Giant anharmonicity controls terahertz vibrations and the boson peak anomaly in metallic glasses

Zeng-Yu Yang\textsuperscript{a,b}, Yun-Jiang Wang\textsuperscript{a,b,*}, Alessio Zaccone\textsuperscript{c,d,e,**}

\textsuperscript{a}State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China
\textsuperscript{b}School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China
\textsuperscript{c}Department of Physics “A. Pontremoli”, University of Milan, via Celoria 16, Milan 20133, Italy
\textsuperscript{d}Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB3 0AS, UK
\textsuperscript{e}Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK

Abstract

The boson peak (BP) is a universal feature in the Raman and inelastic scattering spectra of both disordered and crystalline materials. The current paradigm presents the boson peak as the result of a Ioffe-Regel crossover between ballistic (phonon) and diffusive-type excitations, where the loss of coherence of phonons is described as a purely harmonic process due to structural disorder. This “harmonic disorder” paradigm for the BP has never been challenged or tested at the atomistic level. Here, through a set of atomistically-resolved characterizations of amorphous metallic alloys, we uncover a robust inverse proportionality between the intensity of boson peak and the activation energy of excitations in the potential energy landscape (PEL). Larger boson peak is linked with shallower basins and lower activation barriers and, consequently, with strongly anharmonic sectors of the PEL. Numerical evidence from atomistic simulations indicates that THz atomic vibrations contributing the most to the BP in atomic glasses are strongly anharmonic, as evidenced through very large values of the atomic- and mode-resolved Grüneisen parameter found for the atomic vibrations that constitute the BP. These results provide a direct bridge between the vibrational spectrum and the topology of the PEL in solids, and point towards a new “giant anharmonicity” paradigm for both generic disordered materials and for the phonon-glass problem in emerging materials for energy applications. In this sense, disorder and anharmonicity emerge as the two sides of the same coin.

Keywords: Disordered materials; Boson peak; Potential energy landscape; Giant anharmonicity
1. Introduction

The spectra of atomic vibrations in disordered materials, such as glasses, have been the object of tremendous experimental, computational and theoretical efforts over the last decades. Understanding the vibrational Raman and inelastic neutron/X-ray scattering spectra of glasses is a central step for the quantitative prediction and understanding of the thermodynamic and thermal transport properties of disordered materials. While the electronic properties of disordered systems are now fundamentally understood thanks to the pioneering work of Mott, Anderson, van Vleck, Efros, Shklovskii and others, such a fundamental understanding for the vibrational and thermal properties of structurally disordered materials is currently missing. Understanding the vibrational properties of amorphous materials is also crucial to solve the longstanding problem of amorphous elasticity [1] and plasticity [2].

The vibrational density of states (VDOS), in this context, plays a central role since it is the key factor entering the integrals in terms of which the specific heat and thermal conductivity of glasses are expressed [3]. Since the early 1960s, at least, experimental evidence from Raman and Brillouin scattering of glasses showed the presence of a large peak in the Debye-normalized Raman intensity (i.e. divided by Debye’s law $\sim \omega^2$), in the THz regime [4]. The Raman intensity of glasses at low energy is given by $I(\omega) \sim g(\omega)[n(\omega, T) + 1]$, with $n(\omega, T) + 1 = [1 - \exp(-\hbar\omega/k_BT)]^{-1}$ the Bose function, where $k_B$ is the Boltzmann constant [5]. Since the peak intensity appeared to depend on temperature $T$ according to the Bose distribution (likely because the exponential character of the latter obscures all other dependencies), this prompted researchers to believe that the boson peak is insensitive to temperature and therefore its origin must be purely “harmonic”.

In spite of this, the early theoretical approaches to explain the boson peak vibrational glassy anomalies were based on double-well anharmonic models [6–10], following in the wake of Ilya M. Lifshitz’s pioneering work on atomic vibrations around defects in solids. Further experimental evidence were collected later on, revealing the profound effects of anharmonicity on the attenuation of sound waves in glasses in the GHz and THz regions, supporting the anharmonic origin of

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*Corresponding author.
**Corresponding author.

