Universal link between the boson peak and transverse phonons in glass

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The physical properties of a topologically disordered amorphous material (glass), such as heat capacity and thermal conductivity, are markedly different from those of its ordered crystalline counterpart. The understanding of these phenomena is a notoriously complex problem. One of the universal features of disordered glasses is the 'boson peak', which is observed in neutron and Raman scattering experiments. The boson peak is typically ascribed to an excess density of vibrational states. Here, we study the nature of the boson peak, using numerical simulations of several glass-forming systems. We discovered evidence suggestive of the equality of the boson peak frequency to the Ioffe–Regel limit for 'transverse' phonons, above which transverse phonons no longer propagate. Our results indicate a possibility that the origin of the boson peak is transverse vibrational modes associated with defective soft structures in the disordered state. Furthermore, we suggest a possible link between slow structural relaxation and fast boson peak dynamics in glass-forming systems.

Vibrational states of crystals with periodicity can be well understood as quantized plane-wave phonon modes, but the nature of vibrations in disordered systems remains elusive. Glassy and amorphous materials exhibit a number of peculiar low-temperature properties that are considered anomalous in comparison with those of their crystalline counterparts¹⁻⁴. The universality of these properties in various types of glass has fascinated many researchers. For example, the specific heat (C_p) below 1 K increases linearly with the temperature T instead of T^3 expected from the Debye model. This anomaly below 1 K is explained by two-level tunnelling systems at least on a phenomenological level¹. At higher temperatures (10-30 K), all disordered materials including biological matter (for example, proteins³) also exhibit some unusual dynamical properties that are practically independent of the detailed structure of the material. These properties include anomalous acoustic behaviour, the existence of a plateau in the T dependence of the thermal conductivity, the peak in the T dependence of C_p/T^3 and the boson peak observed in inelastic scattering of light or neutrons. These indicate the existence of an excess vibrational density of states over the prediction of the Debye model: corresponding to the maximum in C_p/T^3 , the vibrational density of states (VDOS), $D(\omega)$, scaled by the square of the angular frequency ω , $D(\omega)/\omega^2$, goes through a maximum, which is called the 'boson peak' (typical energy scale: a few millielectronvolts) (refs 1-4). There is a consensus that the boson peak is a manifestation of some sort of disorder, but its physical origin has remained a serious puzzle in condensed-matter physics and materials science¹⁻⁵. The boson peak is believed to be the key to the fundamental understanding of the vibrational states of glassy and amorphous materials, which are beyond the simple plane-wave phonon picture for crystals.

For a long time, it has been well recognized in the glass community that the strength of the boson peak increases with a decrease in the fragility. The fragility characterizes how steeply the viscosity increases on cooling^{3,6}. Liquids in which the viscosity

obeys the Arrhenius law are called 'strong' (for example, covalent liquids such as silica and germania), whereas 'fragile' liquids (many organic liquids) have super-Arrhenius behaviour. It is an intriguing open question why there is such a relation between the boson peak characterizing the high-frequency excitations and the fragility characterizing the slowest flow behaviour⁷.

Recent advances in experimental and computational techniques provide us with further information on the microscopic dynamics of glass. For example, Rufflé et al. found that the boson peak frequency is closely related to the Ioffe-Regel limit of longitudinal phonons⁸ for many glasses, using Brillouin scattering of light and X-rays⁹. Note that the Ioffe–Regel limit is reached when the mean free path of the phonons approaches their wavelength. However, Scopigno et al.¹⁰ found that there exists a well-defined Ioffe-Regel limit even well above the boson peak energy for a metallic glass (Ni₃₃Zr₆₇). This controversy has made it unclear whether the Ioffe-Regel limit has a connection to the boson peak frequency or not^{11,12}. The fact that the boson peak has predominantly transverse character has been well known for decades from its high depolarization ratio in the Raman scattering intensity^{13,14}. This has recently been confirmed by numerical studies, which suggest that the boson peak in a soft sphere glass¹⁵ and silica^{16,17} has a transverse character. However, it should be noted that there are still ongoing debates on whether the boson peak has an acoustic or non-acoustic nature¹⁸⁻²⁰.

A number of theoretical models have been proposed to explain the anomalous low-energy excitations, for example, localization of vibrations²¹, soft anharmonic nature of the potentials^{22–24}, frequency resonance or localization of phonons due to cohesive clusters²⁵, the mode-coupling approach²⁶, vibrational modes of a system of randomly fluctuating elastic constants^{27–29}, a crossover between a minima-dominated phase (with phonons) and a saddle-point-dominated phase (without phonons) in the complex energy landscape³⁰, strongly anharmonic transitions between the local minima of the energy landscape³¹, the elastic–granular



Figure 1 Structural relaxation and high-frequency dynamics (boson peak). a, Temperature dependence of the structural relaxation time τ_{α} of the liquid (P = 0.5, N = 1,024) for $\Delta = 0.6, 0.65, 0.7, 0.75$ and 0.8. T_g is the glass-transition temperature. Solid curves are Vogel–Fulcher fits. **b**, Density of states divided by the angular frequency ω of the glass (P = 0.5, N = 4,096) for $\Delta = 0.6, 0.65, 0.7, 0.75$ and 0.8. T_g is the glass-transition temperature dependence of τ_{α} of the liquid ($\Delta = 0.8, N = 1,024$) for P = 0.5, 1.0, 1.5, 2.0 and 3.0. Solid curves are Vogel–Fulcher fits. **d**, Density of states divided by ω for the glass ($\Delta = 0.8, N = 4,096$) for P = 0.5, 1.0, 1.5 and 2.0. Inset: The density of states for P = 0.5 compared with the Debye value (horizontal solid line) calculated from longitudinal and transverse sound velocities (see text).

