Universal correlations in vibrational spectra of complex crystals

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We study spectral statistics of lattice modes in a disordered crystal and in a crystal with a complex unit cell. The correlations of the eigenmode frequencies of a block of a disordered solid is found to obey the GOE Wigner-Dyson statistics. In contrast, the set of eigenfrequencies of a crystal with a complex unit cell taken at the same point $Q \neq 0$ in the Brillouin zone exhibit correlations specific to the GUE universality class.
The Wigner and Dyson statistical approach is extensively used to analyse the spectra of complex dynamical systems [1]. It has been proven theoretically and confirmed experimentally that the quantum energy levels in objects with chaotic dynamics universally obey the same mutual correlations as the eigenvalues of random symmetric, Hermitian or symplectic matrices [2]. Although an original statistical analysis of level correlation was focused at the spectra of microscopic quantum objects, such as nuclei and molecules [1], a similar idea may be applied to any spectral problem related to random matrices, for example, to the spectra of electromagnetic or electron waves in mesoscopic cavities [3]. Below, we report the results of a statistical analysis of vibrational spectra of a solid where complexity and chaos in the phonon spectrum are introduced via a random distribution of masses of the nuclei.

A priori, two spectral problems can be formulated for a complex solid. One is about statistical properties of resonances in the absorption spectra of a finite-size crystalline specimen, which can be regarded as a very big molecular cluster. A similar problem has been investigated experimentally [4] in chaotic solid resonators where the spectra reveal correlations specific to Gaussian symmetric real random matrices (the Gaussian orthogonal ensemble - GOE [2]), which is reproduced by numerical simulations reported below. The other problem is related to the spectrum of vibrations in a crystal with a unit cell composed of many different atoms - that is, of the optical phonons - taken at a point in the Brillouin zone of the complex solid. One can measure such spectra in the inelastic scattering experiments. We show that the latter spectra obey the statistics and correlation laws of the eigenvalues of Hermitian Gaussian random matrices (unitary ensemble, GUE [2]), which are usually attributed to the energy spectra of electrons in chaotic cavities in a magnetic field [3].

As a model of a chaotic acoustic resonator, we simulate numerically an fcc-crystal consisted of $12 \times 10 \times 8$ atoms along the $[010], [101],[\bar{1}01]$ cubic crystallographic directions, with random masses of sites and identical pair interactions between atoms. The latter choice allows us to avoid complications of a search of an appropriate ground state of the system. Each configuration of site masses, $\{m_j\}$ is produced by a random number generator. The latter is characterized by an amplitude of a fluctuation $|\delta m|/\langle m \rangle = 0.3$ around the mean value $\langle m \rangle$. 

For $|\delta m|/\langle m \rangle \ll 1$, this is the model of a solid mixture of isotopes. The Debye frequency, $\omega_D \approx 2.9\sqrt{k/\langle m \rangle}$ is determined by $\langle m \rangle$ and the interatomic force constant $k$, and it sets us a unit to express the values of eigenfrequencies. Below, we treat such a model in the harmonic approximation. The dynamics of a lattice is described by the linearized equations of motion for atomic displacements $u_j$ with respect to the equilibrium positions $j$ in the lattice. In the nearest-neighbor approximation, $m_j \ddot{u}_j^\alpha = -\sum_i K_{ij}^{\alpha\beta} u_i^\beta$, where $K_{ij}^{\alpha\beta} = k(l_{ij}^{\alpha}l_{ij}^{\beta} - 4\delta_{ij}\delta^\alpha\delta^\beta)$, $l_{ij}^{\alpha} = (j-i)^{\alpha}/|j-i|$, and $(j-i)$ is taken from the first coordination sphere. We find the set of eigenfrequencies, $\{\omega_n\}$, by solving numerically the eigenvalue problem

$$det(D - \omega^2 I) = 0, \quad D = M^{-1/2}KM^{-1/2},$$

(1)

where the randomness is brought in by a random diagonal matrix $M_{ij}^{\alpha\beta} = m_i\delta^\alpha\delta^\beta_{ij}$. The dynamical matrix $D$ is diagonalized by a standard NAG library black box routine for each given distribution of masses over the lattice.