Email addresses: yjwang@imech.ac.cn (Yun-Jiang Wang), alessio.zaccone@unimi.it (Alessio Zaccone)
Brillouin (or Akhiezer) diffusive linewidths $\Gamma \sim q^2$ up to the Ioffe-Regel crossover between ballistic and diffusive propagation of vibrations [11–14]. Similar evidence for the strong anharmonic damping of transverse acoustic phonons has been recently found also for metallic glasses [15]. Subsequently, the Ioffe-Regel crossover between ballistic propagation and diffusive-like $\Gamma \sim q^2$ (transverse) excitations has been established, based on numerical simulations, as the fundamental process behind the boson peak [16]. It has been confirmed more recently in theoretical calculations [17, 18] that the crossover from a regime at low $\omega$ dominated by the real (acoustic) part of the excitation into a regime dominated by the imaginary (diffusive) part provides a universal mechanism for the boson peak. The origin of the diffusive linewidth being traced back to anharmonicity [19], this mechanism is able to provide an explanation to the many recent observations of boson peak in the spectra of perfectly ordered or minimally-disordered crystals [20–23], where clearly the structural disorder plays no role.

In spite of these many conceptual and experimental evidences suggesting a leading role of anharmonicity as the main driving factor for the phonon decoherence leading to Ioffe-Regel crossover and the boson peak, there is no doubt that the current dominant paradigm to explain the boson peak is based on the idea of “dissipationless” or “harmonic” disorder as manifested e.g. in spatially fluctuating elastic constants. In this framework, as developed in several papers by W. Schirmacher, G. Ruocco and co-workers [24, 25] and known as “heterogeneous elasticity theory” (HET), the loss of phonon coherence at the Ioffe-Regel crossover has nothing to do with anharmonicity and stems uniquely from disorder.

In this paper we settle this debate and provide a conclusive answer to this fundamental question (i.e. whether the boson peak in glasses stems from “harmonic” or “anharmonic” processes), based on atomistic simulations. For the first time, we are able to directly quantify the harmonic/anharmonic character of each atomistically-resolved vibrational eigenmode that contributes to the boson peak, in a paradigmatic atomic glass. It is demonstrated that the eigenmodes that make up the boson peak in the THz regime are strongly anharmonic, as reflected in their erratic trajectories through shallow regions of the potential energy landscape (PEL). Furthermore, huge values of the atomistically- and mode-resolved Grüneneisen parameter are found for the atomic vibrations that contribute to the boson peak. This rich evidence points to a new paradigm of “giant
anharmionicity” in glasses as the root cause of glassy thermal anomalies, in analogy with emerging thermoelectric materials [26–29].

2. Methods

2.1. Molecular Dynamics

Extensive molecular dynamics simulations are conducted via the open source code LAMMPS [30]. Prototypical binary Cu$_x$Zr$_{100-x}$ ($x = 30, 40, 50, 60, 70$) MG models, each containing 19652 atoms, are constructed based on the many-body Finnis-Sinclair-type embedded-atom potential [31] implemented to describe the interatomic interactions. For the model preparation process, a $NPT$ ensemble (constant number of atoms, constant pressure, and constant temperature) is utilized, and the pressure remains zero by Parrinello–Rahman barostat [32]. The temperature is controlled through the Nosé–Hoover method [33]. Each system with randomly distributed lattice atoms are first heated and equilibrated at 2000 K for 2 ns to achieve a fully melting state. The liquid is then quenched to the glassy state at 0 K, with cooling rates spanning multiple orders of magnitudes, i.e., from $10^9$ K/s to $10^{14}$ K/s. To prepare the inherent structures at different temperature, we further thermally equilibrate the systems at the desired temperature with $NVT$ (constant number of atoms, constant volume and constant temperature), and then perform energy minimization using the conjugate gradient algorithm. Periodic boundary conditions (PBCs) are imposed to all the three directions. The MD time is set to be 0.002 ps.

