Phonons in supercooled liquids: a possible explanation for the Boson Peak

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Glasses are amorphous solids, in the sense that they display elastic behaviour. In crystals, elasticity is associated with phonons, quantized sound-wave excitations. Phonon-like excitations exist also in glasses at very high frequencies (THz), and they remarkably persist into the supercooled liquid. A universal feature of these amorphous systems is the Boson peak: the vibrational density of states \( g(\omega) \) has an excess over the Debye (squared frequency) law, seen as a peak in \( g(\omega)/\omega^2 \). We claim that this peak is the signature of a phase transition in the space of the stationary points of the energy, from a minima-dominated phase (with phonons) at low energy to a saddle-point dominated phase (without phonons). Here, by studying the spectra of inherent structures (local minima of the potential energy), we show that this is the case in a realistic glass model: the Boson peak moves to lower frequencies on approaching the phonon-saddle transition and its height diverges at the critical point. The numerical results agree with Euclidean Random Matrix Theory predictions on the existence of a sharp phase transition between an amorphous elastic phase and a phonon-free one.

Vibrational excitations of glasses in the THz region, and the related vibrational density of states (VDOS), play a crucial role in their thermodynamic properties. Recent results suggest that the VDOS is determined by the properties of the potential energy landscape (PEL), a crucial tool to understand the slow dynamics of supercooled liquids. Indeed, the VDOS and the dynamic structure factor can be qualitatively reproduced from the (harmonic) vibrational spectrum obtained from the diagonalization of the Hessian matrix of the potential energy evaluated at the minima (or inherent structures [IS]) of a Lennard-Jones system. The same numerical procedure led to quantitative agreement with inelastic X-ray scattering experiments in amorphous silica (O. Pilla et al., preprint condmat/0209519). Here we will show that a Boson peak must be present in the VDOS as a consequence of the PEL geometry, and make quantitative predictions which can be checked fastly quenching supercooled liquids below their glass temperature.

The high-frequency (0.1–10 THz) excitations have been experimentally shown to have linear dispersion relations in the mesoscopic momentum region (\( \sim 1–10 \) nm\(^{-1} \)). Although clearly not plane waves, they are highly reminiscent of phonons because they propagate with the speed of sound and because the VDOS, \( g(\omega) \), is Debye-like (\( g(\omega) \propto \omega^2 \)) at
low enough frequency. These excitations have in fact been dubbed “high-frequency sound” and a coherent theoretical picture of their properties was obtained using Euclidean Random Matrix Theory (ERMT).

However, there is more to the low frequency VDOS of glasses than the Debye law. A characteristic feature is that the VDOS departs from the Debye form, displaying an excess of states, which has been named “Boson peak” (BP). As observed in many materials, the BP is in a region of frequencies where the dispersion relation for phonons is still linear ($\omega \sim$ a few THz). Several non-equivalent ways of experimentally defining the BP have been introduced. One approach defines it as a peak in Raman-scattering data, another as a peak in the difference between the VDOS of the glass and the corresponding crystal. Other authors extract $g(\omega)$ from their neutron scattering data and look for a peak in $g(\omega)/\omega^2$. This is the definition we adopt, since we believe it unveils universal properties of glasses.

The origin of the Boson peak can be understood if we consider the ensemble of generalized inherent structures (GIS): for each equilibrium configuration the associated GIS is the nearest stationary point of the Hamiltonian. If we start from an equilibrium configuration at low temperature, the GIS is a local minimum, and it coincides with the more frequently used IS (i.e. the nearest minimum of the Hamiltonian). On the contrary, if we start from high temperature, the GISs are saddle points. In the GIS ensemble there is a sharp phase transition separating these two regimes. It takes place in glass-forming liquids at the Mode Coupling temperature ($T_{MC}$), above which liquid diffusion is no longer ruled by rare “activated” jumps between ISs but by the motion along the unstable directions of saddles. Phonons are present in the spectrum of the VDOS in the low temperature phase (IS dominated) but are absent in the saddle phase (see ref. 23 for a different approach).

The key point, following both from analytic computations in soluble models and simulations, is that the minima obtained starting from configurations below $T_{MC}$ and the saddles obtained starting above $T_{MC}$ join smoothly at $T_{MC}$. Thus we can study GIS as a single ensemble, parametrized by the initial temperature or the final energy. We expect that the GIS ensemble belong to a large universality class.

