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Universality in the vibrational spectra of weakly-disordered two-dimensional clusters

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Abstract

We numerically investigate the vibrational spectra of single-component clusters in two dimensions. Stable configurations of clusters at local energy minima are obtained, and for each the Hessian matrix is evaluated and diagonalized to obtain eigenvalues as well as eigenvectors. We study the density of states so obtained as a function of the width of the potential well describing the two-body interaction. As the width is reduced, as in three dimensions, we find that the density of states approaches a common form but the two-peak behavior survives. Further, calculations of the participation ratio show that most states are extended, although a smaller fraction of the degrees of freedom are involved in these modes compared to three dimensions. We show that the fluctuation properties of these modes converge to those of the Gaussian orthogonal ensemble of random matrices, in common with previous results on three-dimensional amorphous clusters and molecular liquids.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The study of vibrational spectra has long provided important insights into the understanding of amorphous states of matter [1], such as molecular glasses. However, many key questions still remain unanswered. The vibrational disorder that is present in systems such as glasses is mainly topological in origin, and over the years a lot of effort has been given to the study of glass and glass transitions in terms of the underlying potential energy surface (PES) [2–9]. One of the main focuses has been the study of inherent structures, i.e. local minima of PES, and properties like ageing have also been studied as a function of inherent structures [10]. Regarding vibrational spectra of systems having a topological disorder [11–17, 20–28], a popular approach relies on the study of the statistical properties of random matrices, as within the harmonic approximation the dynamical or the Hessian matrix contains all the dynamical features [11–17].

Recently, studies of the vibrational spectra of amorphous systems have revealed some interesting universal

aspects. In particular, studies of three-dimensional amorphous clusters [21–23] have demonstrated the universality in the functional form of the density of states (DOS), and further, the statistical fluctuations have been shown to obey the characteristics of the Gaussian orthogonal ensemble (GOE) of random matrices to a very high degree of accuracy. Recent studies on periodic three-dimensional molecular network-forming liquids have also shown that the statistical fluctuations obey the characteristics of the GOE [24] at various temperatures and for various densities. Even in amorphous alloys [28], the statistical fluctuations have been reported to obey the characteristics of random matrix theory. Another universal feature that has been reported in earlier and recent studies on periodic three-dimensional amorphous systems using various model potentials is the density of states function approaching a limit that is independent of the explicit functional form of the potential in the amorphous regime. The reasons for this universality have been suggested in [18–20].

The concept of localization and delocalization of vibrational states has also been a focus in these studies, with delocalized states being associated with GOE statistics [17, 27] and localized states resulting in Poissonian statistics [17].

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A popular measure of localization is the participation ratio [15–17, 20–27]. Values for participation ratios for three-dimensional amorphous clusters [20–23], network-forming liquids [24] and atomic liquids [27] indicate that the majority of the states are delocalized, supporting the apparent universality of GOE behavior in the statistical fluctuations.

Recent years have also seen an increase in studies of the vibrational properties of nanocrystalline materials, both theoretically [29] and experimentally [30]. The new experimental techniques and methods have made it possible to explore the systems that are very small in size [31] and increased computational power has even made it possible to explore such systems in reduced dimensions [32].

In the present work we numerically investigate the vibrational spectra of two-dimensional clusters. It is well known (e.g. in critical phenomena) that dimension has a strong effect on universal behaviors, and a detailed study in a lower dimension would be a severe test of the robustness of the observed universalities in three-dimensional systems. For example, as suggested in [33], in quantum mechanical systems such as two-dimensional kicked rotors for lower dimensions ($d \leq 2$), all the electronic states are exponentially localized, while for higher dimensions ($d > 2$) there are extended as well as localized states. Also, disordered molecular systems display novel behavior in two-dimensions, e.g. the occurrence of the hexatic liquid phase that has a long range bond order without translational order [34]. Hence, checking the universality of the vibrational spectra for two-dimensional clusters is a severe test. We are interested in seeing the effect of dimensionality on the states being localized or delocalized, with the main focus being on statistical fluctuations for the present two-dimensional case.

