Universal properties of high-frequency spectra in glass formers

P. Verrocchio

*Dipartimento di Fisica, Università di Trento Povo (TN) Italia*

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The vibrational spectra of glass formers follow different laws with respect to crystals. A rationale for their anomalous behaviour is provided by the euclidean random matrix theory. Experiments on glass formers at different densities might be a suitable route to test the prediction of the theory.

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I. INTRODUCTION

The high frequency (THz) dynamics of the density fluctuations in highly viscous supercooled systems is presumably due to purely vibrational modes. However, with respect to their crystalline counterpart these systems show a number of puzzling features whose theoretical interpretation is still controversial (see e.g. [1]). The purpose of this work is to focus on two of them describing a theoretical approach which is able both to explain the physical processes beyond such features and to make rigorous predictions.

**Brillouin-Peak** X-rays and Neutron inelastic scattering experiments probe excitations of momentum $q$ comparable to the characteristic momentum $q_0$, the position of the first diffraction peak in the static structure factor. In other words the wavelength is of the same order of magnitude of the inter-particle distance and an hydrodynamic approximation does not make much sense. Nevertheless the position $\omega$ and the width $\Gamma$ of the Brillouin Peak are reported to show hydrodynamic-like features:

$$\omega_{\text{peak}} \propto q, \quad \Gamma_{\text{peak}} \propto q^2$$

(1)

The agreement regarding the exponent 2 in the scaling law of $\Gamma$ between hydrodynamics and experiments is likely fortuitous. In fact the magnitude of $\Gamma$ has a very slight dependence on temperature (if any) while it should be strongly temperature dependent in case the decay of hydrodynamic modes was induced by the viscosity [8].

**Boson Peak** Raman experiments and neutron scattering experiments at large $q$ (see below) may be useful to determine the vibrational density of states (VDOS) $g(\omega)$. Glass formers are quite peculiar with respect to crystals since in the frequency region where the main hypothesis of Debye holds (linearity of the dispersion relation) one finds that the VDOS has a different behaviour from the Debye law:

$$g(\omega)/g_{\text{Debye}}(\omega) >> 1.$$  

(2)

This excess of states over the Debye VDOS is termed *Boson Peak* (BP).
II. THEORY

Within the harmonic framework one assumes that the VDOS is simply given by the eigenvalues of the Hessian Matrix $K_{ij;\mu\nu}$. At low enough frequency this approximation breaks down since the relaxational modes start playing a relevant role. One could roughly claim that the harmonic approach holds whenever $\omega$ is larger than the inverse of the fastest relaxation mode time-scale. Since this quantity in all the realistic cases is unknown, one must content to assess empirically the range of reliability of the harmonic approach by means of the comparison between the experimental spectra and the numeric spectra. Aiming to modelize the vibrations in glass-formers one has to take into account the role played by the disorder. As a matter of fact the positions around which the atoms vibrate harmonically do not form in general a regular lattice. The disorder of the positions $\{ \vec{x}_i \}$ of the center of oscillation is described by a suitable distribution of probability $P[\{ \vec{x}_i \}]$. Different choices for $P$ describe different physical situations. Furthermore this topological disorder induces a broad distribution of probability of the spring constant $K$. The theoretical effort is greatly simplified if the macroscopic quantities are assumed to be self-averaging, i.e if their value remains the same when different realizations of the disorder are taken. This allows to replace the computation of (say) the VDOS for a given realization of the disorder (involving the knowledge of an infinite number of positions $\vec{x}_i$) with the computation of the averaged VDOS (which involves the knowledge of $P$).