Repeated periodically, the same block of atoms represents the model of a solid with a complex unit cell. The spectrum of optical lattice vibrations of such an object may be derived independently for each value of wavevector $Q$ within the reduced Brillouin zone, whereas the box size plays now the role of a complex lattice period. The spectrum of optical modes can be found by solving Eq. (1) with a modified dynamical matrix which incorporates the boundary condition on the edges of a unit cell imposed by the finite wave-number induced phase shift in the lattice displacements:

$$K_{ij}^{\alpha\beta}(Q) = \sum_h k(l_h^{\alpha}l_{h+i,j}^{\beta} e^{iQh} - 4\delta_{h+i,j}\delta^\alpha\delta^\beta),$$

where $h = Lh_1 + Mh_2 + Nh_3$ belongs to the Bravais lattice of a complex crystal and $i,j$'s are the atomic positions within the unit cell. Note that for $Q \neq 0$, the matrix elements of $D(Q)$ related to the sites on the edges of the unit cell acquire complex phase factors, which make the whole dynamical matrix complex,

$$D(Q) = D_s(Q) + iD_A(Q).$$
where $D_S(Q)$, $D_A(Q)$ are real symmetric and antisymmetric matrices, respectively. In the particular cases of $Q = 0$, or $Q$ taken in the corners of the Brillouin zone of a complex crystal, such as $Q = (0, \pi/|h_2|, \pi/|h_3|)$, $D_A(Q) = 0$ and $D(Q) = D^S(Q)$ is real symmetric, as in the case of acoustic resonances in an isolated block.

The numerically calculated spectrum of modes $\{\omega_n\}$ enables us to derive the distribution function $P(s)$ of the nearest-level-spacing, $s = (\omega_{n+1} - \omega_n)/\Delta$. It is natural to measure spacings in units of the mean level spacing $\Delta = 1/\nu(\omega)$, where $\nu(\omega)$ is the calculated disorder-average density of states. The function $P(s)$ is built upon a two-step averaging procedure. The first one is to use an ensemble of 50 random realizations of the distribution of masses in the crystal. A further averaging can be applied after considering ergodicity in the chaotic scattering regime: we average $P(s)$ over a broad frequency range, namely, $\omega \in [0.35, 1]$, for each of the calculated spectra by using an observation that they become self-similar after having been rescaled by $\Delta$.

The nearest-level-spacing distribution function for a disordered solid resonator is indistinguishable from that for the optical phonon spectrum at $Q = 0$, and it is shown in Fig. 1(a). It coincides with the random matrix theory prediction for real symmetric matrices given by the Wigner-Dyson distribution function for the GOE (plotted with dashed line).
In contrast, optical lattice vibrations with wavevector \( \mathbf{Q} \neq 0 \) show the nearest-level-spacing statistics which is best fitted by the Wigner-Dyson distribution function for random Hermitian matrices (GUE). A typical numerically found \( P(s) \)-histogram is plotted in Fig. 1(b), in comparison with the GUE analytical result \( \mathbb{E} \) quoted in the inset. A similar observation has been recently made about chaotic electronic band structures for a finite Bloch momentum \( \mathbb{F} \). As a test, the inset in Fig. 1(c) shows the \( P(s) \)-histogram for the corner of the Brillouin zone, which should be of a GOE-type, since \( D([0, \pi/|\mathbf{h}_2|, \pi/|\mathbf{h}_3|]) \) is real.

The evolution of the correlation function \( P(s) \) as a function of the wave number is illustrated by one example in Fig. 1(c). It is apparent from this plot that the crossover between two distinct limits - from GOE to GUE - takes place at relatively small values of
$|\mathbf{Q}|$ (which is the parameter responsible for the imaginary part of a dynamical matrix). A high sensitivity of correlations in the spectrum of optical phonons in a complex crystal to the rise of an imaginary part of $D$ is in agreement with what is known about the crossover between GOE and GUE symmetry classes in chaotic electronic billiards [6], and it seems that it cannot be reduced to a trivial mixing of two typical (GOE and GUE) distribution functions [7–9].

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