Spectral fluctuations of the atomic vibrations in glasses: random matrix theory and beyond

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It is demonstrated on a realistic model of amorphous alloy Si$_{0.9}$Ge$_{0.1}$ with 1000 atoms, that short-range spectral fluctuations of propagons and diffusons are universal and in agreement with random matrix theory. The universality ceases at distances greater than Thouless number $N_T$, where propagons obey the Altshuler-Shklovskii power law, $\Sigma_2 \sim N^{3/2}$ for the variance $\Sigma_2$ of the number of levels $N$, while a new power law, $\Sigma_2 \sim N$, is observed for diffusons.

Complexity of the atomic structure of glasses results in a wonderful variety of vibrational eigenmodes. Topological defects and the lack of a long-range order lead to mode localization, inhibition of ballistic motion, or resonance; only a small portion of the modes resemble phonons–vibrations in periodic crystals. It is a difficult computational task to build a respectable-size atomic model of a glass and obtain the vibrational eigenstructure by diagonalizing huge dynamical matrices; no analytical treatment is available. By applying the methods of random matrix theory, this Letter reports on certain statistical analytical rules, universal (parameter free) and not, shared by similar modes. In particular, it is found that short-range spectral correlations of diffusons (non-propagating extended modes) and propagons (phonon-like modes) are universal and agree with random matrix theory, similarly to what have been observed in many other complex physical systems. However, correlations at distances greater than Thouless number $N_T$ cannot be described by random matrix theory. Spectral fluctuations become idiosyncratic: the statistics acquires a parameter ($N_T$) and the functional dependence is different for different mode classes. Propagons follow the Altshuler-Shklovskii “3/2” power law for the fluctuations $\Sigma_2$ of the number of levels, while diffusons have the fluctuations growing linearly with increasing number of levels. This is likely a general feature of strongly scattered (diffusion-like) waves in random media.

The following picture of vibrational modes in glasses has emerged from numerical studies of realistic models of vibrational disorder. Figure shows the calculated vibrational density of states for a model of a glass used in this paper (amorphous Si$_{0.9}$Ge$_{0.1}$), with three specified spectral regions. At the lowest frequencies vibrations are acoustic-phonon-like propagons, weakly scattered sound waves with well defined momentum and polarization. At low frequencies one also finds resonance modes which have unusually large amplitude at certain inhomogeneous regions, while resembling propagons elsewhere. As the frequency increases, propagon momenta become less and less certain until the frequency reaches the so called Ioffe-Regel limit where the mean free path becomes comparable to the wavelength and the wave vector concept is no longer valid. The emerging modes are diffusons–extended modes not able to propagate ballistically, rather spreading out in a special diffusive fashion. Diffusons, forming the majority of the spectrum, are the most natural modes for glasses. Atoms in glasses display a short-range order by globally preserving local quantities like interatomic distances or coordination numbers. But at large distances the order is lost. Diffusons have the same property: displacements of neighboring atoms are strongly correlated, while those between distant atoms are uncorrelated and the global displacement pattern, like the structure of the glass, appears random. Finally, the highest-frequency modes are localized–locons. The purpose of this letter is to compare spectral properties of propagons and diffusons with random matrix theory and theories of wave-like modes in disordered systems, to sort out universal and nonuniversal features.

Random matrix theory was originally devised to deal with the spectra of complicated nuclei, but by now it has been successfully applied in many areas of physics. The main assumption is that certain spectral properties of complex (as opposed to simple) Hamiltonians are universal, not dependent on the concrete realization of complexity; these properties can be therefore calculated, in many cases analytically, as averages over an ensemble of (similarly) complex Hamiltonians. I focus here on the Gaussian orthogonal ensembles (GOE) which are sets of real symmetric matrices with elements randomly selected from a Gaussian probability distribution. Dynamical matrices which determine the frequencies of atomic vibrations are also real symmetric so, if their structure is sufficiently complicated, their properties should be similar to the properties of the GOE. For the latter theory predicts that neighboring levels (frequencies) repel each other: there is a zero probability of finding two equal levels. A convenient measure of level repulsion is the level-spacing distribution (LSD) $\rho$ which, for the GOE ensembles, is very accurately expressed by the Wigner surmise