In order to compute the spectral properties of the matrix $K$

$$K_{ij;\mu\nu} \equiv \delta_{ij} \sum_k \partial_{\mu\nu} V(|\vec{r}_{ik}|) - \partial_{\mu\nu} V(|\vec{r}_{ij}|) \quad \vec{r}_{ij} \equiv \vec{x}_i - \vec{x}_j. \quad (4)$$

we introduce a complex valued tensor $G_{\mu\nu}$ called resolvent, which can be split in its longitudinal and transversal parts:

$$G_{\mu\nu}(z,q) \equiv \frac{1}{N} \sum_{jk} e^{i\vec{q} \cdot \vec{r}_{jk}} \left[ \frac{1}{z - K_{jk;\mu\nu}} \right] \equiv G_L(z,q) \frac{q_{\mu}q_{\nu}}{q^2} + G_T(z,q) \left( \delta_{\mu\nu} - \frac{q_{\mu}q_{\nu}}{q^2} \right) \quad (5)$$

$z$ is a complex number related to the value $\lambda$ of the eigenvalues of the Hessian matrix $K$ by $z \equiv \lambda + i\epsilon$.

The resolvent is related to the VDOS and the VDSF. However $G_{\mu\nu}$ is defined in the space of eigenvalues which nothing prevents from being negative. On the other hand the VDSF and the VDOS are functions of the frequency, and the frequencies are related to the eigenvalues only in the positive eigenvalues region ($\lambda = \omega^2$). Then the following relations hold only in that region:

$$S(q,\omega) = -\frac{2kTq^2}{\omega \pi} \text{Im} G_L(q,\omega^2 + i0^+), \quad g(\omega) = \lim_{q \to \infty} \frac{\omega^2}{kTq^2} S(q,\omega) \quad (6)$$
However we will show that the existence of the resolvent at negative $\lambda$ leads to important consequences. Note that only isotropic modes survive in the VDOS because $G_{\mu\nu}(q = \infty, z) \propto \delta_{\mu\nu}$. Thus the polarization is approximately defined only for $q \sim 0$. This is very different from lattice models, where $g(\omega) \propto \int dq S(q, \omega)$.

The resolvent can be computed in a non perturbative way if the $n$-th moment of $P$ is assumed to be factorized (superposition approximation): $g^{(n)}(\vec{x}_1 \ldots \vec{x}_n) = g(\vec{r}_2) \ldots g(\vec{r}_{n-1\, n})$ where $g(r)$ is the pair probability distribution. With this approximation the resolvent is given by:

$$G_{\mu\nu}(q, z) = \left[ \frac{1}{z - \rho f(0) + \rho f(q) - \Sigma(q, z)} \right]_{\mu\nu}$$

$$\Sigma(q, z)_{\mu\nu} = \frac{1}{\rho} \sum_{\alpha\beta} \int \frac{d^3k}{(2\pi)^3} V_{\alpha\mu}(q, k) G_{\alpha\beta}(k, z) V_{\beta\nu}(k, q)$$

where $\rho$ is the density, $V_{\mu\nu}(k, q) \equiv \rho \left( \hat{f}_{\mu\nu}(k) - \hat{f}_{\mu\nu}(q - k) \right)$ and $\hat{f}_{\mu\nu}(q) \equiv \mathcal{F}[g(r) \partial_{\mu\nu} v(r)] (v(r)$ is the pair interaction).

The quantity $\Sigma$ is called self-energy and describes the loss of energy of phonons due to the disorder. It vanishes in the limit of infinite density, where phonons propagate without dissipation. In this limit one has:

$$S(q, \omega) = \delta (\omega - \omega_{\text{peak}}(q)) \quad \omega_{\text{peak}}(q) \equiv \sqrt{\rho \left( \hat{f}(0) - \hat{f}_L(q) \right)}$$

This does not imply that the disorder vanishes when $\rho \to \infty$. Rather his effects on the propagations of phonons are averaged out by the infinite number of particles within each wavelength. On the other hand at finite $\rho$ the self-energy starts playing a relevant role, modifying the position and the width of the peak.