This transition from the phonon phase to the saddle phase is a quite general phenomenon that it is not restricted to glasses. It has been studied in the framework of the Euclidean Random Matrix Theory (ERMT), showing that close to this transition, a BP is present in
the phonon phase, whose position shifts to lower frequencies on approaching the transition point, while its height grows without bound. The BP actually signals a crossover at frequency ω_{BP} between a (phonon dominated) ω^2 scaling of g(ω) to an ω^γ scaling (γ < 2) that is present at the phase transition point. More precisely, at frequencies small respect to the Debye frequency, the VDOS should satisfy the scaling law

\[ g(\omega, \Delta) = \omega^\gamma h(\omega \Delta^{-\rho}) \tag{1} \]

where Δ is the distance from the critical point and depends on the actual control parameter (pressure, temperature, etc.) and h(x) is such that \( h(x) \sim x^{2-\gamma} \) for \( x \ll 1 \) and \( h(x) \sim \) constant for \( x \gg 1 \). This scaling law implies that

\[ \omega_{BP} \propto \Delta^\rho, \quad \frac{g(\omega_{BP})}{\omega_{BP}^2} \propto \Delta^{-\beta}, \tag{2} \]

where \( \beta = \rho(2 - \gamma) \). Under the resummation of a given class of diagrams, ERMT predicts that \( \rho = 1 \), \( \gamma = 3/2 \) and \( \beta = 1/2 \). Of course the actual (universal) values of these critical exponents in three dimension may differ slightly from the values found in this approximation.

We now analyze numerically the existence of such a transition by studying the soft sphere binary mixture, a model of a fragile glass\textsuperscript{25}. We simulate this system with the Swap Monte Carlo algorithm\textsuperscript{26}, and compute the VDOS of the ISs obtained starting from equilibrium configurations at temperatures below \( T_{MC} \). Except were stated, we used 2048 particles, and runs were followed until the energy of the IS, \( e_{IS} \), reached a stationary value. The predictions above agree with the numerical data, taking \( \Delta = e_c - e_{IS} \) (\( e_{IS} \) being the energy of the ISs and \( e_c \) the critical value).

Given the numerical results of Kob et al.\textsuperscript{27}, one expects that \( g(\omega) \) depend only on \( e_{IS} \), and thus that \( e_{IS} \) be the relevant control parameter. To check this, we compare the VDOS of two systems at different temperatures (one in equilibrium, the other not) but with the same \( e_{IS} \). The equilibrated system has 2048 particles, while the other has 20000 and is in the regime where \( e_{IS} \) has not yet stabilized after a quench (Fig. 1b). As Fig. 1a shows for a representative case, the VDOS obtained at the same \( e_{IS} \) for the two systems coincides, confirming that \( e_{IS} \) is the control parameter. We can thus proceed to investigate the scaling laws \[2\].

The VDOS at three representative temperatures is shown in Fig. 2. For temperatures up to \( T = 0.69 T_{MC} \), a Debye behaviour (\( g(\omega) \propto \omega^2 \)) is found for the lowest frequencies that can
be resolved in a system of this size. In the $g(\omega)/\omega^2$ plot (Fig. 2a), a peak is clearly identified, which is seen to grow in height and shift to lower frequency on rising the temperature. The peak shifts to frequencies below our resolution for $T > 0.69 T_{MC}$, but we can identify a Debye region up to $T = 0.83 T_{MC}$. Above this temperature the Debye region is not well defined, and it disappears completely for $T \geq 0.9 T_{MC}$. At these temperatures, $g(\omega)/\omega^2$ seems to diverge (at least within the frequency range that we can resolve). Experimentally, this behaviour may be difficult to observe due to the presence of the elastic peak, but $\text{B}_2\text{O}_3$ data\textsuperscript{20} seem to support this prediction. For frequencies immediately above $\omega_{BP}$, the VDOS scales as $\omega^\gamma$, with $\gamma \approx 1.5$ (Fig. 2b). Note that these changes of the VDOS with temperature go practically unnoticed if one plots $g(\omega)$ directly (Fig. 2c). In particular, the BP is completely unrelated to the first maximum of $g(\omega)$, whose position is insensitive to temperature changes.

Since we know that $e_{IS}$ decreases slowly with time after a quench\textsuperscript{27} (see also Fig. 1b), the above results enable us to make predictions about the *ageing* of the VDOS, and in particular of the BP. With increasing time the system moves farther from the critical point, and thus the BP should decrease in height and shift to higher frequencies. Moreover, at a given frequency (below the asymptotic $\omega_{BP}$) $g(\omega)$ should decrease, since it will be of order $\omega^\gamma$ at short times and of order $\omega^2$ at very long times. Similarly, one should expect a cooling rate dependence of the shape of the BP: the slower the cooling, the lower the asymptotic $e_{IS}$ and thus a larger $\omega_{BP}$ and less pronounced BP. An effect of this kind has been observed in $\text{As}_3\text{Se}_2$,\textsuperscript{28} although here it is difficult to disentangle the physical effect from the chemical changes of the sample due to dissociation. To our knowledge, a clear-cut experimental observation of these effects has not been reported.

