority of them (93%) are not plane waves.

In numerical experiments⁴⁰ the truly localized modes were discovered at the very end of the frequency spectrum. It is worthwhile to mention that at low frequencies the calculated DOS has a part with linear ω dependence just in the region of delocalized states. The same results were obtained for amorphous selenium.⁴¹ The modes with frequencies above 0.5 THz were delocalized (again just above the boson peak for this glass).

To conclude, we have established for the first time the correlation between the boson peak frequency and the Ioffe-Regel crossover frequency. We proved that this correlation occurs because of the bilinear coupling between sound waves and quasilocal harmonic vibrations in glasses.

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- ¹See, for example, the *Proceedings of 7th International Workshop on Disordered Systems*, Molveno, Italy, edited by A. Fontana and G. Viliani [Philos. Mag. **79** (1999)].
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