### III. EVOLUTION OF THE BOSON PEAK WITH DENSITY

Solving the integral equation in the limit of $q \to \infty$ one obtains the density of eigenvalues from which the VDOS $g(\omega)$ is obtained. Due to the complexity of the equation, the result for a given choice of $\hat{f}_{\mu\nu}(q)$ can be computed only numerically. However it is possible to deduce some important mathematical properties of the solution which are not dependent on $\hat{f}$ (hence, on the model). Keeping fixed the other thermodynamic parameter, it can be shown that at low enough densities the Hessian matrix has both negative and positive eigenvalues, while at high densities all the eigenvalues are positive. A critical density $\rho_c$ separates the two regions. In the low density regime implies that $g(\omega) \propto \omega$ when $\omega \sim 0$ while at very high densities one has the standard Debye behaviour $g(\omega) \propto \omega^2$. The change of exponent in $g(\omega)$ is due to the occurrence of a sort of phase transition. The parameter which induces such phase transition is not necessarily the density, a change in any of the other thermodynamic quantities may lead the system from the region with only positive eigenvalues of $\mathcal{K}$ to the region where also the negative ones are allowed. For example it has been shown that the value of the potential energy of the stationary points (minima or saddles) around which a glass system remains for a long time (termed generalized inherent structures) is one of those quantities. For the experiments however the stationary points are not a suitable observable, while it is surely conceivable perform measurements of spectra at different densities putting the system under a very high pressure. In the following we will identify the region without negative eigenvalues with the glass forming liquid.
detail the behaviour of the VDOS in this phase. In the region of frequencies where the dispersion relation is still linear one finds the following universal form:

\[ g(\omega) = \omega^\gamma h(\Delta^{-\alpha}), \quad h(x) \sim \begin{cases} 
  x^{2-\gamma} & x \ll 1 \\
  \text{const.} & x \gg 1 
\end{cases} \]  

(9)

If we define a distance \( \Delta \) from the critical point as \( \Delta \equiv (\rho - \rho_c) \) we see that at a characteristic frequency \( \omega_{BP} \) it occurs a crossover from the Debye behaviour \( g(\omega) \sim \omega^2 \) to a different law \( g(\omega) \sim \omega^\gamma \). One obtains furthermore that:

\[ \omega_{BP} \sim \Delta^\alpha, \quad g(\omega_{BP})/g_{\text{Debye}}(\omega_{BP}) \sim \Delta^{-\eta} \]  

(10)

where the universal exponents are:

\[ \begin{array}{c|c|c}
\eta & \alpha & \gamma \\
\hline
1/2 & 1 & 3/2 \\
\end{array} \]  

(11)

The main consequence of the a critical point is the modification of the Debye law at \( \omega_{BP} \). This is highly remindful of the Boson Peak found in experiments. This suggests to identify \( \omega_{BP} \) with the position of the Boson Peak and \( g(\omega_{BP})/g_{\text{Debye}}(\omega_{BP}) \) with its height. Since (11) does not hold at low \( \omega \) the predicted singularity at \( \rho_c \) is not approached in real systems. However the proximity of such singularity is enough to break the Debye law.

We can test our theoretical prediction by performing numeric simulations of a simple glass former. We performed MonteCarlo simulations at different temperatures and densities of a simple glass former (see [7] of the details). The VDOS’s have been computed by diagonalizing at least 50 different realizations of the Hessian matrix.

In fig (1) we show the VDOS for \( T = 0.897T_{mc} \) (\( T_{mc} \) is the Mode Coupling temperature [5]). At \( \omega_{BP} \sim 1 \) (where the dispersion relation is still linear) there is the crossover in the VDOS from the Debye law to the \( \omega^{3/2} \) behaviour. This is the signature of the Boson Peak, as predicted by the theory. In fig (2) we see the large variations of the VDOS for different densities at \( T = 4.420T_{mc} \) (left). The position of the Boson Peak moves linearly with the density while its the growth of its eight seems to be compatible with a power law whose exponent is 1/2 (right). Thus even those theoretical predictions are in reasonable agreement with the numeric data.
IV. THE COMPLEX BEHAVIOUR OF THE BRILLOUIN PEAK