(affine–non-affine) crossover at a certain mesoscopic length^{32,33} and resonant or localized modes associated with locally favoured structures³⁴ (LFSs). However, the physical origin of the boson peak and the link between slow and fast dynamics still remain elusive even on a qualitative level. Here, we tackle these challenging problems, using numerical simulations of three standard glass-forming systems³⁵ as well as a recently developed two-dimensional (2D) glass-forming system (2D spin liquid (2DSL))³⁶, where the fragility can be systematically controlled over an extremely wide range just by modifying the interaction potential or changing the pressure (see the Methods section).

Figure 1a shows the so-called Angell plot³ of 2DSL where the structural relaxation time (τ_{α}) is plotted against T_g/T (T_g : the glass-transition temperature) for five different degrees of frustration Δ , or the strength of the anisotropic part of the potential (see the Methods section), at pressure P = 0.5. We set $T \equiv T_g$ when $\tau_{\alpha} = 10^6$. The data can be well fitted by the Vogel–Fulcher relation $\tau_{\alpha} = \tau_{\alpha}^0 \exp[DT_0/(T - T_0)]$, where D is the so-called fragility index and T_0 is the Vogel–Fulcher temperature. Note that the smaller D means 'less' fragile. The fragility can also be characterized by the so-called fragility parameter (steepness index) *m* (ref. 3): $m \equiv d(\log_{10} \tau_{\alpha})/d(T_g/T)|_{T=T_g}$. Note that the larger value of *m* means that the liquid is more fragile (opposite to D). The reason why we prefer D rather than the more popular m is that m depends on the choice of T_{g} , which is rather arbitrary in simulations. We list the values of D and m in Supplementary Information, Table SI. We found that the fragility index D increases, that is, the fragility decreases, with an increase in Δ : D = 7.4, 10.9, 17.2, 29.7 and 84.3 for $\Delta = 0.6$, 0.65, 0.7, 0.75 and 0.8, respectively. This range of D almost extends from the fragile (for example, organic liquids) to the strong extremes (for example, silica) in real liquids. Figure 1b shows the Δ dependence of VDOS at P = 0.5. The peak position of $D(\omega)/\omega$, that is, the boson peak, shifts towards a lower frequency and the intensity of the boson peak becomes stronger as the degree of frustration Δ increases. This result is consistent with the well-known experimental fact that the intensity of the boson peak becomes stronger for a stronger liquid^{3,7}. Figure 1c shows the Angell

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Figure 2 Longitudinal and transverse phonon dynamics and the dispersion relations. a, Longitudinal and transverse dynamical structure factors of the glass ($\Delta = 0.8$, P = 0.5). Solid lines are the damped harmonic oscillator fits. **b**, Dispersion relations for longitudinal (L) and transverse (T) motion of the glass ($\Delta = 0.8$, P = 0.5). Ω_{α} and $\pi \Gamma_{\alpha}$ ($\alpha = L$ or T) are fitted by q (solid line) and q^2 (solid curve). The horizontal thick grey line is ω_{BP} .

plot for five pressures for $\Delta = 0.8$. The higher the pressure, the more fragile the liquid: D = 84, 24, 14, 10 and 7.4 for P = 0.5, 1.0, 1.5, 2.0 and 3.0, respectively. This result is also consistent with our prediction³⁷. Figure 1d shows the pressure dependence of VDOS. The boson peak frequency shifts towards a higher frequency and the intensity of the boson peak becomes weaker with an increase in the pressure, which is exactly the characteristic feature observed experimentally^{4,38}.

Now we briefly consider the dependence of the fragility on Δ and *P*. The increase in Δ , which characterizes the strength of the anisotropic part of the potential, leads to stronger bond-forming ability. The increase in P, on the other hand, leads to weaker bond-forming ability, because the local symmetry preferred by the potential occupies a larger specific volume than random structures without bonding. This is an explanation based on the correlation of the bond-forming tendency and the fragility³. In our two-order-parameter model of glass transition³⁷, the fragility is determined by the energetic frustration between long-range ordering towards crystallization and short-range bond ordering towards the formation of LFSs. The degree of frustration is correlated with the ability to form the LFSs with five-fold symmetry (pentagons) in 2DSL (ref. 36), which decreases with an increase in *P* or with a decrease in Δ . Thus, the above results are also consistent with this scenario. In our scenario37, even if the bond-forming ability is high, if the local symmetry favoured by bonding is consistent with that of crystal, then a liquid should be a poor glass former and not be a strong liquid. This prediction should be checked in the future.