2.2. Single-particle intensity of boson peak

The vibrational analysis of the glass state is performed by direct diagonalization of the Hessian matrix of the inherent structures, which correspond to local energy minima positions in the PEL. The single-particle vibrational density of states (VDOS) for the $i$th atom is defined as

$$ g_i(\omega) = \frac{1}{3N} \sum_j \delta(\omega - \omega_j) |e_j|^2, \quad (1) $$

where $N$ is the total number of atoms. $\omega_j$ and $e_j$ represent the phonon frequency and the corresponding polarization vector. The sum of $g_i(\omega)$ equals to the total VDOS $g(\omega)$ of the system. Further, the reduced VDOS, i.e., the value divided by $\omega^2$ can be used to characterize the boson
peak. The intensity of single-particle boson peak is thus formulated as the maximum value of the reduced VDOS, i.e., \( I_{BP} = \max \left[ g_i(\omega)/\omega^2 \right] \).

2.3. Single-particle activation energy

To explore the underlying topological feature of the PEL, including the energy minima and the surrounding saddle points, the activation-relaxation technique nouveau (ARTn) [34, 35] is utilized to extract the single-particle activation energy. In the framework of ARTn, an initial perturbation is introduced to a central atom and its neighbors by imposing a random small displacement vector. The magnitude of the perturbation displacement vector is fixed as 0.1 Å, while the activation direction is chosen randomly. To restrict the perturbation to a specific atom, the cutoff distance of the atom cluster is set to be 2 Å, which is shorter than the first maximum of the radial distribution function of the CuZr glasses. The state is pulled towards high energy along the weakest Hessian direction. When the lowest eigenvalue of Hessian matrix is less than \(-0.30 \text{ eV/Å}^2\), the system is pushed towards the saddle point automatically using a Lanczos algorithm. The system is considered to converge to the saddle point state when the force on any atom is below 0.05 eV/Å. Thereafter, the energy difference between the saddle point and the initial state is calculated as the corresponding activation energy of an atom’s hopping. For a statistical purpose, each atom is activated for 20 times with random initial perturbation. The average activation energy of the 20 events for each atom is further used as a single-particle activation energy.

3. Results and discussion

3.1. Correlating boson peak with topology of PEL

In order to understand what kind of excitations contribute to the boson peak, we start from the analysis of the PEL of the model binary metallic glass Cu\(_{50}\)Zr\(_{50}\), and we study its relation to the boson peak. Fig. 1a shows a 3D illustration of the PEL, where the minima (or basins of the landscape) represent the inherent structures, while saddle points (or hills of the landscape) characterize the dynamical bottlenecks on the pathways of structural excitations and relaxations. As sketched in Fig. 1a, the short-time vibration around a minimum or valley is shown by the orange trajectory. The long-time transition from one local energy minimum to a neighbouring one
is characterized by the red line. Clearly, the short-time vibrations within a single basin are mainly “harmonic”, whereas the red trajectories are associated with strongly anharmonic eigenmodes. The goal of the subsequent analysis is to disentangle the relative prevalence of these two types of excitations among those that form the boson peak in the VDOS.

In amorphous materials, the existence of extra low-energy modes in excess with respect to the Debye law \( \propto \omega^2 \), defines the boson peak anomaly, which can be quantified by the maximum value of the \( \omega^2 \)-normalized VDOS, as shown in Fig. 1b. To our knowledge, none of the approaches that can be found in the literature have attempted to understand this phenomenon from the perspective of its relation to the PEL.

Fig. 1c shows the energy difference between the saddle point and the initial local minimum, which is defined as the activation energy to structural excitations. On the basis of atomistic molecular dynamics (MD) simulations, we have access to both sets of information, i.e. the activation energies in the PEL and the eigenmodes, in an atomistically resolved way. In other words, for each atom we can extract its contribution to the vibration spectrum and to the BP, as well as its ramblings through the PEL and the activation energies that it goes through.

Hence, to seek quantitative correlations between eigenmodes and activation energies, the particle-level intensity of boson peak \( I_{BP} \) and the activation energy \( \Delta Q \) are calculated for each atom. The raw data are plotted in Fig. S1 in the Supplementary Information (SI). Even though the correlation is somewhat broad in terms of the original scattered data points, qualitatively the trend is clear: \( \Delta Q \) increases with decreasing \( I_{BP} \). This observation applies for both Cu and Zr atoms. In Fig. 2, we compare \( \Delta Q \) for the group of atoms with the 10% lowest and the 10% highest \( I_{BP} \) values in Cu\(_{50}\)Zr\(_{50}\). The atoms which more prominently contribute to the BP effectively experience a lower magnitude of activation energy in their dynamics, and, thus, are more susceptible to structural rearrangement under thermal and/or mechanical stimuli. Also, importantly, their motions are markedly anharmonic, as shallow activation basins are obviously linked to larger anharmonicity, whereas deep valleys and steep barriers are related to harmonic-type dynamics [36].