$$\rho_W(s) = \frac{\pi}{2} s \exp(-\pi s^2),$$  \hspace{1cm} (1)
distant levels. Such correlations can be quantified in several ways. Here I use the \( \Sigma_2 \) statistics which measures, given an interval of size \( N \), the variance of the number of levels in that interval. For GOE at large \( N \):}

\[
\Sigma_{2,\text{GOE}}(N) \approx \frac{2}{\pi^2} \left[ \ln(2\pi N) + \gamma + 1 - \frac{\pi^2}{8} \right],
\]

where \( \gamma \approx 0.5772 \) is Euler’s constant. The logarithmic dependence expresses the rigidity of a GOE spectrum.

I evaluate LSD and \( \Sigma_2 \) for the vibrational spectrum of a model of amorphous Si\(_{0.9}\)Ge\(_{0.1}\) alloy whose atomic coordinates and interatomic forces are taken from the realistic model of amorphous silicon \cite{13} generated by randomizing a crystalline silicon structure (Wooten-Winer-Weaire recipe \cite{12}) and then relaxing the atoms to a local minimum of the Stillinger-Weber interatomic potential \cite{13}. The model structure and physical properties agree very well with experiment \cite{14}. Here I use a model with 1000 atoms arranged in a cube of side 27 Å. The Si\(_{0.9}\)Ge\(_{0.1}\) alloy is obtained by substituting germanium atomic masses for the masses of randomly picked 10% silicon atoms. The mass disorder is small to qualitatively change the vibrational properties of the original amorphous silicon model (similar amorphous silicon-germanium alloys were studied in Refs. \cite{7,14}), but large enough to generate a useful ensemble. Below I use \( N_r = 3500 \) different mass-disorder realizations of the alloy. The model has 3000 vibrational frequencies whose spectrum is in Fig.\( \square \) (averaged over the ensemble), along with the alloy inverse participation ratio \( 1/p \) (averaged over 15 samples), allowing an identification of the mobility edge at about 70 meV. The Ioffe-Regel limit is also indicated at 13 meV (taken from the studies of the pure silicon models \cite{4,7,8} the actual transition is probably quite broad, perhaps plus and minus 2 meV). For the statistics, I take for propagons all the modes, about 200, from 5 to 13 meV (this includes a small number, less than 5%, of resonance modes which behave mostly as propagons anyway) and for diffusons all the modes, about 1000, from 35 to 65 meV (which is enough away from the locons and from the anomalous quasi-localized region around 30 meV at the DOS dip and \( 1/p \) peak).

To calculate spectral averages that can be compared with the predictions of random matrix theory, the vibrational spectrum has to be “unfolded,” that is, locally rescaled to compensate for the spectral variations of the local average level spacing. A standard unfolding procedure \cite{5} involves finding the average cumulative DOS (a staircase function) of the spectral region of interest. The unfolded spectrum is then the set of values of the average function at the original frequencies. There are two ways of finding the average: by ensemble averaging or by analyzing a smooth fit to a single spectrum. The latter method works fine if an analytical behavior of the cumulative DOS is known. Without an analytical guidance, however, the procedure is more art than science \cite{13}. This is why I use amorphous alloy Si\(_{0.9}\)Ge\(_{0.1}\) (rather than just pure amorphous silicon) for spectral statistics: first, there is no analytical formula available for DOS of amorphous silicon and, second, mass disorder is much easier to implement than structural disorder. With a sufficiently large ensemble at hand, the averages are straightforward to evaluate. If \( \rho_i(\omega) \) is the cumulative DOS of the \( i \)-th sample at frequency \( \omega \), the average...
The scaling parameter $N_L$ is the Thouless number, $N_T = hD/\delta^2$, the uncertainty in the energy (in the units of the average local level spacing $\delta$) of a wave-packet-like state diffusing with diffusivity $D$ throughout a sample of size $L$. Equation (3) is valid for $N \gg N_T$, (up) and propagons obey it with $N_T \approx 1.1$ (see Fig. 3). Figure 3 plots $N_T$ as a function of vibrational frequency for the pure silicon 1000-atom model, calculated from the model diffusivity $D$. The result for the alloy would look identical, perhaps being smaller by a few percent ($D$ for a similar alloy with 25% of substituted Ge atoms differs only slightly from $D$ of the pure silicon sample [6]). We see that $N_T$ is frequency dependent—it varies from below 0.1 to above 4 in the propagon region. Considering that Eq. 3 comes with some effective $N_T$, biased towards lower values, the result for the effective $N_T \approx 1.1$ is reasonable (the average of 1/$N_T^{3/2}$ over the propagon frequencies gives about 1.7; for the alloy it will be slightly less), confirming the theory of Ref. [6].