Figure 2a shows the wavenumber (q) dependence of the longitudinal and transverse dynamic structure factor, $S_L(q, \omega)$ and $S_T(q, \omega)$ (see the Methods section). At low ω , these can be fitted with a damped harmonic oscillator model:

$$S_{\alpha}(q,\omega) \propto \frac{\Omega_{\alpha}(q)^2 \Gamma_{\alpha}(q)}{(\omega^2 - \Omega_{\alpha}(q)^2)^2 + \omega^2 \Gamma_{\alpha}(q)^2},$$

where $\alpha = L$ and T for a longitudinal and transverse mode respectively. $\Omega(q)$ corresponds to the excitation frequency and $\Gamma(q)$ corresponds to the full-width at half-maximum of the excitations. Figure 2b shows the dispersion relation for a liquid of $\Delta = 0.8$ at P = 0.5. Linear dispersion relations are observed for $\Omega(q)$ for both longitudinal and transverse phonons. As the degrees of translational and rotational freedom are 2N and N respectively, the Debye value $D_{\text{Debye}}(\omega)$ of the translational motion should satisfy $\int d\omega D_{\text{Debye}}(\omega) = 2/3$. Thus, we have

$$D_{\text{Debye}}(\omega) = rac{V}{6\pi N} \left(rac{1}{
u_{ ext{L}}^2} + rac{1}{
u_{ ext{T}}^2}
ight) \omega,$$

where $v_{\rm L}$ and $v_{\rm T}$ are the longitudinal and transverse sound velocity respectively. For $\Delta = 0.8$ and P = 0.5, we compared it with VDOS in the inset of Fig. 1d, which shows that the peak has excess VDOS over the Debye value: the distinct signature of the boson peak. Both $\Gamma_{\rm L}(q)$ and $\Gamma_{\rm T}(q)$ obey a q^2 law, consistent with experimental results^{10,39,40}: $\Gamma_{\rm L}(q) = (\eta_{\rm L}/\rho_0)q^2$ and $\Gamma_{\rm T}(q) = (\eta_{\rm T}/\rho_0)q^2$, where ρ_0 is the density and $\eta_{\rm L}$ and $\eta_{\rm T}$ are longitudinal and transverse viscosity, respectively. The Ioffe–Regel limit condition is given by

$$\Omega(q) = \pi \Gamma(q).$$

From Fig. 2b, we determine the Ioffe–Regel limit for the longitudinal wave (ω_{IR}^L) as 2.5 and that for the transverse wave (ω_{IR}^T) as 1.5. In Fig. 2b, we also show the boson peak frequency (ω_{BP}) for comparison. This result clearly indicates that a well-defined longitudinal acoustic wave continues to exist well above the boson peak frequency ω_{BP} , which is consistent with the experimental results of Scopigno *et al.*¹⁰. The most striking finding is that $\omega_{IR}^L \gg \omega_{BP}$, but $\omega_{IR}^T = \omega_{BP}$.

To check the generality of the latter relation, we calculated the dependence of $\omega_{\text{IR}}^{\text{L}}$ and $\omega_{\text{IR}}^{\text{T}}$ on Δ and P and compared them with $\omega_{\rm BP}$ (see Supplementary Information, Table SII and Supplementary Information, Fig. S2). Figure 3a shows the relation $\omega_{\text{TR}}^T = \omega_{\text{BP}}$ holds well in a very wide range of the fragility. We also calculated ω_{IR}^{L} , ω_{IR}^{T} and ω_{BP} for three other systems, 2D and 3D binary Lennard-Jones systems (2DLJ and 3DLJ) and a 2D binary soft-core system (2DSC) (see Supplementary Information, Table SII and Supplementary Information, Fig. S3). Figure 3b clearly demonstrates that the relation $\omega_{IR}^T = \omega_{BP}$ holds very well for all of the systems studied, irrespective of the dimensionality and the detail of the interaction potential. This suggests the intimate and universal link of the boson peak with transverse phonons, but not with longitudinal phonons. In disordered materials, however, the longitudinal sound wave is often hybridized with the transverse one that has the same energy and vice versa⁴¹. This is particularly the case for strong liquids having directional covalent bonding, such as silica. This is why ω_{IP}^{L}

is located near $\omega_{\rm BP}$ in some materials and causes the dispute^{11,12} about whether $\omega_{\rm IR}^{\rm L}$ is correlated with $\omega_{\rm BP}$ or not. However, it was recently reported for some materials (for example, NiZr₂) that $\omega_{\rm IR}^{\rm L}$ is much higher than $\omega_{\rm BP}$ (ref. 10), which is consistent with the result shown in the inset of Fig. 3b. We argue that the longitudinal sound wave can propagate as a plane wave even far above $\omega_{\rm BP}$, when it is only weakly hybridized with the transversal sound wave.