Our explanation for the weak correlation shown in Fig. S1 is that the collective vibrational anomaly and the structural excitation are not exactly controlled by the first-shell local structure, but rather their structural fingerprint is embedded in several shells of the radial distribution function.
(RDF) via spatial correlations. We therefore plot the $I_{BP}$ vs $\Delta Q$ correlation as a function of the coarse-graining size in Fig. 3. The best correlation, quantified by the Pearson’s coefficient, can be achieved with the coarse-graining length $L = 5.9$ Å. In Fig. 4a, we plot the activation energy versus the reciprocal of the BP intensity for the spatial coarse-graining size that yields the strongest correlation. Finally, Fig. 4b shows the corresponding result after numerical coarse-graining with bin size of $\sim 100$ atoms. It shows a strong, well-defined $\Delta Q \sim I_{BP}^{-1}$ scaling law. This intimate correlation between boson peak and activation energy in the PEL implies a nonlocal scenario for the thermodynamics and dynamics in glasses [37–40].

The $I_{BP}$–$\Delta Q$ correlation can be studied in terms of spatial coarse-graining. The spatial distributions of the particle-level intensity of boson peak $I_{BP}$ and activation energy $\Delta Q$, as well as their coarse-grained counterparts, i.e., $[1/I_{BP}]_{CG}$ and $\Delta Q_{CG}$, are shown in Fig. 5a–d. The 3D rendering is further provided in Figs. S2 and S3. All of them consistently imply that the high-$I_{BP}$ regions and the low-barrier regions overlap with each other significantly, once a certain (optimal) value of spatial coarse-graining length is chosen. Again, the best correlation is established with coarse-graining size of 5.9 Å. This value arises as the characteristic decay length of the spatial autocorrelation function for both quantities. Here, the normalized spatial autocorrelation function of a physical entity is defined as

$$C (r) = \frac{\langle \Delta P_{n} \Delta P_{n+r} \rangle - \langle \Delta P_{n} \rangle^{2}}{\langle \Delta P_{n}^{2} \rangle - \langle \Delta P_{n} \rangle^{2}},$$

where $P_{n}$ and $P_{n+r}$ denote the values of the property “$P$” at a reference position $r_{0}$, and that at a distance of $r$ from the reference atom, respectively. Here, $\Delta$ denotes the deviation from the ensemble averaged value. The operator $\langle \cdots \rangle$ represents the operation of ensemble average. As shown in Fig. 5e, the spatial autocorrelation function for the particle-level intensity of the boson peak, and that for the activation energy, exhibit exactly the same decay with distance $r$, with exactly the same value of correlation length, namely 5.9 Å. When $r = 5.9$ Å, $C (r)$ decays to approximately $\exp (-3)$ of the reference value for both quantities, which corresponds to an optimal compromise, since lower values would imply losing the effect of medium-range correlations, whereas larger values would see the correlation vanish altogether.
3.2. Direct evidences for the anharmonic origin of boson peak

As mentioned above, a spatial region with a high-boson-peak contribution can be used as predictor of a locally shallow basin with lower activation energy. The universality of this relationship is demonstrated by examining different glasses. As shown in Fig. 6 and Fig. 7, such correlation is robust against variation in both composition and cooling history. Since low barriers are usually associated with asymmetry in PEL topology [27], one may deduce that it is the anharmonicity that causes the boson peak anomaly in glasses. On the contrary, large activation energy is linked with deeper valleys in PEL, which are usually well described by the harmonic transition state theory. In this sense, lower $\Delta Q$ means stronger deviation from harmonicity, hence “soft” and anharmonic regions of the PEL. This idea will be justified in the following with plenty of evidence at the atomic scale.

