From random matrix theory to linear-in-$T$ specific heat in glasses

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The low-temperature properties of glasses present important differences with respect to crystalline matter. In particular, models such as the Debye model of solids, which assume the existence of an underlying regular lattice, predict that the specific heat of solids varies as the cube of temperature at low temperatures. Since the 1970s at least, it is a well established experimental fact that the specific heat of glasses is instead just linear in $T$ at low temperature. The most popular model that has been proposed in an attempt to explain this anomaly, is based on the assumption of two-level tunnelling states between isolated groups of atoms. Here we present numerical calculations and analytical theory which demonstrate that the linear-in-$T$ behaviour of the specific heat is a direct consequence of random matrix behaviour in the vibrational density of states (VDOS) of the solid. Hence, the specific heat anomaly and its universal appearance are a genuine result of structural disorder at the classical (non-quantum) level, and it is possible to directly link the temperature dependence of thermal quantities to the scaling of the eigenvalue distribution of random solids. The model is also able to reproduce, for the first time, the experimentally observed inverse proportionality between the specific heat peak and the shear modulus.

Disordered systems  |  Phonons  |  Lattice dynamics

Introduction

Because of the absence of long-range order and the unavoidable heterogeneity due to strong disorder the search for a microscopic description of glasses has attracted a lot of effort in the condensed matter community in the last decades. The nature of glasses and the transport features of amorphous solids in general are surprisingly still far from being under theoretical control. Glasses present interesting and still unexplained anomalies with respect to the Debye model in both the vibrational density of states (VDOS) $D(\omega)$, the specific heat $C(T)$ and the thermal conductivity $\kappa(T)$. Two emblematic examples of such anomalies are the famous Boson peak excess of eigenmodes in the normalized density of states $D(\omega)/\omega^2$ and the linear in $T$ scaling of the specific heat at low temperatures in contrast with the Debye prediction $C(T) \sim T^3$.

The current, and in fact unique, paradigm for the explanation of the thermal anomalies in glasses relies on hypothetical double-wells in the energy landscape of glasses at low $T$ (1–3). Assuming a random distribution of such double-wells and implementing quantum tunnelling between nearly-degenerate states, a Hamiltonian can be obtained which leads to a linear-in-$T$ specific heat at low temperatures (on the order of $1K$). The Two-Level-States (TLS) model has had an enormous success in its ability of providing an interpretation to experimental results, and it has been also extended within the mosaic picture of the Random-First order Theory (RFT) of glasses (4, 5).

Yet, the TLS model has not been fully validated in the sense that, on one hand, the two-level states have been somewhat elusive to identify in physical systems. On the other hand, a series of papers by Leggett and co-workers (6, 7) have highlighted how unlikely it is that a random distribution of tunnelling states could produce universal values of ultrasonic absorption constant and thermal conductivity for any material. Finally, discrepancies with recent experimental observations have also been reported (8–12).

Here we challenge the current paradigm based on TLS, and present an altogether different model, called Random Matrix Model (RMM), to explain the linear-in-$T$ specific heat anomaly

Significance Statement

It has been observed experimentally since the 1970’s that the specific heat of amorphous solids at low-$T$ does not follow the $T^3$ law predicted by the Debye law based on assumptions of regular lattice. The universally accepted explanation for this effect relies on quantum tunnelling between two-level states. Here we show, instead, on a minimal model of amorphous solids, that the structural disorder alone is sufficient to account for this anomaly in the specific heat, and we provide a direct quantitative connection between the specific heat and the random matrix behaviour of the vibrational spectrum.

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in glasses. We show that the root-cause of this behaviour can be identified with a flattening regime in the VDOS, which is dominated by a random matrix scaling. Previous derivations and discussions of the VDOS using Random matrix theory have been already proposed in (13–18). Most of the previous results are either directly based on or related to analytical results obtained in the Gaussian or Wishart ensembles for which spectral distributions converge to the form of the well-known Wigner and Marchenko-Pastur distributions. Recently, however, it has been rigorously demonstrated (19, 20) that the Marchenko-Pastur spectral distribution corresponds to random Laplacian block matrices with \( d \times d \) blocks, where \( d \) is the space dimension, and with connectivity \( Z \), only in the limit \( d \to \infty \) with \( Z/d \to \infty \) fixed. The Wigner semi-circle is recovered for adjacency matrices in the limit \( Z/d \to \infty \) with \( d \) fixed, while for the same matrices in the limit \( d \to \infty \) with \( Z/d \to \infty \) fixed one recovers the effective medium approximation of Ref. (21).

