Physical Origin of the Boson Peak Deduced from a Two-Order-Parameter Model of Liquid

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We propose that the boson peak originates from the (quasi-) localized vibrational modes associated with long-lived locally favored structures, which are intrinsic to a liquid state and are randomly distributed in a sea of normal-liquid structures. This tells us that the number density of locally favored structures is an important physical factor determining the intensity of the boson peak. In our two-order-parameter model of the liquid-glass transition, the locally favored structures act as impurities disturbing crystallization and thus lead to vitrification. This naturally explains the dependence of the intensity of the boson peak on temperature, pressure, and fragility, and also the close correlation between the boson peak and the first sharp diffraction peak (or prepeak).

The dynamics of glass-forming liquids has been extensively studied in order to reveal the physical mechanism of the liquid-glass transition. One of the most mysterious dynamic modes, which universally exists in many different types of glasses, is the low-frequency vibrational motion giving rise to the so-called “boson peak” in the inelastic scattering of light or neutrons. The boson peak originates from low-energy excitations having the energy of approximately 0.2-2 THz \( \approx 10-100 \) K and reflects the excess density of vibrational states (DOS) in comparison with the Debye value. This excess DOS is, thus, also the origin of the low-temperature anomaly of specific heat \( C_p \), namely, a hump in \( C_p/T^3 \), which is again universally observed for different kinds of glasses. The physical origin of the low-energy excitations, or the low-temperature anomalies, remains to be clarified in the physics of condensed matter.

The anharmonic contribution below 2 K was, on the other hand, successfully explained by two-level-systems models at least on a phenomenological level, although the microscopic origin of a two-level-systems feature and its universality are still not clear. The connection of this behavior to the excess vibrational states is suggested by the soft potential model, based on the concept that there are generally two types of local structures, reflecting complex many-body interactions. The former is favored by density order parameter \( \rho \), which attempts to maximize the local density and leads to crystallization, while the latter is favored by bond order parameter \( S \), which originates from the symmetry-selective parts of the interactions and attempts to maximize the quality of bonds. Locally favored structures are icosahedra for metallic glass formers, and tetrahedra and their ring organization for covalent-bonding glass formers. The locally favored structure may have the local symmetry of a crystal, which is different from that of the equilibrium crystal, for a system with polymorphism. Thus, we view a liquid as follows: locally favored structures with medium-range order are randomly distributed in a sea of normal-liquid structures [see Fig. 1 (a)]. It should be noted that a locally favored structure

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has its own specific packing symmetry. A simple thermodynamic model of the two states with different degeneracies \[16-23\] tells us that the average fraction of locally favored structures, \( S \), is given by

\[
S \sim \frac{g_S}{g_P} \exp[\beta(\Delta E - P\Delta v)],
\]

where \( \beta = 1/k_B T \) (\( k_B \): Boltzmann’s constant), \( \Delta E \) and \( \Delta v \) are the energy gain and the volume increase upon the formation of a locally favored structure, respectively, and \( P \) is the pressure. Here \( g_S \) and \( g_P \) are the degrees of degeneracy of the states of locally favored structures and normal-liquid structures, respectively. We assume that \( g_S \ll g_P \). This is the direct consequence of the uniqueness of locally favored structures and the existence of many possible configurations of normal-liquid structures. Thus, there is a large loss of entropy upon the formation of a locally favored structure, which is given by \( \Delta S = k_B \ln(g_S/g_P) \). The validity of eq. (1) was confirmed by the successful physical description of water’s anomalies in terms of our model \[21-23\]. The lifetime of a locally favored structure can be estimated as \( \tau_{LFS} = \tau_0 \exp(\beta \Delta G) \), where \( \tau_0 \) is the inverse of the attempt angular frequency and \( \Delta G \) is the energy barrier to be overcome upon the transformation from a locally favored structure to a normal-liquid structure.