To demonstrate the anharmonicity of the energy basins which contribute to the BP, we run MD in Cu$_{50}$Zr$_{50}$ glass sample for 1 ps at 100 K, after sufficient thermal equilibration. The potential energy and the root mean-squared displacement (RMSD) of the system are recorded in Fig. 8 as a function of time. We pick two extreme atoms, with strongest and weakest contribution to the boson peak, respectively, for demonstration. For the low-boson-peak atom with ID = 7565 shown in Fig. 8a, each fragment of PEL closely resembles a quadratic function. However, the PEL fragment of the high-boson-peak atom with ID = 1633 shown in Fig. 8b strongly deviates from the harmonic approximation. This indicates that the atomic motions contributing to boson peak explore the more anharmonic topology of the local PEL. These atoms are found to move far away from their equilibrium positions, as further evidenced by the trajectory shown in Fig. 8d. Instead, atoms that do not participate in the boson peak are limited in their motions to the harmonic basins of the PEL. Low-boson-peak atoms are found to vibrate near their local equilibrium position, as shown in Fig. 8c. Moreover, it is interesting to find that the high-$I_{BP}$ experiences string-like collective motion, as shown in the inset of Fig. 8b, in analogy to the atomic-scale pattern of $\beta$ relaxation [41–43]. This new link that we found between BP and stringlets aligns well with very recent results of Douglas and co-workers [44]. Further, the generality of the anharmonic diffusive dynamics of high-$I_{BP}$ atoms is verified by applying this analysis to more atoms in Figs. S4 and S5.

Temperature dependence provides further insights into the anharmonic origin of the boson
peak. If the local PEL were completely harmonic for a certain vibration mode, there would be no dependence on temperature. Figure 9 shows the VDOS and its Debye-normalized at different temperatures. Increasing temperature leads to the shift of VDOS and boson peak towards smaller values of frequency. Meanwhile, the intensity of boson peak is enhanced as temperature increases in agreement with the behaviour seen for polymer glasses [45]. The phenomena are more conspicuous across the glass transition temperature, $T_g = 650$ K for Cu$_{50}$Zr$_{50}$. Thus, temperature-dependent VDOS points to the anharmonic origin of the boson peak. Note that some early experiments observed that the Raman scattering intensity is proportional to $n(\omega) + 1$. Therefore, the peak in the VDOS was concluded to be temperature independent. This is possibly caused by either 1) the Bose-Einstein exponential function at room temperature, which makes the temperature dependence of the BP not visible, or 2) experimental error bars, or a combination of 1) and 2).

The final “smoking gun” evidence, which further demonstrates and quantifies the strong anharmonicity of boson peak vibrations, comes from the mode- and atomic-resolved Grüneisen parameter $\gamma$, which is directly associated to the third- and higher-order anharmonic coefficients in the Taylor expansion of the interatomic interactions [27, 46–48]. The atomistic Grüneisen parameter can straightforwardly quantify the level of anharmonicity of a local PEL fragment experienced by a given atom, furthermore the linewidth of acoustic phonons can be shown [16, 19] to be $\Gamma \sim Dq^2$, with the vibration diffusivity $D$ being proportional to the average Grüneisen parameter $\gamma$ of the material at hand [48, 49]. First of all, the mode-Grüneisen parameter, $\gamma_k$, is calculated according to the derivative of the phonon frequency with respect to volume variation

$$\gamma_k = -\frac{V}{\omega_k} \frac{\partial \omega_k(V)}{\partial V}, \quad (3)$$

where $V$ is the volume, and $\omega_k$ is the phonon frequency of the $k$th normal mode. It can be approximated by the numerical differentiation method [50]:

$$\gamma_k = -\frac{V}{\omega_k} \left( \frac{\Delta \omega_k(V)}{\Delta V} \right), \quad (4)$$