Clearly the dynamical (or Hessian) matrix of an amorphous solid can be most realistically represented by a Laplacian random block matrix with \( 3 \times 3 \) blocks (\( d = 3 \)). Nevertheless, as shown in (19), the Marchenko-Pastur distribution which is exact only for \( Z/d \to \infty \) still captures the salient qualitative features also of the spectral distribution at finite \( d \). In the impossibility of formulating an exact analytical description of the spectrum for finite \( Z/d \) (20), this motivates us to use a suitably modified Marchenko-Pastur distribution as the starting point for an analytical description of random matrix behavior in the VDOS of amorphous solids, and the successful fittings presented below indirectly justify this choice and the proposed RMM model. The analytical RMM description of VDOS data can then be used to evaluate the specific heat and is shown to reproduce the linear-in-\( T \) scaling at low \( T \), and its occurrence over a broader range of \( T \) upon increasing the disorder.

**Numerical calculations**

As a model system we use random networks of harmonic springs derived from Lennard-Jones (LJ) glasses. The details about the preparation of the numerical system can be found in previous work (22). In short, a system of LJ particles is quenched into a metastable glassy minimum using a random block matrix with \( 3 \times 3 \) blocks (\( d = 3 \)). This system presents several analogies with jammed packings of soft frictionless spheres (23): the shear modulus \( G \) goes to zero as \( \sim (Z - Z_c) \) exactly like at the unjamming transition of compressed soft spheres, and the crossover frequency \( \omega^* \) at which the VDOS drops and corresponding to which there is an excess of modes (the Boson peak) also exhibits scaling with \( Z - Z_c \) (24). Furthermore, the VDOS for these elastic networks is very similar to the VDOS of jammed packings and presents the same features (23, 25): there is a Debye \( \omega^2 \) regime extending from \( \omega = 0 \) up to \( \omega^* \), approximately, which shrinks upon decreasing \( Z \) until it vanishes at \( Z = Z_c \). Previous discussions about jamming, marginal stability and low-temperature anomalies in structural glasses have already appeared in (26–28).

An advantage of our system is that, being all bonds harmonic springs, there are no complications that may arise from anharmonicity, which is also known to generate a boson peak, and hence one can properly isolate the effect of structural disorder on the vibrational and thermal properties.

**Random matrix model**

We start out from the well known Marchenko-Pastur distribution of eigenvalues for random matrices drawn from the Wishart ensemble of matrices \( M \). The Wishart ensemble is created by starting from a \( m \times n \) gaussian random matrix \( A \) using \( M = \frac{1}{n} A A^T \). This matrix has the eigenvalue distribution \( (M v = \lambda v) : \)

\[
p(\lambda) = \frac{\sqrt{((1 + \sqrt{\rho})^2 - \lambda)(\lambda - (1 - \sqrt{\rho})^2)}}{2\pi \rho \lambda}
\]

where we introduced the parameter \( \rho = m/n \). Since we are interested in the vibrational density of states \( D(\omega) \) of the eigenfrequencies \( \omega = \sqrt{\lambda} \) we transform \( p(\lambda) \) to the frequency space: \( p(\lambda)d\lambda = D(\omega)d\omega \)

\[
D(\omega) = \frac{\sqrt{((1 + \sqrt{\rho})^2 - \omega^2)(\omega^2 - (1 - \sqrt{\rho})^2)}}{\pi \rho \omega}
\]

We now shift this distribution in the frequency space by \( \delta \) and introduce the width of the spectrum \( b \) by the transformation:

\[
\omega \to \frac{2}{b} (\omega - \delta)
\]

which gives:

\[
D(\omega) = \frac{\sqrt{((1 + \sqrt{\rho})^2 - \frac{1}{b^2}(\omega - \delta)^2)((\omega - \delta)^2 - (1 - \sqrt{\rho})^2)}}{\pi \rho \frac{2}{b} |\omega - \delta|}.
\]
This spectrum belongs to a matrix $M'$ that can be derived by the original Wishart matrix $M$ in the following way:

$$(M')^{1/2} = b \frac{M^{1/2}}{2} + \delta 1$$ \[5\]

where $\delta$ and $b$ both depend on the minimal and maximal eigenfrequencies of the system, which define the support of the random matrix spectrum. In particular, the value of $\delta$ coincides with the lower extremum of the support of the random matrix distribution, and thus its value controls the frequency $\omega^∗$ which is associated with the Boson peak.