It is highly desirable to experimentally observe the dynamics of the transverse acoustic phonons of these materials and confirm the relation $\omega_{\rm BP} = \omega_{\rm IR}^{\rm T}$. It is worth noting the physical message of our finding. First we note that

$$\omega_{\rm BP} \equiv \omega_{\rm IR}^{\rm T} = v_{\rm T} q_{\rm IR} = v_{\rm T}^2 / \pi (\eta_{\rm T} / \rho_0) = \mu / (\pi \eta_{\rm T}) = 1 / (\pi \tau_{\rm T}),$$

where μ is the shear modulus and $\eta_{\rm T}$ and $\tau_{\rm T}$ are the dissipation and characteristic time associated with transverse vibrations, respectively. Note that $\eta_{\rm T}$ is different from the macroscopic viscosity η . Experimentally it was confirmed that η_L is temperature independent in a wide temperature region ranging from values well below T_{g} up to the liquid phase^{39,40}. Thus, we speculate that $\eta_{\rm T}$ may also be temperature independent, although this is to be confirmed. Two possible origins for this temperature-independent sound absorption have been proposed: static^{28,40,41} and dynamic origin²³. This is also related to the nature of the Ioffe-Regel crossover and the origin of the boson peak. For example, it was suggested⁴¹ that the Ioffe-Regel crossover is ascribed to 'elastic' scattering of acoustic phonons from a static disorder (Rayleighlike scattering). Schirmacher et al.^{28,29} suggested that the static disorder leads to microscopic random spatial fluctuations of shear modulus and the boson peak arises from a band of random transverse acoustic vibrational states. Klinger and Kosevich²³, on the other hand, suggested that there can be Ioffe-Regel crossover for 'inelastic' (resonant) scattering of acoustic phonons from harmonic soft-mode vibrations. Our results suggest that there is no anomaly in the excess DOS at $\omega = v_L q_{IR}^T$ (see Fig. 1), which means that longitudinal phonons with wavenumber around q_{IR}^T propagate without any anomaly. q_{IR}^T of 2DSL is markedly different from those of 2DLJ and 2DSC (see Supplementary Information, Table SII), despite their rather similar structures. These facts indicate that the length scale associated with q_{IR}^T is not relevant to the phonon scattering, which seems to be inconsistent with a scenario in which spatial inhomogeneity of the local shear modulus leads to elastic scattering of phonons. Thus, our results seem to suggest the importance of $\omega_{\text{IR}}^{\text{T}}$ rather than q_{IR}^{T} and support an inelastic (resonant) scattering scenario, but specifically 'transverse' soft modes (not longitudinal ones). However, further study is necessary to settle this fundamental issue.

Next we consider the boson peak intensity. The boson peak intensity is known to increase with a decrease in the fragility and the pressure. Such behaviour is indeed observed in Fig. 1. Recent experimental studies, however, have suggested that the boson peak intensity after scaling by the Debye level is independent of the pressure⁴² or even increases with an increase in pressure^{43,44}. Thus, we study how the boson peak intensity scaled by the Debye level, $A_{\rm BP} \equiv D(\omega_{\rm BP})/D_{\rm Debve}(\omega_{\rm BP})$, behaves as a function of Δ and P. Because in the above we learned that the boson peak has a close connection to transverse phonons, we also scaled the boson peak intensity by the Debye level of the transverse phonons alone, $A_{\rm BP}^T \equiv D(\omega_{\rm BP})/D_{\rm Debye}^T(\omega_{\rm BP})$. The results are shown in Fig. 4. After scaling the angular frequency by $\omega_{\rm BP} \cong \omega_{\rm IR}$, the scaled boson peak can be surprisingly well collapsed on a single curve for $\omega \leq 3\omega_{\rm BP}$ for 2DSL at various Δ values and P values, 2DLJ and 2DSC for both types of scaling. The lowest angular frequency points always lie below the Debye level, but this may be due to a too small number of points in that low- ω region, which leads to significant errors. The



Figure 3 Relation between the boson peak frequency and the loffe–Regel limit frequencies for longitudinal and transverse phonons. a, Δ and *P* dependencies of $\omega_{\rm IR}^{\rm L}$, $\omega_{\rm IR}^{\rm L}$ and $\omega_{\rm BP}$. Left panel: *P*=0.5; right panel: Δ =0.8. Dotted lines are guides for the eye. **b**, Relationship between $\omega_{\rm BP}$ and $\omega_{\rm R}^{\rm T}$ for various *P*, Δ and systems. The solid line is $\omega_{\rm IR}^{\rm T} = \omega_{\rm BP}$. Inset: The relation between $\omega_{\rm IR}^{\rm L}$ and $\omega_{\rm BP}$. The solid line is $\omega_{\rm IR}^{\rm T} = \omega_{\rm BP}$. Although there is a positive correlation between $\omega_{\rm IR}^{\rm L}$ and $\omega_{\rm BP}$, we do not see any simple relation between them.

larger excess density of states over the Debye level in 3D than in 2D (see, for example, Supplementary Information, Fig. S3) may be due to extra degrees of freedom of transverse vibrational modes in 3D. Our results suggest a remarkably simple relation for the boson peak intensity for 2D:

$$\frac{D(\omega_{\rm BP})}{\omega_{\rm BP}} \propto \frac{D_{\rm Debye}(\omega_{\rm BP})}{\omega_{\rm BP}} \propto \frac{1}{K} + \frac{1}{\mu} \quad \text{or} \quad \frac{1}{\mu}.$$
 (1)

As the bulk modulus *K* is usually more than a few times larger than μ and furthermore the *P* (or Δ) dependence of *K* is similar to that of μ , the difference in the above two relations is not so significant. Nevertheless, because the scaling by $D_{\text{Debye}}^T(\omega_{\text{BP}})$ is better than that by $D_{\text{Debye}}(\omega_{\text{BP}})$ (compare Fig. 4b and d), we are tempted to claim that the boson peak amplitude is inversely proportional to μ for 2D. The above relation indicates that variations of the boson peak can