Using all the spectra for which the peak position can be clearly identified, we find that the relationship between $\omega_{BP}$ and the energy of the IS is linear (Fig. 3a). The energy at which $\omega_{BP}$ becomes zero, $e_c$, is found from a linear fit as $e_c = 1.74 \epsilon$ ($\epsilon$ is the energy scale). As for the height of the peak, the points up to $T = 0.83 T_{MC}$ are compatible with a power-law divergence of the form \textsuperscript{2} (Fig. 3b). Fixing $e_c$ at the value $1.74 \epsilon$ arising from the linear fit of $\omega_{BP}$ vs. $e_{IS}$, a power-law fit yields an exponent $\beta = 0.40(15)$, while if one fixes the exponent $\beta = 1/2$, then the critical value is obtained as $e_c = 1.752(2) \epsilon$. Thus the numerical data are compatible with the theoretically predicted scaling, although we have not been able to work close to the critical point, and thus cannot get a great accuracy on the critical exponents or the critical point.
The present discussion applies to experiments as long as one is in the regime where the inverse frequency is much larger than the structural relaxation time, when the harmonic approximation makes sense\textsuperscript{29}. Thus, while the BP observed in liquids can be understood by the present considerations, one should not expect to actually arrive close to the critical point in equilibrium measurements. Rather, one should generate a glass by hyperquenching (see e.g. talk by C. A. Angell in [http://www.df.unipi.it/workshop/oral/OL6.pdf](http://www.df.unipi.it/workshop/oral/OL6.pdf)): for this we predict that the BP measured at low T should obey the scaling \( e_{c} = 1.74(1) \), the control parameter being the fictive temperature, which in our instantaneous quench is just the temperature at which the hyperquench starts, but in experiments involves also the cooling rate. In this way one should also alleviate the problem of the swamping by the quasielastic peak.

The significance of the value \( e_{c} = 1.74(1) \) is twofold. First, it is the value of \( e_{IS} \) that corresponds, in equilibrium, to \( T = T_{MC} \), the Mode-Coupling critical temperature (which we have independently determined as in ref. \textsuperscript{22}, using a standard Monte Carlo without swap). Second, it coincides within errors with the threshold energy below which the ratio of the number of saddle points to the number of minima vanishes exponentially with the number of particles\textsuperscript{6} (our numerical accuracy on \( e_{c} \) is similar to that of \textsuperscript{6}). Thus we find a link between the onset of slow dynamics, the appearance of phonon-like excitations and a geometrical phase transition of the PEL in fragile glasses. At variance with previous PEL studies, the clear link between the PEL geometrical transition and high-frequency dynamics allows it to be studied experimentally by following the evolution of the BP.

In summary, we have studied numerically the VDOS of a fragile glass-former liquid undergoing its Mode-Coupling transition. We have found that in the ensemble of the stationary points near the equilibrium configurations (GIS) there is a transition from a mechanically unstable phase where saddles are present to a stable phase where phonon-like excitations appear. The scaling laws predicted by ERMT are compatible with the numerical results we have obtained for the soft sphere model. This approach is equivalent to other microscopic descriptions of the glass transition based on the geometry of the potential energy landscape (PEL)\textsuperscript{4,5,6,30}. But this point of view emphasizes quantities accessible to experiment, like the VDOS, and proposes an interpretation of an universal feature of glasses, the Boson peak. The BP appears in the phonon phase, and it is a signature of a cross-over from a phonon-dominated spectrum with a Debye \( \omega^{2} \) scaling to an \( \omega^{\gamma} \), \( \gamma \approx 1.5 \) spectrum, resulting from the hybridization of acoustic modes with high-energy modes that soften upon approaching
the saddle-phonon transition. The ERMT predictions (eqs. 1 and 2) could be checked experimentally in hyperquenching experiments, where the Boson peak should strongly depend on the fictive temperature. We expect that the saddle-phonon transition point of view will be able to bridge the realms of experiment and numerical studies of the PEL, allowing to test many geometrical ideas and to use the PEL insights in the detailed analysis of the experimental glass transition.