Since the symmetry of locally favored structures is usually not consistent with that of the equilibrium crystal, locally favored structures act as impurities for density ordering, namely, crystallization. Thus, we can apply the knowledge of random-spin systems to this problem. Due to the random disorder effects of locally favored structures, a liquid enters into the Griffiths-phase-like frustrated state below \( T_m^* \), which is the melting point of the corresponding pure system and should be located near the real melting point \( T_m \) of the material (note that \( T_m^* \) is usually located near the so-called mode-coupling \( T_c \) \[10-13\]). Namely, below \( T_m^* \), the free energy of a system starts to exhibit a complex multi-valley structure. This leads to the non-Arrhenius behavior of the structural relaxation. The Vogel-Fulcher temperature \( T_0 \) is then defined as a transition temperature from the Griffiths-phase-like state to the spin-glass-like nonergodic state.

This physical explanation provides a satisfactory answer to the question of which physical factor governs the fragility of liquid \[16-19\]. In our model, fragility is determined by the strength of random disorder effects, namely, \( S \). Thus, a liquid with larger \( S \), which suffers from stronger disorder effects, should be “stronger”, or “less fragile”. This leads to a larger distance between \( T_m^* \) and the Vogel-Fulcher temperature \( T_0 \) for a stronger liquid, which is consistent with experimental results \[16-19\]. It is worth noting that the only way for a liquid to eliminate these random disorder effects, is “global crystallization”. While a system is in a liquid state, it is inevitably under the influence of frustration effects.

On the basis of this model, we seek the physical origin of the boson peak. We assign the boson peak to the (quasi-) localized cooperative vibrational modes associated with a locally favored structure and/or a cluster made of a few locally favored structures. Locally favored structures are characterized by a particular spatial symmetry which is not consistent with the symmetry of the “equilibrium” crystal, and are distributed randomly in space. Their lifetime \( \tau_{LFS} \) is much longer than that of normal-liquid structures, which are in a disordered state. Thus, a locally favored structure can have the cooperative vibrational eigen mode with an angular frequency of \( \omega_{bp} \) unique to that structural unit if \( \tau_{LFS} \) is longer than \( 1/\omega_{bp} \). This condition determines the high-temperature stability limit of the boson peak, \( T_{bp} \). \( \omega_{bp} \) can be roughly estimated as \( \omega_{bp} \sim 2\pi v_s/R \), where \( v_s \) is the velocity of the transverse sound and \( R \) is the average characteristic length of a locally favored structure and a cluster made of a few locally favored structures. It is worth mentioning here that Uchino and Yoko \[14,15\] specified the modes characteristic of particular types of medium-range ordering regions, which should correspond to our locally favored structures, for \( \mathrm{B}_2\mathrm{O}_3 \) and \( \mathrm{SiO}_2 \) by \textit{ab initio} molecular orbital calculations.

In the light of this explanation, we now consider the questions (i)-(v) (see the introduction). The answers are
as follows: (i) A locally favored structure with medium-range order and its cluster are responsible for the boson peak and the low-temperature anomaly. Their characteristic size, $R$, is larger than that of the intermolecular bond, $a$. Thus $\omega_{bp}$ is several times smaller than $\omega_g$. (ii) Locally favored structures and clusters are isolated locally ordered structures [see Fig. 1 (a)] and are not an average structure of supercooled liquid or glass, which is usually described by the term “medium-range order”. Thus, it may not be appropriate to simply say that the boson peak is due to disorder effects. (iii) It is a locally favored structure that causes frustration disturbing crystallization and is thus responsible for vitrification. In our model, thus, the boson peak is crucially related to the glass-transition phenomena. (iv) The boson peak should universally exist in any glass-forming liquid in principle since in our two-order-parameter model of the liquid-glass transition it is the existence of locally favored structures that is the primary cause of vitrification. (v) Locally favored structures, which are responsible for the boson peak, exist not only in a supercooled or glassy state, but also in a liquid state if $T_{bp} > T_m$.

