

Discrete breathers properties obtained from *ab initio* calculations in graphene and graphane

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The density functional method was used for the simulation of discrete breathers in graphane (fully hydrogenated graphene) and strained graphene. It is demonstrated that breathers can exist with frequencies lying in the gap of the phonon spectrum of both systems. The gap in graphane is a consequence of high mass difference between carbon and hydrogen atoms, while in graphene the gap is induced by uniaxial tension of carbon layer in the “zigzag” direction (axes X). Breather core atoms in graphane are moving along Z direction which is perpendicular to the carbon sheet. In graphene discrete breathers are polarized in the “armchair” direction (axis Y). In both systems breathers are highly localized dynamical objects. The frequency on amplitude dependence found for breathers possess soft nonlinearity type. The results are of fundamental importance, as far as for discrete breathers in crystals molecular dynamics calculations based on empirical potentials should be revised by means of more reliable methods.

Keywords: discrete breathers, *ab initio* calculations, density functional theory, quasibreathers.

1. Introduction

Localized dynamical objects in nonlinear discrete systems that have translational symmetry were first studied in the work of Ovchinnikov [1]. Dolgov examined the time-periodic symmetric and antisymmetric localized solutions of nonlinear equations for the chain of Fermi–Pasta–Ulam of β type by means of Fourier series expansion [2]. The article of Sievers and Takeno [3] drew the attention of the scientific community to the study of objects, which later became known as discrete breathers (DB). By definition, they are oscillations in a homogeneous (without impurities and defects) Hamiltonian lattice, localized in space and periodic in time. Discrete breathers can be directly observed in mesoscopic systems, which resulted in their discovery in a number of such systems of different physical nature [4]. In particular, they were found in the chains of superconducting Josephson junctions [5], arrays of optical waveguides [6] and mechanical microcantilevers [7], in granular crystals [8], etc. On the other hand, experimental studies of discrete breathers in real crystals [9–14] face serious technical difficulties [15], whereby the methods of computer simulation become of special significance. Using these methods, it was possible to predict the possibility of the existence of discrete breathers in alkali halide crystals [16–18], metals Ni and Nb [19] and V, Fe, and W [20], semiconductors Si and Ge [21], an ordered Pt₃Al alloy [22] and strained graphene [23–25].

In the vast majority of works, the mathematical simulation of discrete breathers is carried out using the methods of molecular dynamics, considering a crystal as a system of mass points; the interaction between the points is described by some phenomenological potentials (we will refer to it as MT models). The selection of appropriate interatomic

interaction potentials is of crucial importance in this approach and especially for the study of discrete breathers. In the simulation of breathers in crystals of different types, various kinds of potentials were used. The complexity of them ranges from the simple pair potentials such as the Lennard–Jones, Morse, and Born–Mayer to the highly sophisticated multi particle potentials like Brenner, Tersoff, AIREBO, and so on. The choice of the phenomenological potential in the study of the dynamics of specific crystal structures is often a difficult task. An example of a comparative analysis of the correctness of various empirical potentials is the work [26], which addresses the discrete breathers in covalent crystals of silicon and germanium.

Breather oscillations induce polarization of the outer electron shells of atoms, which is very difficult to fully capture in the frame of the model considering interaction between mass points. There exist several works where polarization of electron shells induced by breather oscillations is partly taken into account. As an example, we refer to the works [27, 28] where a simplified model was used to discuss the effect of polarization induced by DBs in the perovskite structure.

The above discussion suggests the importance of *ab initio* simulations of DBs in crystals. Such simulations in the present work are held by means of electron density functional method, which is implemented the ABINIT package [29–31]. In fact calculations are made in the framework of the following approximations. The pseudopotentials (in the Troullier–Martins form) approach allows to distinguish valent and core electrons, the latter are considered as a part of the ion. The Born–Oppenheimer approximation takes into account the significant differences in the masses of the ions and electrons. The motion of heavy ions is described by the classical equations, while the motion of light valent electrons

is controlled by the quantum mechanics equations. The forces acting on the ions depend on the electronic subsystem state, which quickly adapts to the ions current positions. Kohn-Sham equations [32, 33] are solved by ABINIT for each nuclei configuration.

