Properties of discrete breathers in graphane from \textit{ab initio} simulations

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A density functional theory (DFT) study of the discrete breathers (DBs) in graphane (fully hydrogenated graphene) was performed. To the best of our knowledge, this is the first demonstration of the existence of DBs in a crystalline body from the first-principle simulations. It is found that the DB is a robust, highly localized vibrational mode with one hydrogen atom oscillating with a large amplitude along the direction normal to the graphane plane with all neighboring atoms having much smaller vibration amplitudes. DB frequency decreases with increase in its amplitude, and it can take any value within the phonon gap and can even enter the low-frequency phonon band. The concept of DB is then used to propose an explanation to the recent experimental results on the nontrivial kinetics of graphane dehydrogenation at elevated temperatures.

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Discrete breathers (DBs), also termed as intrinsic localized modes, are spatially localized, large-amplitude vibrational modes in defect-free nonlinear lattices. They have been identified as exact solutions to a number of model nonlinear systems possessing translational symmetry\textsuperscript{[1]}. DBs were successfully observed experimentally in various physical systems such as two-dimensional array of optical waveguides\textsuperscript{[2]}; Bose-Einstein condensate\textsuperscript{[3]}; one-dimensional micromechanical array of coupled cantilevers\textsuperscript{[4]}; two-dimensional nonlinear electrical lattices\textsuperscript{[5]}; underdamped Josephson-junction array\textsuperscript{[6]}; quasione-dimensional biaxial antiferromagnet\textsuperscript{[7]} and others.

Diversity of physical systems supporting DBs suggests that they are very common in nonlinear lattices. Crystals are natural nonlinear lattices and many studies, both experimental\textsuperscript{[8,11]} and numerical\textsuperscript{[12,13,14]};\textsuperscript{[16,17,18]}, have been done to prove the existence of DBs and to use them for explanation of various physical effects in crystals\textsuperscript{[10,20–24]}. Let us mention the detection of DBs from the resonant Raman scattering measurements in a complex compound termed as PtCl\textsuperscript{8}; from inelastic x-ray and neutron scattering data in α-uranium\textsuperscript{10}; from inelastic neutron scattering spectra in NaI\textsuperscript{11}. It should be noted that experimental observation of DBs in crystals is a challenge because their contribution to the vibrational density of states is masked by the contribution from thermal lattice vibrations\textsuperscript{[25]}. In these circumstances the importance of numerical studies cannot be overestimated. Molecular dynamics based on empirical interatomic potentials was used to identify DBs (or, more precisely, quasi-breathers\textsuperscript{[26]}) in NaI\textsuperscript{12}, in Si and Ge\textsuperscript{13}, in Ni and Nb\textsuperscript{14}, in C\textsubscript{60} fullerite nanocrystals\textsuperscript{15}; in carbon nanotubes\textsuperscript{16}, graphene\textsuperscript{17,18} and graphane\textsuperscript{19}.

Molecular dynamics studies rely on the quality of interatomic potentials, which is always a question. For instance, the authors of the work\textsuperscript{13} report that they have tried different interatomic potentials to model DBs in Si and have succeeded only with the Tersoff potential. The reason is that the interatomic potentials are often fitted to the elastic moduli and phonon spectra of crystals (calculated from linearized equations of motion) as well as to some experimentally measurable energies, such as the sublimation energy, vacancy energy, etc. (for which not the exact profile of the potential functions but their integral characteristics are important since the change in potential energy is path independent). On the other hand, DB, being an essentially nonlinear vibrational mode, is sensitive to the exact shape of the potentials. In this study it will be demonstrated that the molecular dynamics simulation of DBs in graphane\textsuperscript{19}, performed using the LAMMPS package\textsuperscript{[28]} with the AIREBO potential\textsuperscript{[29]}, gives an adequate estimation of DB frequency only for small amplitudes and shows a dramatic error for large amplitudes. At the same time, the AIREBO potential has been successfully used in a countless number of studies of various properties of hydrocarbon systems, meaning that indeed DBs provide a very severe test of the interatomic potentials.

Breather oscillations induce polarization of the outer electron shells of atoms, which is very difficult to fully capture in 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\textsuperscript{[20]} 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 \textit{ab initio} simulations of DBs in crystals. So far, to the best of our knowledge, no such studies have been undertaken, possibly, because the application of DFT theory to dynamical problems is computationally costly. In this sense, graphane\textsuperscript{30,31} is a very good choice for...
the study because the highly localized DBs in a two-dimensional crystal can be analyzed using a computational cell with a small number of atoms. Furthermore, graphene is a new material promising for many applications \[32\]. Particularly, graphene holds a potential for hydrogen storage due to its lightweight structure and high performance \[31 \, 34\]. It was shown that graphene can easily absorb hydrogen at low temperatures and desorb at high temperatures \[31 \, 32 \, 36\].

Dehydrogenation kinetics during annealing of graphene turns out to be not as simple as expected. It was found that there are two types of dehydrogenation mechanisms with different dehydrogenation barriers \[36\]. It is challenging to find a theoretical explanation of this effect.

In the present work, DB in graphane is studied with the aid of ab initio calculations. We use the ABINIT software package \[37\] implementing the methods of the density functional theory \[38\] (the corresponding algorithms can be found in \[39\]). The above package allows one to study dynamics of molecules and crystals in the framework of the Born-Oppenheimer approximation, which takes into account the significant differences in the masses of the atom nuclei and electrons \[40\]. The motion of heavy nuclei (ions) is described by the classical equations, while that of light electrons is controlled by the quantum mechanics equations. The forces acting on the nuclei depend on the electronic subsystem state, which quickly adapts to the nuclei current positions. Kohn-Sham equations \[38\] are solved by ABINIT for each nuclei configuration. Our calculations were performed based on the local density approximation and Troullier-Martins pseudopotentials. Plane waves are used as a basis set (with kinetic energy cutoff 40H) for the decomposition of electron eigenstates.