Here we summarize important experimental findings, which any physical model of the boson peak has to explain and thus can be used as criteria for determining the validity of a model. (a) The boson peak and the low-temperature anomaly of $C_P$ are more pronounced in stronger glass formers [24–26, 28]. (b) The boson peak intensity [32] becomes weaker with increasing either temperature or pressure [33–35]. (c) A boson peak has its own unique instability point, $T_{bp}$, which accompanies the appearance of quasi-elastic contributions. It is often located above the melting point $T_m$ for strong glass formers [24–26, 28], as confirmed in SiO$_2$, B$_2$O$_3$, ZnCl$_2$, and glycerol. These results seem to be contrary to the conjecture that $T_{bp} \sim T_g$ [27, 28], although we cannot completely deny the possibility that they are exceptional cases. More importantly, they indicate that the boson peak can exist even in an equilibrium liquid state above $T_m$ (i.e., $T_{bp} > T_m$). This cannot be explained by conventional models since they assume that an equilibrium liquid is completely homogeneous and has no specific structures, while a supercooled liquid has some medium-range order or specific disorder which is considered to be responsible for the boson peak. (d) There is much evidence [36–39] which suggests the correlation between the boson peak and the first sharp diffraction peak (FSDP) (or prepeak) [10]. Although there are experimental results [40] contrary to this prediction about the correlation [41], it may be true that the boson peak and the FSDP share some common origin in many systems. This is also supported by the fact that the FSDP has many features similar to the boson peak; for example, it often survives above $T_m$, and its intensity decreases with increasing either temperature or pressure [42].

An explanation of all the above-described findings (a)-(e) in a coherent manner at least on a qualitative level should be the first step toward an understanding of the physical mechanism of the boson peak. Thus, we attempt to define a coherent physical scenario rather than to quantitatively explain a particular experimental finding. Hereafter, we evaluate the validity of our explanation in terms of the above criteria (a)-(e). (a) According to our model, the magnitude of excess DOS, which is correlated with the intensity of a boson peak and the low-temperature anomaly of $C_P$, should be proportional to the number density of the locally favored structure, $S$. The two-order-parameter model of liquid [11] indicates that stronger liquids suffer from stronger disorder effects, which are characterized by larger $S$. Thus, the criterion (a) is naturally satisfied in our model. In our model [16–20], locally favored structures can be regarded as impurities disturbing crystallization and this view is consistent with a recent conjecture by Quitmann and Soltwisch [28] that the medium-range order responsible for a boson peak disturbs crystallization. (b) Our model indicates that the intensity of a boson peak [32] may be constant below $T_g$, but should decrease in proportion to the fraction of locally favored structures, $S$, in a liquid state above $T_g$, with increasing temperature. Figure 1(b) shows the $T$-dependence of the boson peak intensity for four strong glass formers, which is reasonably explained by our prediction. The boson peak intensity should also decrease with increasing pressure in proportion to $S$ above $T_g$. However, there have been few experiments on the pressure effects in a liquid state. On the other hand, there are many experiments in a glassy state below $T_g$, which clearly demonstrate the decrease of the boson peak intensity upon densification (see, e.g., Refs. 33 and 34). Such behavior is consistent with our model, but it may not be described by the thermodynamic relation, eq. (1), in an exact sense because of the intrinsically nonequilibrium nature of the densification process. Detailed studies on the temperature and pressure dependencies of the boson peak intensity “above $T_g$” are highly desirable to more unambiguously confirm our prediction that the boson peak intensity is proportional to $S$ between $T_{bp}$ and $T_g$. We could determine $\Delta E$, $\Delta s$, and $\Delta v$ from such analyses. (c) In our model, a boson peak becomes unstable for $\omega_{bp} T_{LFS} \leq 1$. The temperature of the instability of a boson peak, $T_{bp}$, is determined as

$$T_{bp} \sim -\Delta G/[k_B \ln(\omega_{bp} \tau_{LFS})].$$

(2)