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a. $N=2048$, equilibrium, $T=0.9 \ T_{MC}$

$b. N=20000$, out-equilibrium, $e_{IS}=1.731 \epsilon$

N=20000

Asymptotic $N=2048$ value

Monte Carlo time
FIG. 1: The VDOS \( g(\omega) \) at low frequencies depends only on the energy of the inherent structure, \( \epsilon_{\text{IS}} \).

a. \( g(\omega)/\omega^2 \) for an equilibrated 2048 particle system at \( T = 0.9T_{\text{MC}} \) compared to that obtained from ten inherent structures of the same \( \epsilon_{\text{IS}} \) from a 20000-particle system out of equilibrium. The larger system was quenched from infinite temperature to \( T = 0.54T_{\text{MC}} \) and the inherent structures obtained by minimizing instantaneous configurations between \( 1.9 \cdot 10^4 \) and \( 2 \cdot 10^4 \) Swap Monte Carlo steps. Similar results are obtained at all the temperatures for which comparable \( \epsilon_{\text{IS}} \) are obtained in the quench. IS were found by minimizing instantaneous configurations with a conjugate gradient algorithm. The Hessian was diagonalized with standard library routines in the case of the small system, and with the method of moments for the big one. Each VDOS was obtained from at least 200 IS as the histogram of the square root of the eigenvalues.

b. Monte Carlo history of \( \epsilon_{\text{IS}} \) in logarithmic time-scale, for the system of 20000 particles, suddenly quenched from infinite temperature to \( T = 0.54T_{\text{MC}} \). The soft-sphere binary mixture is made of 50% of particles of type A and 50% of type B, both with the same mass. The interaction potential is
\[
V_{\alpha\beta}(r) = \epsilon(\sigma_\alpha + \sigma_\beta)/r^{12} + C_{\alpha\beta} \ (\alpha, \beta \in \{A, B\}),
\]
with \( \epsilon \)’s fixed by the conditions \( \sigma_B = 1.2\sigma_A \), and
\[
(2\sigma_A)^3 + 2(\sigma_A + \sigma_B)^3 + (2\sigma_B)^3 = 4\sigma_0.
\]
A smooth cutoff is imposed at \( r_c = \sqrt{3}\sigma_0 \): for \( r_c \leq r \leq a \), we set \( V_{\alpha\beta} = B_{\alpha\beta}(a - r)^3 \), and \( V_{\alpha\beta} = 0 \) for \( r > a \). In the results, lengths are given in units of \( \sigma_0 \), energies in units of \( \epsilon \) and frequencies in units of \( \omega_0 \equiv (m\sigma_0^2/\epsilon)^{-1/2} \). Using Argon parameters (\( \sigma_0 = 3.4\AA \), \( \epsilon = 120\text{K}k_B \), \( m = 39.96 \text{ u.a.m.} \)) the frequency unit \( \omega_0 \) is 0.46\( \text{Thz} \) and the Mode Coupling temperature \( T_{\text{MC}} \) is 26.4\( K \). All runs are at constant volume, with particle density \( \rho = \sigma_0^{-3} \). For temperatures down to \( T = 0.9T_{\text{MC}} \) thermalization was achieved, as checked by ensuring that the equilibrium fluctuation-dissipation ratio is reached. For \( T < 0.9T_{\text{MC}} \), the run was followed until \( \epsilon_{\text{IS}} \) reached stationarity.
FIG. 2: Vibrational density of states $g(\omega)$ of the soft-sphere binary mixture at three representative temperatures (the full set of temperatures was $T/T_{MC} = 0.9, 0.83, 0.78, 0.69, 0.61, 0.54, 0.49$, frequencies are given in units of $\omega_0$).  

**a.** The $g(\omega)/\omega^2$ plot shows a Boson peak at low temperature (shown $T = 0.54T_{MC}$). When temperature is risen, the peak shifts to lower frequencies and grows without bound. 

**b.** The divergence seen in **a** is due to an $\omega^\gamma$ (with $\gamma < 2$) scaling of $g(\omega)$. At temperatures where the Boson peak is still seen, a crossover between $\omega^2$ and $\omega^\gamma$ scaling can be noted comparing **a** and **b**. While $\gamma$ cannot be extracted very accurately from the data, it is compatible with $\gamma = 2 - \beta/\rho \approx 1.6$, with $\beta$ and $\rho$ taken from the fits of Fig. 3. 

**c.** The high frequency features of $g(\omega)$ do not change drastically with temperature.
FIG. 3: Scaling of the position, $\omega_{BP}$, and height of the Boson peak near the saddle-phonon transition (energies and frequencies in units of $\epsilon$ and $\omega_0$ respectively). 

a. $\omega_{BP}$ is linear in the control parameter, in this case the energy of the inherent structure $e_{IS}$. Extrapolating with a linear fit, $\omega_{BP}$ goes to 0 at $e_{IS} = e_c = 1.74(1) \epsilon$.

b. The height of the Boson peak diverges as a power law (the leftmost point has been left out of the fit). Height and position of the BP were obtained by fitting a parabola to the peak of $g(\omega)/\omega^2$ at $T/T_{MC} = 0.49, 0.54, 0.61, 0.69, 0.78, 0.83$. The corresponding $e_{IS}/\epsilon$ are 1.668, 1.671, 1.674, 1.682, 1.689, 1.707.