At finite densities the propagation of phonons is affected by the loss of energy due to the disorder which make the time-life of phonons finite. Actually it is not entirely correct to describe the effect of disorder on the phonons in topologically disordered systems in terms of phonon-disorder interaction. In fact as we said above in the infinite density limit the phonons propagate freely even if the positions of the particles remain disordered. Actually, when the disorder has a topological nature it is not possible to find a limit where the disorder vanishes, even if his effects may disappear. This is at odds with lattice systems, where phonons propagate freely only when the disorder is not present. The position and the width of the Brillouin peak are affected by the self-energy in the following way:

\[ \omega_{\text{peak}}(q) \sim \sqrt{\rho \left( \hat{f}(0) - \hat{f}_L(q) \right)} + \text{Re} \Sigma_L(\omega_{\text{peak}}) \]

\[ \Gamma_{\text{peak}}(q) \sim \frac{\text{Im} \Sigma_L(\omega_{\text{peak}})}{\omega} \]

Aiming to obtain model independent results we limit to the asymptotic region where \( q \) is small with respecto to \( q_0 \). The general result is:

\[ \omega_{\text{peak}}(q) \sim c q \]

\[ \Gamma_{\text{peak}}(q) \sim A \frac{g(\omega_{\text{peak}})}{\omega_{\text{peak}}^2} q^2 + B q^4 \]

(\( c \) is the speed of sound and \( A, B \) two model dependent constants). While the eq. (14) signals trivially the existence of propagating phonons, eq. (15) reveals a quite rich behaviour of the width of the Brillouin peak. When the frequency of the Brillouin Peak lie below \( \omega_{BP} \) the leading term of \( \Gamma_{\text{peak}} \) is \( \propto q^2 \) while at larger frequencies there is a crossover to \( \Gamma_{\text{peak}} \propto q^{3/2} \). Then \( \omega_{BP} \) signals not only the frequency with the maximum excess of states with respect to the Debye law but even a crossover in the power law of the width of the Brillouin Peak. Moreover at large enough momenta there exists another crossover frequency \( \omega_* \) where the \( q^4 \) term becomes dominant.

We have seen in the previous section that for very large densities the BP moves a very large frequencies hence it is reasonable to expect that in this situation one should observe only the crossover at \( \omega_* \) from the \( \Gamma \propto q^2 \) to \( \Gamma \propto q^4 \). Not
only $\omega_{BP}$ changes with the density (see eq. (10)), even the characteristic frequency $\omega_*$ does, though with a different behaviour. At high densities $A \propto 1/\rho^2$, $B \propto 1/\rho$ hence $\omega_* \propto 1/\sqrt{\rho}$ at $\rho >> 1$.

V. CONCLUSIONS

The euclidean random matrix theory provides a coherent description of the anomalous features found in the vibrational spectra of glass formers. It provides furthermore well defined quantitative laws which should be compared with the numeric and experimental findings. In this paper we presented mainly the laws describing the evolution of the Boson Peak and of the Brillouin Peak when the density of the system is changed.

How many chances do the experiments have to investigate such laws? The main restraint we see is given by the limited frequency windows where the harmonic modes describe entirely the dynamics. In fact already in the $GHz$ region the relaxational modes (accounted for example by the Mode Coupling theory) could become important. Optimistically we might argue that the harmonic approach holds at most over three decades (say for frequencies $\in [0.01 - 10]THz$). This raises some problems in the verification both of eq. (10) and of eq. (15). In the former case one cannot get very close to the critical point underlying the Boson Peak since the low frequency region is not described by harmonic effects. Still, the numeric results in fig. 2 suggest that the singularity might be discerned and studied quantitatively even in experiments. In the latter case the possible presence of two crossovers is hard to detect having only three decades of frequencies available. Not surprisingly different experimental groups interpret the results in this region in different ways. In that kind of measurement it might be useful to remind that playing with density is it possible to change the values of $\omega_{BP}$ and $\omega_*$ exalting a particular behaviour with respect to the others.

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