Above $T_{bp}$, where $\tau_{LFS} < 1/\omega_{bp}$, the vibrational modes characteristic of locally favored structures should be overdamped. It is natural to expect a correlation between $\Delta E$ (the strong nature of a liquid) and $\Delta G$. Thus, a strong glass former with large $\Delta G$ should have a high $T_{bp}$ (sometimes above $T_m$). This is consistent with the observed behaviors [24–29, 28]. Our model can also naturally explain the existence of the boson peak in a liquid...
state above $T_m$. A fragile glass former with small $\Delta G$, on the other hand, should have a low $T_{\text{bp}}$. For a very fragile liquid, thus, the boson peak may not be observed in the liquid state. The fact that a boson peak survives above $T_m$ rules out the possibility that it is due to small clusters of the equilibrium crystal. (d) We propose that the FSDP or prepeak observed in the structure factor $S(q)$ should reflect locally favored structures and their aggregates or clusters, in many cases. Recently, Mas-sobrio et al. [3] studied FSDP in GeSe$_2$ by comparing their first-principles molecular dynamics simulations with neutron structure factors and found that the FSDP originates from the medium-range order of tetrahedral symmetry, GeSe$_4$, and its intensity decreases with increasing temperature. This is consistent with our explanation. Furthermore, Dzugutov et al. [4] demonstrated that the FSDP is due to well-defined atomic-scale voids, which is associated with icosahedral local order for a simple monoatomic liquid. On noting that the locally favored structures for such a liquid are icosahedral structures, their finding is consistent with our explanation that the FSDP reflects the pseudo-periodic atomic density fluctuations associated with locally favored structures and their clusters. This explanation naturally leads to the conclusion that there should be a strong correlation between the boson peak intensity and the intensity of the FSDP (or prepeak). Indeed, this is consistent with the observations [5–7]. Furthermore, this is consistent with the finding that in many cases the boson peak intensity and the intensity of the FSDP (or prepeak) [2] both decrease with increase of either $T$ or $P$. However, it should be noted that the intensity of the FSDP (or prepeak) is a function not only of the number density of locally favored structures, $\bar{S}$, but also their spatial arrangement.

Finally, we provide other evidence to support our explanation. It is widely known that the addition of another component into a liquid changes its fragility. The famous example is a mixture of SiO$_2$ and Na$_2$O. Usually, Na$_2$O is considered to act as a network modifier. We propose, more specifically, that Na$_2$O is the breaker of locally favored structures (probably, 6-member ring structures in the case of SiO$_2$). This concept naturally indicates that the addition of Na$_2$O increases the fragility of liquids, and weakens the boson peak [8], the low-temperature anomaly of $C_P$ [9], and the FSDP, since it induces the reduction of the number density of locally favored structures, $\bar{S}$. The same scenario may also be applied to a mixture of B$_2$O$_3$ and Li$_2$O [10].

We also mention a recent simulation study by Jund et al. [11], which systematically changes the strength of directional interactions ($\Delta E$ in our terminology) for SiO$_2$-type liquids. It demonstrated [11] that (i) an increase in the strength of directional interactions increases the intensity of a boson peak and the FSDP and also the number density of ring structures (locally favored structures in our terminology) and (ii) a liquid with a more medium-range order is stronger, or less fragile. These findings are all highly consistent with our physical explanation.

In summary, we propose a physical origin of the boson peak on the basis of the two-order-parameter model of liquid: Cooperative vibrational modes localized resonantly to locally favored structures and their clusters may be the origins of the boson peak. This model can explain most of the experimental findings, at least on a qualitative level. We stress that locally favored structures exist not only in a supercooled or glassy state of liquid, but also in an equilibrium liquid state if $T_{\text{bp}} > T_m$. This is consistent with the experimental finding that the boson peak exists even above $T_m$ for some strong liquids, which is difficult to explain using previous models.

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Throughout this paper, the boson peak intensity means that scaled by $\omega_n(\omega) + 1$, where $\omega$ is the angular frequency and $n(\omega) = \exp(\hbar\omega/k_B T) - 1$ is the temperature bose factor, where $\hbar$ is Planck’s constant. It is proportional to the density of vibrational states, $g(\omega)$.