2. Methodology and density of states

The model used for the interactions between the particles is the Morse potential [35]. Over the years various studies have demonstrated the usefulness of this potential in simulations (for example [36, 37]). The form of the potential energy V of the system is

$$V = \sum_{j>i} \{ \exp[-2\alpha(r_{ij} - 1)] - 2 \exp[-\alpha(r_{ij} - 1)] \}. \quad (1)$$

The potential is thus a function of inter-particle distance r_{ij} and the (positive) parameter α ; the sum is over all pairs of particles in the system. The α parameter can be tuned to fit a variety of systems, ranging from metals such as sodium with $\alpha = 3.15$, van der Waals bonded systems such as rare gases with $\alpha = 6$, to the very short-ranged interactions of the C_{60} molecule with $\alpha = 13.62$ [37]. The values of α that have been used in the present study are 3.5, 6.0, 10.0, 13.0 and 16.0. Using these values of α for the interaction potential, we first generate stable two-dimensional clusters with $N = 4000$, where N is the number of particles in a cluster. For some calculations, clusters with $N = 500$ and 2000 particles are used.

In order to generate stable clusters, we begin by initializing the particle positions within the limiting distance $r = \sqrt{N/\pi}$ on the x - y plane. Figure 1(a) shows an example

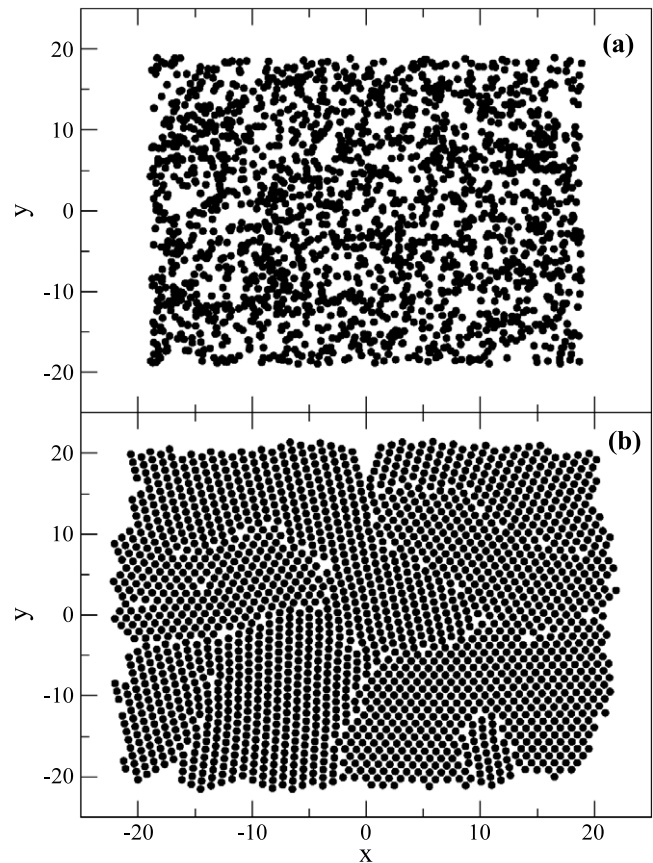


Figure 1. (a) A typical starting configuration of a two-dimensional cluster with $N = 2000$. (b) Stable two-dimensional cluster obtained using the method of homotopy with $N = 2000$.

of a typical starting configuration for $N = 2000$. In order to obtain the potential energy minimum for such a configuration, we use the homotopy method of minimization [38, 39]. According to this method, in order to find a local minimum of a function V , we minimize in a series of steps the quantity $\theta V + (1 - \theta)W$, where W is a suitably chosen simple function (e.g. quadratic) and θ is varied from 0 to 1 in a finite number of steps, typically 20. The minimized configuration for one value of θ serves as the initial configuration for the subsequent step. Figure 1(b) illustrates a two-dimensional stable cluster generated by this method.

At each local minimum generated by this method, a Hessian matrix is constructed using the position coordinates of particles at that minimum and is diagonalized using standard methods to obtain the eigenvalues as well as the eigenvectors. The eigenvectors correspond to the normal modes and the eigenvalues (λ) are related to the frequencies (ω) of the obtained normal modes according to $\omega = \sqrt{\lambda}$. The normal modes obtained in this manner are also known as quenched normal modes (QNM). A quantity that is of central physical interest is the density of states (DOS) function, the histogram of values of ω , denoted by $G(\omega)$. In figure 2(a), we plot $G(\omega)$ for several values of α . To improve statistics we combine information from the available distinct quenched configurations (at least 75 for each case) by averaging over all the configurations. After obtaining the raw averaged DOS