To obtain the mode-Grüneisen parameter, a three-step diagonalization of the Hessian matrix is carried out accounting for the variation of phonon frequency at $0.99\ V_0$, $1.0\ V_0$ and $1.01\ V_0$, respectively. $V_0$ is the volume of the system at ground state. As shown in Fig. 10a, $\gamma_k$ is then plotted
as a function of the phonon frequency. Surprisingly, huge values of the apparent mode-Gr"uneisen parameter appear at low frequencies. This indicates that the definition of the $k$th normal mode—sorted by the magnitude of the normal mode frequency $\omega_k$ at ground state $V_0$—is not invariant against volumetric variation. Thus the low-frequency modes contributing to the boson peak are diffusive (or exchangeable due to low activation energy; see Fig. 1) under mechanical deformation. It implies that the boson peak is controlled by the anharmonic interactions, and that the energy flows from one mode to another, in analogy to the anharmonic/nonlinear Fermi-Pasta-Ulam problem. Moreover, the dashed vertical line in Fig. 10a indicates the frequency of boson peak, which appears right at the inflection point of the $\gamma$ vs $\omega$ function. The inset of Fig. 10a is a semi-logarithmic plot, which shows that a large part of data points for the mode-Gr"uneisen parameter are near zero. Only a small fraction of modes contribute to the big absolute value of $\gamma_k$ and thus to the boson peak. The discontinuity in $\gamma_k$ in the inset can be attributed to the periodic boundary condition used in atomistic simulations.

Further, the anharmonic feature is demonstrated also at the system level. In Fig. 10b, $\gamma_{\text{ave}}$, which denotes the average value of the mode Gr"uneisen parameter within $\omega < \omega_0$, is plotted as a function of frequency. Even on a system level, the average $\gamma_k$ has quite large values (in range between 1 and 2), suggesting strong anharmonic effects, especially, at low frequencies. It is interesting to note that $\gamma_{\text{ave}} (\omega < \omega_0)$ has a maximum at 2.5 THz, which is in accord with the position of boson peak (2.5–5.5 THz) as shown in Fig. 9b.

The above picture, where anharmonicity dominates the THz and the lower-energy spectrum, whereas the high-energy spectrum is less anharmonic, is also in line with experiments by Monaco and co-workers on various glasses, which showed that anharmonic damping is active at low wavenumber, while the more “harmonic” Rayleigh scattering/damping [51] dominates at higher frequencies [14].

Finally, to show the robustness of the correlation between intensity of boson peak and anharmonicity, we further define a particle-level Gr"uneisen parameter $\gamma_i$ via summation of all contributions from individual mode-Gr"uneisen parameters projected onto the polarization direction of a
specific atom $i$. That is

$$\gamma_i = \sum_k -\frac{V}{\omega_k} \left( \frac{\Delta \omega_k(V)}{\Delta V} \right) |\mathbf{e}_k^i|^2,$$

(5)

where $\mathbf{e}_k$ is the eigenvector of the $k$th eigenmode, and $\mathbf{e}_k^i$ denotes the corresponding polarization vector of the atom $i$ in the $k$th normal mode. Fig. 10c shows the statistical $I_{BP}-\gamma_i$ correlation. Here, the background shows the raw data colored by the number density, while the scattered points are the result of numerical coarse graining with proper bin size. Throughout the whole frequency domain, the particle-level intensity of boson peak reveals a strong positive correlation with the particle-level Grüneisen parameter, with a robust exponential correlation. Only a slight deviation from the exponential is seen at extremely high $\gamma_i$ values. It is evident from this picture that the atoms with the largest atomic-level Grüneisen parameter values contribute the most to the boson peak intensity. Hence, also the particle-level information strongly indicates anharmonicity as the physical origin of the boson peak in disordered materials.

4. Conclusions

In summary, we presented a detailed quantitative characterization of atomic vibrations in atomic glasses from the point of view of anharmonicity. In contradiction with the current dominant paradigm [24, 25, 52] that postulates that the excess of vibrational modes in the THz range of glasses (known as boson peak anomaly) is due to “harmonic” dissipationless processes induced solely by disorder, we have demonstrated quantitatively at the atomistic level that the boson peak is formed by strongly anharmonic vibrations. This is in line with early theoretical models [7–9] and confirms the universal mechanism proposed in [17] for the origin of the boson peak due to the Ioffe-Regel crossover from ballistic to diffusive anharmonic propagation of vibrational excitations in glasses as well as in ordered crystals [20–22]. The above framework provides a natural connection between PEL and vibrational eigenmodes in solid-state systems. The emerging picture of disorder and anharmonicity being the two sides of the same coin, opens up plenty of opportunities for structure-property relations and for material discovery in the area of amorphous materials for mechanical and thermal transport applications, as well as for crystalline strongly anharmonic thermoelectric materials [26–29] where the boson peak plays an increasingly important
role [29, 53–55].