Figure 4 Scaled shape of the boson peak. a, Δ dependence of the boson peak in which intensity and angular frequency are scaled by the Debye level $D_{\text{Debye}}(\omega)$ and ω_{BP} , respectively. **b**, *P* dependence of the boson peak in which intensity and angular frequency are scaled by the Debye level $D_{\text{Debye}}(\omega)$ and ω_{BP} , respectively. **b**, *P* dependence of the boson peak in which intensity and angular frequency are scaled by the Debye level $D_{\text{Debye}}(\omega)$ and ω_{BP} , respectively. The data for 2DLJ and 2DSC are also plotted after the same scalings. **c**, Δ dependence of the boson peak in which intensity and angular frequency are scaled by the Debye level of the transverse phonons $D_{\text{Debye}}^{T}(\omega)$ and ω_{BP} , respectively. **d**, *P* dependence of the boson peak in which intensity and angular frequency are scaled by the Debye level of the transverse phonons $D_{\text{Debye}}^{T}(\omega)$ and ω_{BP} , respectively. The data for 2DLJ and 2DSC are also plotted after the same scalings.

be described by the transformation of the elastic continuum. This is consistent with a recent report on the pressure effects on the boson peak of Na₂FeSi₃O₈ (ref. 42) and the temperature dependence of the boson peak of silica45; however, it is not compatible with the above-mentioned experimental observations^{43,44}. More importantly, it is known that the boson peak intensity scaled by the Debye level, $A_{\rm BP}$, increases with a decrease in the fragility⁴⁶. It has been proposed recently that this behaviour may be explained by the correlation between the microscopic damping of longitudinal phonons $\eta_{\rm L}/\rho_0$, the fragility *m* and $A_{\rm BP}$ (refs 20,29,47). Our results, however, do not exhibit such a distinct correlation among these quantities: for the 2D systems, A_{BP} is constant (see Fig. 4) and independent of $\eta_{\rm L}$ (or $\eta_{\rm T}$) (see Supplementary Information, Table SII). The above relation (1) holds for the 2D systems studied here, which suggests that $A_{\rm BP}$ does not depend on the fragility. This apparently contradicts experimentally observed correlations of the $A_{\rm BP}$ and the fragility⁴⁶. We speculate that this problem may be related to the relation between the macroscopic and local modulus: $A_{\rm BP}$ may be independent of the fragility only when the mechanical series model connecting the local modulus to the average modulus holds (see below), in other words, when soft regions form a majority matrix phase. For stronger liquids, hard regions become the majority and the mechanical series model does not hold any more and mechanical series–parallel models become necessary. This seems to explain the larger $A_{\rm BP}$ for stronger liquids. As the discussion is speculative, however, further careful study is necessary to reveal what physical factors control the boson peak intensity.

Now we come to another fundamental question: the structural origin of the boson peak. In our 2DSL, there are three structural candidates (see also Fig. 4a–c in ref. 36) that may give rise to quasi-localized vibrational modes with the characteristic frequency $\sim \omega_{BP}$ and couple with transverse phonons: medium-range crystalline (antiferromagnetic) order (MRCO) (dark green particles in Fig. 5b), LFSs (white particles forming pentagons in Fig. 5b) and low-density defective structures (white particles in Fig. 5c) in the



Figure 5 Structural origin of the boson peak. a, Spatial distribution of $D_i(\omega_{\rm BP})$, which is the amplitude of the vibration modes with frequencies around the boson peak frequency. Particles with less boson peak intensity are more blue. The background is coloured the same way (darker for less boson peak intensity), and this same background is repeated in **b** and **c**, to see the correlation of $D_i(\omega_{\rm BP})$ with local order and local volume, respectively. Note that we equilibrated the liquid of $\Delta = 0.6$ at T = 0.18 and P = 0.5 and quenched it to T = 0.02 to prepare this sample. Thus, MRCO is more developed and the number density of LFSs is higher than in samples prepared by a rapid quench. **b**, Spatial distribution of the order parameter $\bar{\Psi}_i(\mathbf{r})$ (see ref. 36 for its definition). Dark green, green and white particles represent MRCO, normal liquids and LFSs, respectively. **c**, Spatial distribution of local volume (the area of Voronoi polygon per particle). Brighter particles have larger local volume (less local density). **d**, $D(\omega) / \omega$ per particle averaged over the one-third of particles having large local volume ('large'), small local volume ('small'), intermediate local volume ('intermediate') and all of the particles.

normal liquid structure. We calculate VDOS per particle, $D_i(\omega_{\rm BP})$ of a glass (see the Methods section), which is the amplitude of the vibrations around the boson peak frequency, and study the correlation between $D_i(\omega_{\rm BP})$ and these structural candidates. Figure 4a shows the distribution of $D_i(\omega_{\rm BP})$ for the glass ($\Delta = 0.6$, T = 0.02, P = 0.5). Here, $\omega_{\rm BP} = 2.1$ and we set $\Delta \omega = 0.5$ (see the Methods section). In Fig. 5a-c, the background (outside a particle) colour is brighter for particles with high $D_i(\omega_{\rm BP})$. Comparison of the colour between particles and their background in Fig. 5b tells us that the vibrational amplitude is small in regions with high MRCO, which is consistent with the above conclusion. Thus, particles inside MRCO seems not to be responsible for the boson peak. As MRCO is the origin of dynamic heterogeneity in our system³⁶, this gives us the impression that the boson peak may not be a direct consequence of dynamic heterogeneity and the resulting elastic inhomogeneity. On noting that main vibrational displacements should be located on the surface of MRCO (see, for example, ref. 31), however, further careful studies are necessary to settle this issue.