Diffusons show nonuniversal behavior too. In Fig. 4, their $\Sigma_2$ grows linearly with increasing $N$ for about a decade, from 30 to almost 400 (the growth slows down for greater $N$, most likely due to finite size effects). Like propagons, diffusons become less spectrally correlated when separated by more than a few other modes (of order 1; the deviation at small $N$ is not visible because of the graph scale). But unlike propagons, the power law is linear, $\Sigma_2 \sim N$. This different dependence is not surprising, as diffusons are not weakly scattered modes envisioned in the derivation of Eq. 3. Diffusons do diffuse with time [8], but in a different way than do propagons or electrons (in weakly disordered systems). Equation 3 was derived by perturbation theory which assumes electron states to be plane waves between scattering events.
In other words, the mean free path of electrons is much greater than their wavelength: the electrons are below the Ioffe-Regel limit and their diffusion resembles a random walk (like propagons). Diffusions, on the other hand, diffuse more like a free-particle quantum mechanical wave packet (this type of diffusion was branded “intrinsic” [4]); diffusions are not perturbative states.

To explore possible sources of differences between $\Sigma_2$ for propagons and diffusions, it is instructive to repeat the qualitative argument [4] which leads to Eq. 3. A given state can mix with neighboring $N \gg N_T$ states if it diffuses a time $\tau_N \approx \hbar/\delta N$, or over a region with size $L_N = (D\tau_N)^{1/2} = (N_T/N)^{1/2}L$. The $N$ states in a volume $(L_N)^3$ will be correlated as predicted by random matrix theory, with the uncertainty in the number of levels of order unity (a rigid spectrum). But states in different regions (all of size $L_N$) of the sample will be uncorrelated, so the uncertainty (measured by $\Sigma_2$) in the number of states in the whole sample will be proportional to the number of the independent regions/spectra. This number is $(L/L_N)^3 = (N/N_T)^{1.5}$, which is Eq. 3. The argument can be made (naively) more general by considering an anomalous diffusive transport $L_N \sim \tau_N^\beta$ ($\alpha = 1/2$ in the usual case) and a fractal filling of volume $L^\beta$ ($\beta = 3$ for uniform filling). Then $\Sigma_2 \sim N^{\alpha\beta}$, and for diffusions one gets $\alpha\beta = 1$. If the space filling is ordinary ($\beta = 3$), the diffusive transport is not ($\alpha = 1/3$). If the transport is ordinary ($\alpha = 1/2$), the spreading is fractal ($\beta = 2$). It is not clear wheather diffusions behave one way or the other (or both), or whether the above reasoning, which is a pure speculation, makes sense.

If there is a scaling of the type $\Sigma_2 \sim (N/N_T)$, the best way to see it is to look at spectral statistics of small diffusion regions of almost constant $N_T$; the regions must contain enough levels to see the systematic deviations from GOE. Figure 2 plots $\Sigma_2$ of six such regions, all displaying the linear law $\Sigma_2 \sim N$, all with different proportionality coefficients (note that the law holds also for the 18-22 region not considered in the calculation of Fig. 3). From the values of the coefficients and the regions’ average $N_T$’s given in the caption, one cannot see any obvious relationship between the coefficients and $N_T$. There is certainly no support from the available data of a scaling of the type $\Sigma_2 \sim (N/N_T)$: by plotting $\Sigma_2$ versus $N/N_T$ (not shown) the curves do not collapse onto or close to a single line. While there definitely is a dependence of $\Sigma_2$ on $N_T$ (explicit or implicit), the present spectrum size does not allow me to decipher it and considering larger models is presently unfeasible.

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