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Figure 1. (a). Schematic of a fragment of PEL illustrating thermodynamic vibration and thermal activation between neighbouring basins. (b). \( \omega^2 \)-reduced VDOS, \( g(\omega)/\omega^2 \), confirms the existence of boson peak in glasses. The inset shows the original VDOS. (c). Schematic of 1D activation pathway defines activation energy for a structural excitation.
Figure 2. (a). Distribution of the activation energies for excitation of Cu atoms in two groups, i.e., the highest and lowest 10% of the intensity of boson peak, respectively. (b). The case for Zr atoms.

Figure 3. Pearson’s correlation coefficient between the intensity of boson peak and the activation energy as functions of spatial coarse-graining length. It shows that best correlation achieved with $L = 5.9 \text{ Å}$. 

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Figure 4. Boson peak correlates inversely with the difficulty of the thermally activated structural excitation in glass. (a). Correlation between the spatially coarse-grained boson peak intensity $[1/I_{BP}]_{CG}$ and the activation energy $\Delta Q_{CG}$ with coarse-graining length $L = 5.9 \, \text{Å}$. The color indicates the number density of atoms. (b). Numerical coarse graining of the data in (a) with binning size of a hundred atoms, which reproduces a $\Delta Q \sim I_{BP}^{-1}$ law.
Figure 5. Spatial correlation between the single-particle boson peak and the activation energy. (a–d) Spatial distribution of $1/I_{BP}$, activation energy $\Delta Q$, as well as their coarse-grained counterparts with coarse-graining length $L = 5.9$ Å, respectively. (e) Semi-logarithmic plot of the spatial autocorrelation function versus distance for $1/I_{BP}$ and $\Delta Q$. The red dashed lines are the best fits according to an empirical equation $C (r) = \exp (-r/\xi)$. When $r = 5.9$ Å, $C (r)$ decays to approximately $\exp (-3)$, as shown by the blue dashed line.
Figure 6. Robustness of the inverse proportionality between the activation energy and the intensity of boson peak against variation in chemical composition. The surveyed glass compositions include a set of Cu$_x$Zr$_{100-x}$ MGs ($x = 30, 40, 50, 60, 70$).

Figure 7. Robustness of the inverse proportionality between the activation energy and the intensity of boson peak against variation in cooling history. The cooling rates applied during sample preparation are varying from $1 \times 10^9$ to $1 \times 10^{14}$ K/s.
Figure 8. Demonstration of the anharmonicity of local energy basins. (a–b). Potential energy as a function of RMSD of the atoms with the weakest and strongest intensity of boson peak, respectively. The color bar corresponds to elapsing time. The insets show the pattern of atomic motions in terms of displacement vector. Only the atoms travelled longer than 1 Å are shown for clarity, with blue spheres representing copper atoms and red for zirconium ones. Higher boson-peak atoms usually experience string-like motion. (c–d) The trajectories of the atoms corresponding to (a) and (b).
Figure 9. Temperature relevance of the boson peak. (a). VDOS of the glassy inherent structures at different temperatures. Inset indicates increasing vibrational soft modes at higher temperature. (b). Reduced VDOS by Debye-squared law. Boson peak intensifies by increasing temperature.
Figure 10. Anharmonicity unveiled by mode- and particle-level Grüneisen parameter. (a). Mode Grüneisen parameter as a function of phonon frequency, with the inset being the semi-logarithmic plot. The dashed vertical line indicates the position of boson peak frequency. Grüneisen parameter is large at low frequencies, indicating a quasi-localized nature of the low-frequency vibration. (b). Mode averaged Grüneisen parameter $\gamma_{\text{ave}}$ as a function of frequency. Error bars denote the standard deviation in the frequency domain below the shown value. (c). Semi-logarithmic plot of the intensity of single-particle boson peak as a function of the single-particle Grüneisen parameter. The background heat map denotes the raw data colored by number density, while the scattered circles represent numerical coarse-grained values with binning size of a hundred atoms.