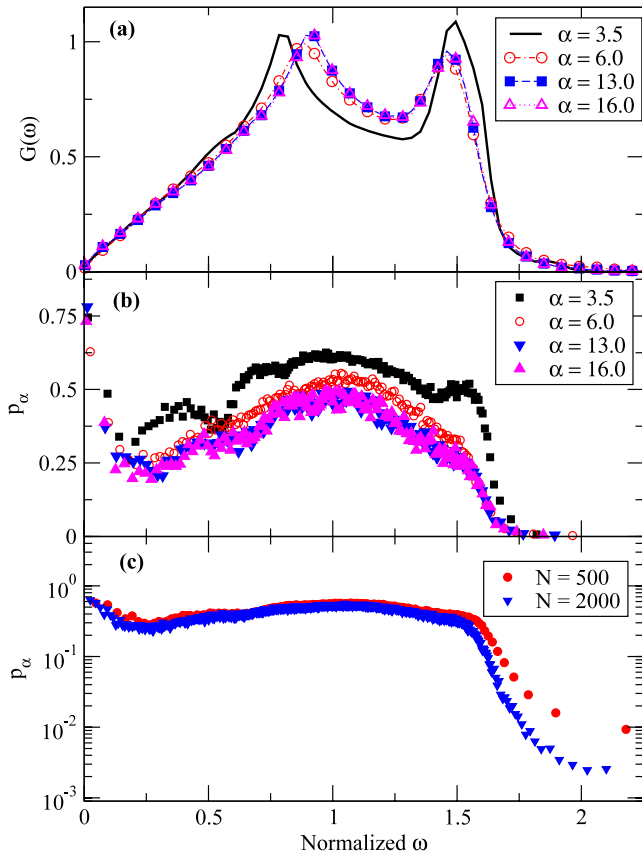


Figure 2. (a) Density of states ($G(\omega)$) versus normalized frequencies of normal modes plotted for various values of α . The area under each curve has been rescaled to unity. $N = 4000$ has been used in this calculation. (b) Participation ratios (p_α) versus normalized frequencies of the normal modes for various values of α . (c) $\log(p_\alpha)$ versus normalized frequencies of the normal modes for $\alpha = 6.0$ for $N = 500$ and 2000 particles.

function, the average frequency is normalized to unity and $G(\omega)$ is rescaled so that the area under the curve is also unity. This process enables us to compare the DOS for different values of α . Figure 2(a) clearly shows the existence of a two-peak behavior for all the values of α studied, suggesting that the obtained local minima have weakly-disordered domains with grain boundaries. This is further evident from figure 1(b). This two-peak nature observed in the DOS function is also consistent with the recent results obtained by Hudon *et al* [32], where bulk nanocrystalline materials in two-dimensions were studied using the Lennard-Jones interaction potential and a similar form for $G(\omega)$ is observed. It also shows that the present system behaves as a ‘normal’ two-dimensional system *as per* the notation used by Hudon *et al* [32]. The peaks shift towards the right with increasing α and the overall structure varies very slowly for higher values of α .

This is also notably different from the earlier study conducted on a periodic three-dimensional system using a similar generalized Morse potential [20, 23]. In the three-dimensional case, it was possible to generate states with variable amounts of disorder and the analysis of disordered states showed that the two-peak behavior of DOS changed over to one-peak behavior as the value of α was increased;

by the time α reached 16 only one peak remained. Further increase in the α value led to small changes in the overall DOS shape [20, 23]. However, in the present case, potential energy minimization results in states that are weakly-disordered rather than totally amorphous, and at present it is not clear how one could generate stable clusters in two dimensions that have variable amounts of disorder. However, a similar feature in both the two- and three-dimensional cases occurs at higher values of α , where the DOS function varies very slowly with further increases in α .

Figure 2(b) shows the participation ratios [15–17, 21–27] calculated using the eigenvectors corresponding to each eigenvalue for all values of α . Mathematically, the participation ratio is defined as

$$p_\alpha \equiv \left[N \sum_i (e_\alpha^i \cdot e_\alpha^i)^2 \right]^{-1} \quad (2)$$

where e_α^i is the projection of the eigenvector (labeled by α) onto particle i . For extended modes, p is of the order of unity and does not depend on system size, while for localized modes it will scale inversely with the system size. Calculations for participation ratios have been done using $N = 500$ and 2000 particles. For each value of α on this plot, information from various quenched configurations is combined to improve statistics. For all the α values studied, maximum values for participation ratios stay below or close to 0.6 which might suggest that more states are localized in two dimensions as compared to three dimensions. However, closer examination of participation ratios plotted on a semi-log scale in figure 2(c) with varying N shows that the states are definitely not localized over the wide spectrum that has been used for studying statistical fluctuations. Since the two systems differ in size by a factor of 4, localized modes in the larger system should have participation ratios approximately 1/4 of those in the smaller system. We find that differences on this scale only occur towards the higher values of ω . Hence, even though the participation ratios in the middle part of the frequency spectrum that is used in the analysis of statistical fluctuations are close to 0.5 or 0.6, these still have behavior consistent with extended modes of the system.