2. Discrete breathers in graphane

The armchair confirmation of graphane is considered with H atoms attached at the opposite sides of the graphene sheet in a staggered manner, as shown in Fig. 1(b). Periodic boundary conditions are applied to exclude the effect of free edges. The calculated phonon density of states (DOS) for graphane is shown in Fig. 1(a). The center of the narrow optical band is at a frequency of about 83 THz, while the width of this band is about 2 THz. The gap in the phonon spectrum extends from $\omega_L = 41.7$ THz to $\omega_H = 81.6$ THz having the width of 39.9 THz.

The paper [34] was the first one in which the simulation of discrete breathers in crystals have been made using *ab initio* calculations based on the density functional theory. Existence of a wide gap in the phonon spectrum of graphane opens the possibility to excite a gap DB. This was achieved by applying a displacement normal to the graphane plane (along the z axis) to the H atom labeled as H_0 [see Fig. 1(b)]. All other atoms in the computational cell had zero initial displacements and zero initial velocities. Varying the initial displacement of the H_0 atom, DBs with different vibration amplitudes were excited. The H_0 atom vibrates with large amplitude while all other atoms have much smaller vibration amplitudes.

The main result for DBs in graphane is the dependence of oscillations frequency ν on breather amplitude A presented in Fig. 2. It can be seen that the $\nu(A)$ curve bifurcates from the upper edge of the phonon gap and then decreases almost linearly with increase in A , entering the lower phonon band. The decrease in frequency with increase in amplitude reveals a soft-type anharmonicity of the DBs in graphane in the entire range of DB amplitudes.

3. Discrete breathers in graphane

A number of works [23, 35, 36] were devoted to the study of the possible existence of discrete breathers in monolayer graphene at zero temperature ($T = 0$ K) in computer simulations. In all these studies, various MT model were used, and the dynamics was described by the conventional Newton equations. Breather-like dynamic objects were studied in [35] for unstrained graphene in the MT model with the Brenner potential [37], which were excited due to the displacement of the two nearest carbon atoms (located on the Y axis) at equal distances towards each other. At sufficiently large amplitudes of such displacement, a strong localization of energy in a small neighborhood of the initial excitation (breather core) took place; the amplitude of the oscillations of atoms decreased rapidly with distance from the core. The localized dynamic object thus obtained, lacking in strict periodicity in time, was not an exact discrete breathers. The time of its life was approximately 26 “periods”, as the fundamental frequency was located above the upper limit of the phonon spectrum.

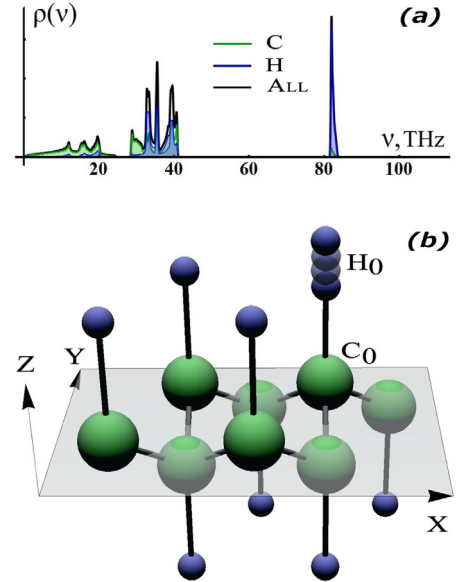


Fig. 1. (Color online) (a) Phonon density of states (DOS) of graphane. Green and blue curves correspond to the states associated respectively with carbon and hydrogen atoms. Black curve displays the entire DOS. (b) Structure of graphane. To excite a DB, the H_0 atom, was displaced along z axes and released with zero initial velocity. All other atoms had zero initial displacements and velocities.