By choosing $\rho = 1.6$, a numerical fitting to the VDOS spectra of Fig. 1 gives: $\delta = (\omega - 2.72 - 0.074(Z - 6))^2$ and $b = (2.4 - 0.056(Z - 6))^2$.

In order to fit our data accurately we need to make two additional modifications that cannot be induced by a corresponding change in the matrix $M'$: first we need to correct the lowest edge of the spectrum by a factor that behaves like $\sim \omega^{-1/2}$ for $\omega \to 0$ and like $\sim 1$ for $\omega >> 0$, and second we need to add peak functions to model the relics of the van Hove singularity peaks which become more prominent for systems with high values of $Z$ due to the topology of the random network becoming influenced by the limiting FCC lattice to which any lattice will converge for $Z = 12$. This second correction is achieved by modelling the two relics of the van Hove peaks with two Gaussian functions. The final result for the fitting formulae of the density of states of the system reads:

$$D(\omega) = \frac{\pi \rho}{Z} \frac{1}{(\omega - \delta)^2 - (1 - \sqrt{2})^2} \left( \frac{\delta}{\omega - \delta} \right)^{1/4} + G_1(Z, \omega) + G_2(Z, \omega)$$

where $G_1 = (0.011(Z - 6)^2 + 0.175)\sqrt{\frac{\pi}{\omega}} \exp(-2(\omega - 1.6)^2)$ and $G_2 = (0.011(Z - 6) - 0.65)\sqrt{\frac{\pi}{\omega}} \exp(-8(\omega - 2.3 - 0.07(Z - 6))^2)$ are the two Gaussian functions used to model the van Hove peaks.

The comparison between Eq. (6) and the numerical data is shown in Fig. 3, whereas Fig. 2 shows the comparison between model and numerical simulations in terms of the corresponding eigenvalue distribution $\rho(\lambda)$. In both cases it is seen that the model parametrization given by Eq. 6 is excellent and provides a very accurate description of the data for all $Z$ values considered in the broad range from $Z = 9$ down to the unjamming transition at $Z = 6$. In particular, the values of all the parameters $\delta$, $b$, $\rho$, and those inside $G_1$, $G_2$, remain fixed upon changing $Z$. Hence, Eq. 6 perfectly captures the variation of the VDOS spectrum upon varying the coordination number $Z$ of the network.

We also note that the random matrix part of Eq. 6, which is given by the first line in Eq. 6, has a leading term which gives the scaling $D(\omega) \sim \omega$. This is very important, as this is the signature of random matrix behaviour. The scaling is, indeed, $D(\omega) = A(1 + B/\omega)$ in the regime just above the crossover frequency, which means that the eigenvalue distribution scales as $\rho(\lambda) = (A/\omega) + (B/\omega)\lambda^{−1/2}$, upon recalling the definition $\omega = \lambda^{2/3}$. Below the Boson peak, and for $Z > 6$, the behaviour is instead $D(\omega) \sim \omega^2$, i.e. fully consistent with Debye law. Upon approaching $Z = 6$, the coefficient $A$ becomes smaller and eventually leaves the clean random-matrix scaling $\rho(\lambda) \sim \lambda^{−1/2}$ found analytically in the Marchenko-Pastur distribution of random matrix theory. For $z > 6$ the Debye regime extends to larger and larger $\omega$ and alters this scaling.

### Specific heat

Equipped with a fully analytical parametrization of the VDOS which explicitly contains the contribution from random matrix behaviour of the eigenvalues of the Hessian, and which correctly reproduces the scaling with $Z - Z_c$, we can now proceed to the evaluation of the specific heat contribution from the part of the VDOS which excludes the Debye regime (the latter is known to provide a $C \sim T^3$ contribution).

Indeed, in order to evaluate the specific heat we do not need anything else than the VDOS, because the specific heat is given by the following integral (29):$

C(T) = k_B \int_0^\infty \left( \frac{\hbar \omega}{2k_B T} \right)^2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) - 2 D(\omega) d\omega \ [6]$

Upon plugging Eq. 6 into the integral, we obtain the specific heat for different values of $Z$ plotted in Fig. 5. It is evident that at low $T$ the specific heat of the random spring network is linear in $T$. For denser networks (larger $Z > 6$) there is also a second linear-in-$T$ regime separated by the low-$T$ regime by a $T^2$ crossover. Importantly, the low-$T$ linear-in-$T$ regime becomes broader and broader as $Z$ decreases until, at the
This peak is well documented also in the experimental literature, which tells us two things: (i) the temperature of the boson peak in the specific heat exhibits critical scaling with respect to the critical point \( Z = Z_c = 2d \); and (ii) the boson peak temperature is proportional to the shear modulus \( G \), since in this system it is known (22, 23, 30) that \( G \sim (Z - Z_c) \).