Next we focus on LFS, which has a unique five-fold symmetry in this system³⁶. The number density of LFS (*S*) increases with a decrease in the fragility and decreases with an increase in the pressure, which is qualitatively consistent with the behaviour of the boson peak intensity (Fig. 1). The fact that white particles in Fig. 5b often have large $D_i(\omega_{\rm BP})$ indicates that LFSs contribute to the boson peak.

Finally, we consider the low-density defective structures. Figure 4c shows the spatial distribution of the local density, calculated from the volume of the Voronoi cell. We can see a positive correlation between the local boson peak intensity and the local (free) volume from the comparison of particle and background colour in Fig. 5c. This relation can also be clearly seen in Fig. 5d, where the boson peak intensity for particles with large, intermediate and small free volume is shown. The particles with larger free volume mainly contribute to the boson peak over the Debye value. This scenario also naturally explains the fact that a hyperquenched glass has a stronger boson peak than an annealed one, as discussed in ref. 38. These findings seem to be incompatible with a scenario that cohesive (dense) regions contribute to the boson peak. Interestingly, the boson peak contribution from less dense structures has higher frequency components, which may suggest smaller $\eta_{\rm T}$ for less dense structures. Now we consider how the relation $I_{\rm BP} \equiv D(\omega_{\rm BP})/\omega_{\rm BP} \propto 1/\mu$ established for 2DSL can be reconciled with the above-mentioned dependence of the boson peak on local structures. Suppose that each type of local structure *i* (fraction Φ_i) has the shear modulus μ_i . Note that $\Sigma_i \Phi_i = 1$. Then the boson peak from each structure may be Φ_i/μ_i and thus $I_{\rm BP} \propto \Sigma_i \Phi_i / \mu_i$. On the other hand, the total boson peak intensity is proportional to the inverse of the average shear modulus μ . This implies that $1/\mu = \sum_i \Phi_i/\mu_i$, suggesting the relevance of the mechanical series model.

Here, we consider the reason why these structures couple with transverse phonons but 'not' with longitudinal phonons. This may be due to the fact that the longitudinal (or, dilatational) resonant frequencies of these local structures are much higher than $\omega_{\rm BP}$ and not well separated from those of the other local structures (or, microscopic vibrational modes). These two factors lead to the absence of resonant couplings between the structures and longitudinal phonons. For example, we confirmed that rotational vibrational states of LFS are located near the boson peak frequency, whereas its longitudinal ones accompanying volume deformation are located at much higher frequencies, where similar vibrational modes for various other particle configurations (including even MRCO) exist. Rotational motions of tetrahedra in silica (see, for example, refs 17,21) are also an example of such soft transverse vibrational modes. Defective structures responsible for the boson peak are much softer against shear deformation than the other structures in glass, whereas there is no such strong inhomogeneity in the softness of local structures against volume deformation. This originates from the general feature that the rigidity of a local structural element against shear deformation is much more sensitive to its particle configuration than that against volume deformation is. So, structural disorder allows particles to have isolated transverse vibrational modes.

From the above findings, we can draw the following scenario concerning the origin of the boson peak: transverse vibrational modes associated with low-density defective structures and LFSs are responsible for the excess VDOS, or the boson peak. These structures are both caused by frustration against crystalline ordering. In other words, energetic³⁶ or geometrical⁴⁸ frustration leads to low-density defective structures in a supercooled liquid and a glass state, which may be the source of (quasi-)localized transverse vibrational modes. The relation $\omega_{\rm BP} = \omega_{\rm IR}^T$ tells us that there exist structural motifs with (quasi-)localized transverse vibrational modes that resonantly couple with transverse phonons and thus govern their dissipation. It may be these transverse vibrational modes that make the vibrational states of disordered solids different from those of periodic crystals, which are characterized only by extended plane-wave phonons. The boson peak frequency probably marks the characteristic frequency of transverse vibrational modes, to which transverse phonons resonantly couple and as a result

transform from propagating to diffusive modes. In our 2DSL, the increase in the degree of frustration (bond-forming ability) leads to the decrease in the fragility and also in the shear modulus μ (see Supplementary Information, Table SII). On noting that the boson peak amplitude is inversely proportional to μ in these systems, this suggests a negative correlation between the fragility and the boson peak intensity (not scaled by the Debye level). To explain the experimentally observed dependence of the boson peak intensity scaled by the Debye level, $A_{\rm BP}$, on the kinetic fragility⁷, however, we need to seek other physical factors, one of which may be the relationship between the average shear modulus μ and the local one μ_i . Further careful study is required to clarify the underlying mechanism.