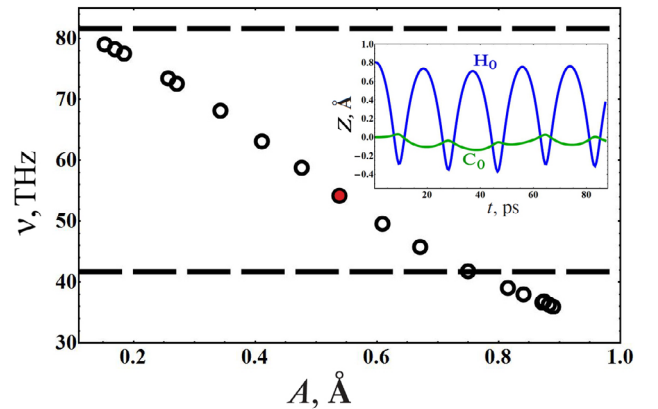


Fig. 2. (Color online) Graphane DB frequency as the function of amplitude obtained from *ab initio* simulation (black circles). Horizontal dashed lines show the edges of gap in the phonon density of states. The inside plot shows the time evolution of C_0 and H_0 (see Fig. 1) atoms displacements from correspondent equilibrium positions for the breather related to the red filled dot of $\nu(A)$ curve.

It is known that to obtain a perfect discrete breather, a very precise selection of the initial displacement of all the atoms of its core along with all its peripheral atoms is required (see, for example, [4, 38, 39]). In the case of an insufficiently good selection of such an initial profile of the localized excitation, one can only expect the construction of a quasi-breather. This concept and a number of numerical characteristics of the “rate of quasi-breatherness” were introduced in [39]. Strict periodicity of a discrete breather assumes a full synchronization of vibrations of all the atoms in the lattice [40]. This synchronization for discrete breathers was implemented in strained graphene [36]. It was shown that despite the possibility to construct a perfect DB in graphane under various types and degrees of strain, all

obtained dynamical objects appear to be unstable.

A fundamentally different type of discrete breathers in strained graphene was studied in [23]. Under the uniaxial deformation along both the “armchair” direction and the “zigzag” direction, a gap opens in the phonon spectrum of graphene. In such a situation, the possibility of the existence of gap discrete breathers arises. The frequency of these dynamic objects is within the gap of the phonon spectrum, and a soft type of nonlinearity takes place; meaning that the frequency of a discrete breather decreases with increasing the amplitude.

In the present paper, we used *ab initio* calculations based on the density functional theory for the study of gap discrete breathers in a graphene monolayer stretched along the “zigzag” direction (the X axis, see Fig. 3). To excite the discrete breather in strained graphene, two adjacent carbon atoms (the core atoms of the discrete breather) are shifted from the equilibrium positions along the Y axis in the opposite directions by the distances equal in absolute value for both atoms, at the initial time. The remaining atoms are in equilibrium positions at this time, and the initial velocity of all the atoms of the lattice are zero.

The dependence of the frequency on amplitude $\nu(A)$ for the gap discrete breathers in strained graphene for the case of uniaxial 20% tension along the X axis (in the “zigzag” direction) is shown in Fig. 4. This figure shows that function $\nu(A)$ decreases monotonically with increasing amplitude, indicating a soft type of nonlinearity of the obtained discrete breathers. The lifetime of these highly localized dynamic objects (they are not exact breathers although) significantly depends on whether the relevant section of the curve of $\nu(A)$ is within the gap of the phonon spectrum, or it goes to the optical band. In the former case, the lifetime reaches hundreds of oscillation periods, and, in the latter case, it does not exceed two or three dozen periods, due to the constant loss of energy for the emission of phonons.