Finally, we can also plot the amplitude of the boson peak in the specific heat, or its reciprocal, as a function of the coordination parameter \( Z - Z_c \). Also in this case scaling is found: the amplitude of the peak is inversely proportional to \( Z - Z_c \); although in this case the scaling law sets in only from \( Z = 7 \), which may suggest the presence of non-mean-field effects close to the critical point \( Z = Z_c \).

Critically, this peak becomes flat at a crossover frequency \( \omega^* \sim T^* \), which turns out to exhibit scaling:

\[ \omega^* \sim (Z - Z_c), \quad Z_c = 6. \]  

As a consequence, the normalized specific heat \( C(T)/T^3 \) displays a maximum (also known as the boson peak in the specific heat) at a temperature:

\[ k_B T^* = \hbar \omega^* \sim (Z - Z_c), \quad Z_c = 6. \]  

This peak is well documented also in the experimental literature, e.g., in metallic glasses. Equation (9) is an important observation, which tells us two things: (i) the temperature of the boson peak in the specific heat exhibits critical scaling with respect to the critical point \( Z = Z_c = 2d \); and (ii) the boson peak temperature is proportional to the shear modulus \( G \), since in this system it is known (22, 23, 30) that \( G \sim (Z - Z_c) \).

Conclusions

We presented a minimal model of a glass at low \( T \) as a random elastic network of harmonic springs. The control parameter in the model is the coordination number \( Z \), because as \( Z \) approach the critical point \( Z_c = 2d = 6 \), which coincides with a rigidity (or unjamming) transition, the maximum degree of disorder is achieved. This type of disorder was characterized in previous work (22) and shown to be related rather to the statistical degree of inversion-symmetry than to bond-orientational order. As \( Z \) decreases towards \( Z_c \), the random matrix character of the vibrational density of states (VDOS) becomes more and more prominent, in the form \( D(\omega) = A\omega^* + B \) with the coefficient \( A \) decreasing as \( Z \) decreases further towards the rigidity/unjamming transition. A fully analytical description of the VDOS called Random Matrix Model (RMM) is provided based on the Marchenko-Pastur spectrum shifted to accommodate the Debye phonons and suitably modified to account for the two reliefs of van Hove singularities corresponding to the reference (FCC) crystalline structure in the limit \( Z = 12 \). The RMM analytical fitting of the numerical VDOS data of the random network gives clear evidence of the random matrix character of the spectrum especially close to the crossover frequency \( \omega^* \) which marks the shoulder below which the random matrix contribution goes to zero and leaves the behind the Debye contribution that occupies the gap between 0 and \( \omega^* \). Using this analytical formula, Eq. 6, we evaluate the specific heat and we found a linear-in-\( T \) law which becomes more and more extended as \( Z \) decreases, i.e., upon moving towards the “epitome” of disorder at \( Z = Z_c \). Hence the linear-in-\( T \) specific heat anomaly of glasses, and its extent, is directly related to the random-matrix form \( D(\omega) = A\omega + B \) in the VDOS (or \( \rho(\lambda) = (A/2) + (B/2)\lambda^{-1/2} \), in terms of eigenvalues). Furthermore, the model also reproduces the well documented peak in the normalized specific heat and, for the first time, shows that also the temperature of the peak exhibits critical scaling with distance \( Z - Z_c \) to the unjamming (rigidity) transition and that the amplitude of the peak is inversely proportional to \( Z - Z_c \) and hence to the shear modulus \( G \sim (Z - Z_c) \), i.e., \( 1/a_{BP} \sim (Z - Z_c) \sim G \). The latter relation between the peak amplitude and the shear modulus is crucial to explain experimental data on specific heat in metallic glasses (see Eq. 4 in Ref. (31)) but has not been proved before.

In conclusion, we presented significant evidence that the well known linear-in-\( T \) specific heat anomaly in low-\( T \) glasses is directly controlled by random-matrix behaviour in the vibrational density of states. Since the elastic random network
model that we studied does not contain any anharmonicities or quantum tunnelling effects, this analysis demonstrates that the linear-in-T anomaly of the specific heat may be caused solely by structural disorder and random matrix character of the eigenvalues of the dynamical matrix, with possibly no role played by quantum mechanics, in contrast with what has been the unique paradigm so far (the so-called Two-level-state model) to explain this effect.

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