METHODS

SIMULATION METHODS

We carried out constant pressure and temperature (NPT) ensemble molecular dynamics with a Nosé–Poincaré–Andersen thermostat to prepare samples for the calculation of dynamical properties³⁶, and carried out standard microcanonical (NVE) ensemble molecular dynamics to calculate the dynamical structure factor for both longitudinal and transversal motion, $S_L(q, \omega)$ and $S_T(q, \omega)$. We used periodic boundary conditions for a system (volume V) consisting of N = 4,096 particles. The model potential we used is the following functional form:

$$U_{ij} = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 - \Delta \left(\frac{\sigma}{r_{ij}} \right)^6 f(\theta_i, \theta_j) \right)$$

Here $f(\theta_i, \theta_j) = (h(\theta_i - \theta_0)/\theta_c) + (h(\theta_j - \theta_0)/\theta_c) - (64/35\pi)\theta_c$, where $h(x) = 1 - 3x^2 + 3x^4 - x^6$ for -1 < x < 1 and h(x) = 0 for $x \le -1$ or $x \ge 1$. θ_i is an angle between the relative vector $\mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i$ and the unit vector \mathbf{u}_i that represents the orientation of the axis of particle *i*. θ_j is an angle between the relative vector $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and the unit vector \mathbf{u}_i that represents the orientation of the axis of particle *i*. θ_j is an angle between the relative vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and the unit vector \mathbf{u}_j . The function $h(\theta - \theta_0)/\theta_c$ $(\theta_0 = 126^\circ \text{ and } \theta_c = 53.1^\circ)$ has a maximum at $\theta = 126^\circ$. Thus, this term stabilizes the LFS of five-fold symmetry. The details of the potential and simulation method are given in ref. 36. Note that Δ represents the strength of frustration against crystallization. Throughout this paper, we use the following scaled units³⁶. We used particle mass M, σ and ϵ as the basic unit of mass, length and energy, respectively. Thus, the moment of inertia *I*, the temperature *T*, the pressure *P*, the distance *r* and the time *t* are scaled as: $I \equiv I/m\sigma^2$, $T \equiv k_{\rm B} T/\epsilon$ ($k_{\rm B}$: Boltzmann's constant), $P \equiv P\sigma^2/\epsilon$, $r \equiv r/\sigma$ and $t \equiv t/\tau_0$ ($\tau_0 = \sqrt{m\sigma^2/\epsilon}$). The scaled angular frequency is given by $\omega = 2\pi \nu \tau_0$, where ν is the frequency.

We investigated the dynamics of liquids with $\Delta = 0.6$, 0.65, 0.7, 0.75, 0.8 and P = 0.5, 1.0, 1.5, 2.0. We prepare the samples by the following procedure. First we equilibrated the liquid at T = 0.8 until t = 100.0 in the NPT ensemble. This system is then cooled to T = 0.02 at a quench rate of $dT/dt = 2.0 \times 10^{-4}$. The quenched glass samples are relaxed for t = 100.0. The final configuration of the NPT ensemble is used as the starting configuration of the NVE ensemble simulation. These samples are relaxed for t = 100.0. If the averaged T and P are different from the target values, we change the kinetic energy and the volume slightly until they reach the target values. These samples are used as the starting configuration for calculating dynamical structure factors. To improve the statistics, ten different configurations of 4,096 particles created in this way were averaged to estimate VDOS and $S(q, \omega)$.

VDOS ANALYSIS

To obtain the VDOS, two different methods were adopted. In the direct diagonalization method, the steepest-descent method is carried out for the final configuration of NVE. The dynamical matrix corresponding to the potential energy minimum reached by the steepest-descent method is given by

$$D_{ij} = \frac{1}{\sqrt{M_i M_j}} \frac{\partial^2 U(x_1, y_1, \phi_1, \dots, x_N, y_N, \phi_N)}{\partial R_i \partial R_j},$$

where M_i is the mass (M) or inertia moment (I) of particle *i* and R_i is the coordinate (x or y) or angle (ϕ) of particle *i*. We directly diagonalize the

dynamical matrix and calculate the VDOS $D_{\rm DD}(\omega)$ as

$$D_{\rm DD}(\omega) = \frac{1}{3N-2} \sum_{\lambda} \delta(\omega - \omega_{\lambda}),$$

where ω_{λ} is the eigenfrequency. In the fast Fourier transformation (FFT) method, we calculate the VDOS without the degree of rotational freedom, $D_{\text{FFT}}(\omega)$, by the Fourier transform of the velocity autocorrelation function as

$$D_{\rm FFT}(\omega) = \int \frac{\mathrm{d}t}{2\pi} \exp(i\omega t) \frac{\left\langle \sum \sqrt{m_i} v_i(t) \cdot \sqrt{m_i} v_i(0) \right\rangle}{\left\langle \sum \sqrt{m_i} v_i(0) \cdot \sqrt{m_i} v_i(0) \right\rangle}$$

We calculate the VDOS with the degree of rotational freedom $D_{\text{FFT,R}}(\omega)$ as

$$D_{\rm FFT,R}(\omega) = \int \frac{dt}{2\pi} \exp(i\omega t) \\ \times \frac{\left\langle \sum \sqrt{m_i} v_i(t) \cdot \sqrt{m_i} v_i(0) + \sqrt{I_i} \omega_i(t) \cdot \sqrt{I_i} \omega_i(0) \right\rangle}{\left\langle \sum \sqrt{m_i} v_i(0) \cdot \sqrt{m_i} v_i(0) + \sqrt{I_i} \omega_i(0) \right\rangle}.$$