3. Fluctuations

We now investigate the statistical fluctuation properties of the DOS. In the present case, the fluctuation properties are computed for λ s, the eigenvalues. For a particular inherent structure, we denote the elements of the obtained spectra by $\lambda(i)$ with $i = 1, 2, \dots, 2N$. Since the present system is two-dimensional, the first three elements in the spectra will be zero and the remaining $(2N - 3)$ positive frequencies are characterized by defining a mean local density as well as the fluctuations around it. The first step in computing the fluctuation properties is to unfold the data [21–24, 40–42]. This process enables us to transform the eigenvalues in such a way that the average spacing between two successive eigenvalues is unity.

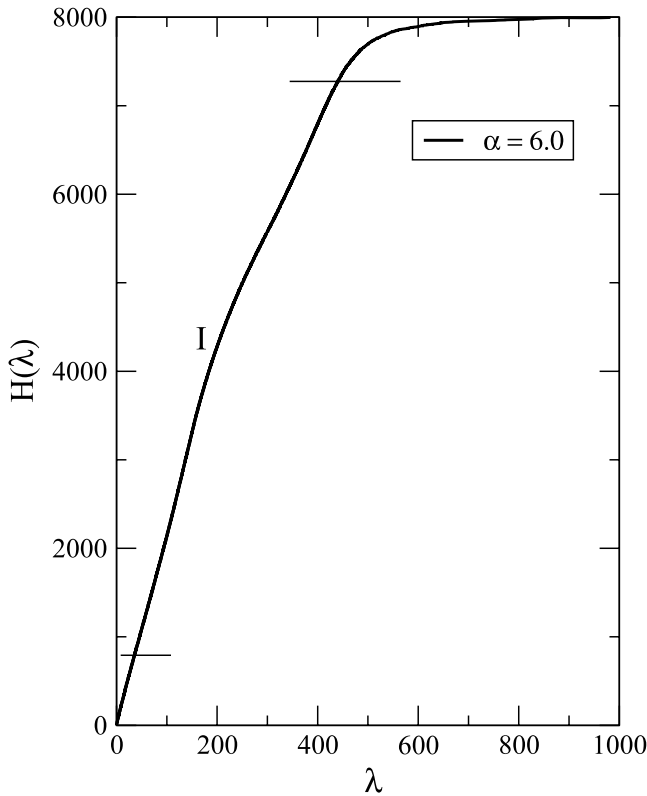


Figure 3. Integrated density of states for a single spectrum for $\alpha = 6.0$ with $N = 4000$. Data in the region I have been used for unfolding and to analyze the statistical fluctuations.

For unfolding the data, we define $H(\lambda)$ to be the number of frequencies equal to or less than λ , as shown in figure 3, and $S(\lambda)$ is a smooth function that passes through the staircase function H in the best-fit sense. In the present case there is no single function that passes smoothly through the whole of H in the best-fit sense. We leave out small regions (about 10% of the levels) from each end of the spectrum and for the remaining levels in the central region marked as I in figure 3, we use a quadratic polynomial $D(\lambda) = a + b\lambda + c\lambda^2$ as an approximation for $S(\lambda)$ over the remaining spectral region. It must be stated that there is no particular reason to leave out the lower end region of I other than to obtain better fitting to the data; however, it is evident from figures 1(b) and (c) that towards the upper end of I, more states are localized and hence, for the analysis of this paper, it is the central regime that we are interested in. The values of a , b and c are obtained by a standard least-square fitting procedure. We also calculate the misfit function [22, 23] corresponding to each of the fits to check how well $D(\lambda)$ approximates $S(\lambda)$. The plot of the misfit function we find is qualitatively similar to the plot in figure 1(b) of [22].