4. Conclusions

In this paper, gap discrete breathers are discussed in graphane and monolayer graphene sheet uniaxially strained along the X axis (the “zigzag” direction). Computer modelling is done using density functional method. DBs in graphane demonstrate the soft-type anharmonicity with frequency monotonously decreasing with increasing amplitude. Atomic vibrations in the constructed discrete breathers in graphane are polarized along the Y axis (the “armchair” direction). These breathers also show a soft type of nonlinearity, and the dependence of the frequency on amplitude $\nu(A)$ is located in the gap of the phonon spectrum.

The investigated discrete breathers are highly localized dynamic objects: only two nearest atoms forming the core of the breather have vibrations of significant amplitude, and the surrounding atoms vibrate at much lower amplitudes.

For the graphene it is essential that the found gap breathers are polarized perpendicular to the axis of deformation of the graphene sheet. However, it should be noted that the gap in its phonon spectrum appears not only upon deformation along the “zigzag” direction (the X axis) but also along the “armchair” direction (the Y axis). We have not found any

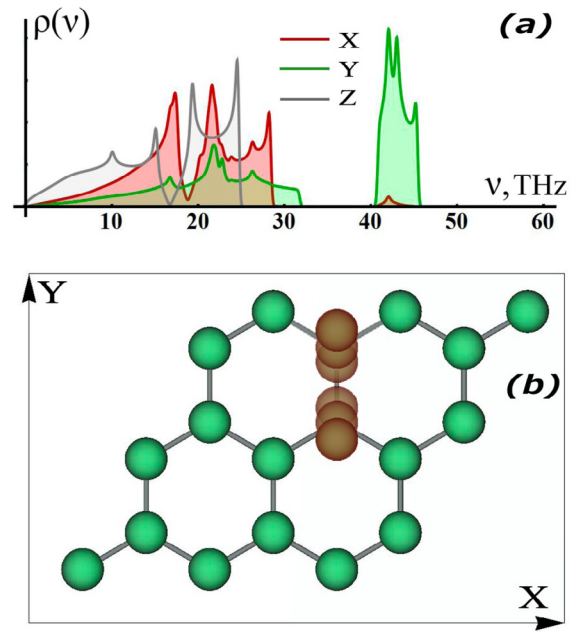


Fig. 3. (Color online) (a) Phonon density of states (DOS) of graphene under the uniaxial 20% stretching along the X . Red, green and gray curves correspond to the normal modes along X , Y and Z axes respectively. (b) Structure of graphene. To excite a DB, two carbon atoms (colored in red), was displaced along Y axes and released with zero initial velocity. All other atoms had zero initial displacements and velocities.

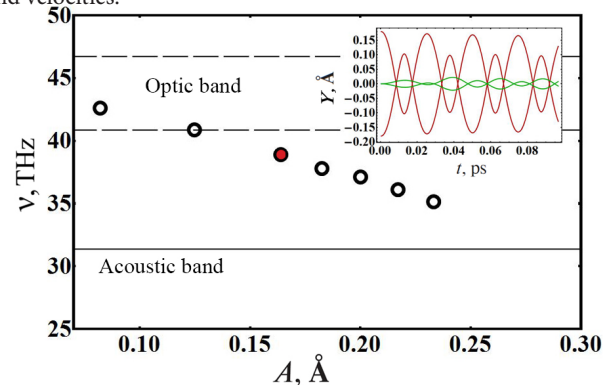


Fig. 4. (Color online) Graphene DB frequency as the function of amplitude obtained from *ab initio* simulation (black circles). Horizontal dashed lines show the optic band while horizontal solid line displays the border of acoustic band of the phonon density of states. The inside plot shows the displacement on time dependency for two DB core carbon atoms (in red) and for two neighbor atoms (in green) for the breather related to the red filled dot of $\nu(A)$ curve.

discrete breathers in this gap. Moreover, in the framework of *ab initio* calculations, we found no breathers with a hard type of nonlinearity (the breathers of this type have been found in [36]).

It should be noted that the *ab initio* calculations are still extremely rare in the studies of the properties of discrete breathers in real crystals and should be expanded, since the results obtained by the methods of molecular dynamics, are dependent, and sometimes significantly, from the use of empirical interatomic potentials.

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