The validity of our simulations is confirmed by the agreement between $D_{DD}(\omega)$ and $D_{\text{FFT,R}}(\omega)$ as shown in Supplementary Information, Fig. S1. Note that the degree of freedom of $D_{DD}(\omega)$ and $D_{\text{FFT,R}}(\omega)$ is 3N (translational and rotational freedoms), whereas that of $D_{\text{FFT}}(\omega)$ is 2N. $D_{DD}(\omega)$ coincides well with $D_{\text{FFT}}(\omega)$ at low ω . At high ω , on the other hand, it is not the case. This indicates that the translational motion is hardly coupled with the rotational motion at high ω . As we are interested in the translational vibrations at low ω , we used $D_{DD}(\omega)$ to evaluate the boson peak frequency ω_{BP} . The coincidence of the direct diagonalization and FFT at the boson peak region confirms the harmonic nature of vibration modes contributing to the boson peak.

LONGITUDINAL AND TRANSVERSE DYNAMIC STRUCTURE FACTORS

We also calculated the longitudinal and transverse dynamical structure factor, $S_{\rm L}(q,\omega)$ and $S_{\rm T}(q,\omega)$, respectively, to determine the Ioffe–Regel limit, above which the phonon decays before propagating its own wavelength. $S_{\rm L}(q,\omega)$ and $S_{\rm T}(q,\omega)$ are given as

$$S_{\alpha}(q,\omega) = \frac{q^2}{2\pi\omega^2 N} \int \mathrm{d}t \, \langle \mathbf{j}_{\alpha}(q,t) \cdot \mathbf{j}_{\alpha}(-q,0) \rangle \exp(i\omega t),$$

where α is *L* or *T* and

$$\mathbf{j}_{\mathrm{L}}(q,t) = \sum (\mathbf{v}_{i}(t) \cdot \hat{\mathbf{q}}) \hat{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}_{i}(t)),$$
$$\mathbf{j}_{\mathrm{T}}(q,t) = \sum (\mathbf{v}_{i}(t) - (\mathbf{v}_{i}(t) \cdot \hat{\mathbf{q}}) \hat{\mathbf{q}}) \exp(i\mathbf{q} \cdot \mathbf{r}_{i}(t))$$

where $\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$. We also calculate $S_L(q, \omega)$ and $S_T(q, \omega)$ by normal mode analysis. $S_{\text{DD},L}(q, \omega)$ and $S_{\text{DD},T}(q, \omega)$ are given as

$$S_{\rm DD,L}(q,\omega) = \frac{k_{\rm B}T}{M} \frac{q^2}{\omega^2} \sum_{\lambda} E_{\lambda,\rm L}(\mathbf{q}) \delta(\omega - \omega_{\lambda}),$$

$$S_{\rm DD,T}(q,\omega) = \frac{k_{\rm B}T}{M} \frac{q^2}{\omega^2} \sum_{\lambda} E_{\lambda,\rm T}(\mathbf{q}) \delta(\omega - \omega_{\lambda})$$

where

$$E_{\lambda,\mathrm{L}}(\mathbf{q}) = |\sum_{i} [\hat{\mathbf{q}} \cdot \mathbf{e}_{\lambda}(i)] \exp(i\mathbf{q} \cdot \bar{\mathbf{r}}_{i})|^{2},$$
$$E_{\lambda,\mathrm{T}}(\mathbf{q}) = |\sum_{i} [\hat{\mathbf{q}} \times \mathbf{e}_{\lambda}(i)] \exp(i\mathbf{q} \cdot \bar{\mathbf{r}}_{i})|^{2},$$

where e_{λ} is the eigenvector and $\{\bar{r}\}$ are the equilibrium positions. We confirmed that both methods give the same results.

VDOS AND THE BOSON PEAK INTENSITY PER PARTICLE

The VDOS per particle *i*, $D_i(\omega_{BP})$, is defined as

$$D_{\text{FFT}}(\omega) = \sum_{i} D_{i}(\omega)$$
$$= \sum_{i} \frac{1}{2Nk_{\text{B}}T} \int \langle \mathbf{v}_{i}(t) \cdot \mathbf{v}_{i}(0) \rangle \exp(i\omega t) dt$$



The sum of $D_i(\omega)$ is equal to the total VDOS, $D_{\text{FFT}}(\omega)$. Then we calculate the boson peak intensity for particle *i*, $D_i(\omega_{\text{BP}})$, as

$$D_i(\omega_{\rm BP}) = \frac{1}{2\Delta\omega} \int_{\omega_{\rm BP}-\Delta\omega}^{\omega_{\rm BP}+\Delta\omega} D_i(\omega') \, \mathrm{d}\omega'.$$

SIMULATION METHODS FOR OTHER SYSTEMS

Simulation methods used for other glass-forming systems are described in Supplementary Information.

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Author contributions

H.T. conceived the project, H.S. carried out numerical simulations and H.S. and H.T. made the analysis and wrote the paper.

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