In order to reduce the mismatch to a lower degree, we eliminate subregions where the mismatch function has a very irregular behavior. In the remaining regular subregions we fit a quadratic function to the misfit function, and we correct $D(\lambda)$ by these quadratic functions to obtain the desired unfolding functions. For each of the fluctuation properties reported in this paper, we combine the data from all the subregions of all the spectra.

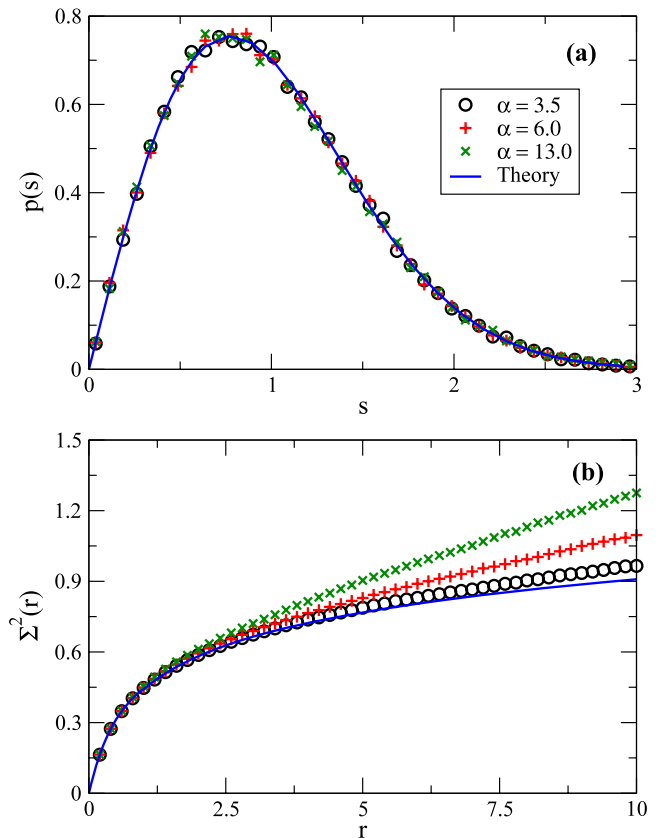


Figure 4. (a) Probability density $p(s)$ for normalized nearest neighbor spacing (s) for various values of α . Also shown is the prediction for the GOE. $N = 4000$ has been used in this calculation. (b) Variance of the number of levels in intervals of length r shown as a function of r for various values of α . Also shown is the prediction for the GOE. $N = 4000$ has been used in this calculation.

Note that this process of unfolding is quite different from the one used in [21–23] in which an exponential function has been used to unfold the data followed by the quadratic correction. In the present case, we could not find any suitable $S(\lambda)$ that could pass through H . Hence we had to resort to this method. However, the advantage of this method of unfolding is that it provides a suitable way of handling more complex functions that have no well-defined analytical form [24].

The first fluctuation property that we report here is $p(s)$, the distribution of the normalized nearest neighbor spacings s of the frequencies of the unfolded spectra. For this, we first complete the process of unfolding described above for each of the spectra using $D(\lambda)$. At this level, we apply the quadratic correction to this $D(\lambda)$ ignoring small regions where the misfit function is very irregular. In this way we obtain the unfolded spectra for each of the spectra. Selection of a random individual spectrum and analysis of each of them separately indicates that the spectrum has fluctuation properties associated with the Gaussian orthogonal ensemble (GOE) of random matrices. To improve statistics, we combine the data of all the available unfolded spectra. These have been plotted in figure 4(a) for three values of α along with the theoretical prediction [40–43]. It can be seen that the agreement with the theoretical prediction is extremely close, in spite of the values

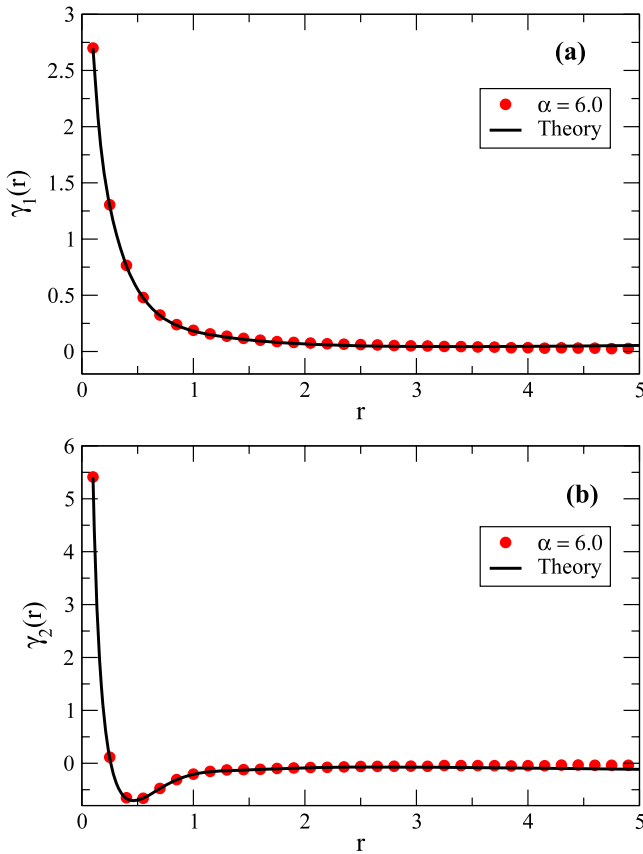


Figure 5. (a) Skewness parameter of the distribution of $n(r)$, the number of levels in intervals of length r , shown as a function of r for various values of α . Also shown is the theoretical prediction for the GOE. $N = 4000$ has been used in this calculation. (b) Excess parameter of the distribution of $n(r)$, the number of levels in intervals of length r shown as a function of r for various values of α . Also shown is the theoretical prediction for the GOE. $N = 4000$ has been used in this calculation.

of the participation ratios being lower than those found in three dimensions.

The second fluctuation property we report is the quantity $\Sigma^2(r)$, the variance of the number of levels $n(r)$ within an interval of length r located randomly in the unfolded spectrum. This is plotted in figure 4(b). It must be emphasized that the quadratic correction applied to the fitting function $D(\lambda)$ is very important in calculating $\Sigma^2(r)$. This calculation is extremely sensitive even to very small errors in the approximation to S . The contribution of any such error to $\Sigma^2(r)$ grows as r^2 , whereas the GOE prediction for $\Sigma^2(r)$ grows only as $\ln(r)$ [21–23]. Values for $\alpha = 3.5$ almost overlap to the theoretical prediction whereas we do see a shift for the other two α values. This may be due to the following possible effects: (i) as explained in [21–23], the exact locations of the irregular regions vary in the contour of the misfit function and this might add to the observed shift. A detailed analysis using a *spectrum-specific* [22, 23] choice of subdomains might help in determining the strength of this effect on the observed deviation. (ii) As observed from figure 1(b), values of participation ratios decrease with increasing α , and this decrease might have a role to play in the observed deviation.

In figures 5(a) and (b), we plot the skewness and excess parameters [43] of the fluctuations. Also included in these plots are the predictions for the GOE. These predictions have been calculated on the basis of a large ensemble of 500×500 matrices belonging to the Gaussian orthogonal ensemble. Again we observe that the agreement with the theoretical prediction is extremely close. Plots show only one value of α just for clarity. Other values of α also have the same level of agreement with the theory as $\alpha = 6$.

4. Conclusions

Our results for the DOS of two-dimensional clusters show the survival of a two-peak behavior when the width of the potential well describing the Morse potential is reduced progressively, thereby indicating a weak disorder in contrast to the three-dimensional case. The participation ratios suggest that the vibrational spectrum has a behavior consistent with the extended modes of the system. Further, the vibrational spectrum has fluctuation properties associated with the GOE of random matrices. For each of the fluctuation properties, agreement with the GOE prediction is extremely close. The observed shifts in the case of the $\Sigma^2(r)$ calculations suggest that the magnitude of the participation ratio might have a role to play in this behavior; however, since calculations of the normalized nearest neighbor spacings distribution and skewness and excess are extremely close to the theoretical prediction, it may not be incorrect to say that the system still follows GOE.

This work leaves us with the following challenges as a part of future work. (1) The first challenge is to generate local minima that have a variable degree of disorder in two dimensions; at the moment it is not clear how to generate such states in two dimensions so as to allow us to do a systematic study with respect to disorder. (2) What should the level of disorder be before we see a convincing departure in the statistics from GOE? The present work shows that the statistics are of GOE type even in weak disorder. The reasons for this effect are yet to be determined. (3) As mentioned by Hudon *et al* [32] in their studies on bulk nanocrystalline materials, density can influence the thermal properties of nanocrystalline materials. Using this argument, it would of great interest to generate local minima as a function of density and repeat the calculations for statistics.

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