The chair confirmation of graphane \[30\] is considered with H atoms attached at the opposite sides of the graphene sheet, as shown in Fig. 1(a). Open (filled) dots show carbon atoms with hydrogen atoms attached above (below) the sheet. The computational cell, shown by the dashed line, includes 32 carbon and 32 hydrogen atoms. Periodic boundary conditions are applied to exclude the effect of free edges.

Using the ABINIT package we have obtained the equilibrium structure of graphane with the C-C bond length equal to 1.520 Å, and the C-H bond length equal to 1.117 Å. Note that these parameters coincide with those reported in \[33\].

The calculated phonon density of states (DOS) for graphane is shown in Fig. 1(b). 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 \(\omega_\text{L} = 41.7 \, \text{THz} \) to \(\omega_\text{H} = 81.6 \, \text{THz} \) having the width of 39.9 THz.

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 z axis) to the H atom in the position \(0\), labeled as \(H_0\) [see Fig. 1(a)]. All other atoms in the computational cell had zero initial displacements and velocities. Varying the initial displacement of \(H_0\), DBs with different vibration amplitudes were excited.

In Fig. 2 the \(\Delta z\) displacements of the central atoms of DB, \(H_0\) and \(C_0\) (left panels), as well as \(\Delta z\) displacements of their nearest neighbors, \(H_1\) and \(C_1\) (right panels), are shown as the functions of time. Black (red) lines show the displacements of C (H) atoms. It can be seen that the \(H_0\) atom shows large-amplitude, quasi-periodic oscillations. The \(C_0\) atom vibrates with one order of magnitude smaller amplitude because carbon is 12 times heavier than hydrogen. Excited DBs are highly localized since the vibration amplitudes of the atoms \(H_1\) and \(C_1\) (and other atoms of the computational cell) are more than one order of magnitude smaller than that of \(H_0\) atom.

In order to quantify the DB amplitude and frequency the \(\Delta z(t)\) curve for \(H_0\) atom is analyzed. The coordinates of the successive minimum and maximum points on the curve, \(\Delta z_{\text{min}}(n), t_{\text{min}}(n), \Delta z_{\text{max}}(n), t_{\text{max}}(n), n\) numbered by the index \(n\) are determined. The amplitude and the oscillation period for the \(n\)-th half oscillation are defined as

\[
A^{(n)} = (\Delta z_{\text{max}}^{(n)} - \Delta z_{\text{min}}^{(n)})/2, \\
\omega_{\text{DB}}^{(n)} = (2t_{\text{max}}^{(n)} - t_{\text{min}}^{(n)})^{-1},
\]

respectively. The quantities \(A^{(n)}\) and \(\omega_{\text{DB}}^{(n)}\) averaged over a few tens of periods are taken as \(A\) and \(\omega_{\text{DB}}\).
In Fig. 2 the DB frequency as the function of amplitude, \( \omega_{DB}(A) \), is given. Edges of the phonon DOS gap are shown by the horizontal dashed lines. Dots labeled as a, b, and c (colored in red) correspond to the DBs presented in Fig. 2 (a,a''), (b,b''), and (c,c''), respectively. It can be seen that the \( \omega_{DB}(A) \) 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. Note that in the molecular dynamics study [19] the \( \omega_{DB}(A) \) curve was predicted to decrease for small \( A \), to increase for moderate \( A \) and again to decrease at large \( A \). Such a non-monotous \( \omega_{DB}(A) \) curve with DB frequency above the phonon spectrum for large DB amplitudes is in a striking difference with our \textit{ab initio} result.

According to the conventional definition, stationary DB is a time-periodic dynamical object \textsuperscript{[1]}. Excitation of a DB in mathematical modeling requires the use of very refined initial conditions \textsuperscript{[11][13]}. In the present study a simple method was used for DB excitation and this is why the DBs presented in Fig. 2 are not exactly time-periodic. The inaccuracy in the initial conditions results in radiation of a part of energy given to the system at \( t = 0 \) in the form of small-amplitude lattice vibrations that disturb the dynamics of DB. Spatially localized modes in nonlinear lattices that do not show exact periodicity in time can be interpreted as quasi-breathers [26].

It is well-known that a stable DB should not have frequency within the phonon spectrum of the crystal, otherwise it will excite the extended normal modes and gradually loose its energy. Therefore, the existence of the long-lived DBs with frequencies below \( \omega_L \) presented in Fig. 2 (c,c''), may look puzzling. The explanation is related to the fact that graphane has rigidity with respect to in-plane deformation much higher than bending rigidity. H\textsubscript{0} atom vibrating with a large amplitude exerts a force normal to the graphane sheet producing primarily bending deformation of the sheet. The bending phonon modes, due to small bending rigidity, have frequencies much lower than \( \omega_L \) and thus they are barely excited by the DB with frequency just below \( \omega_L \). Similar arguments were used to explain the existence of long-lived DBs and DB clusters in strained graphene, having frequencies within the phonon band [17][18].

We now turn to the discussion of recent experiments on thermally activated dehydrogenation of graphene [36]. Reportedly, there are two activation energies of dehydrogenation with the transition temperature at about 200°C. The smaller dehydrogenation activation energy at temperatures below 200°C can be understood by the metastable attachment of the energetic ions to the graphane sheet during plasma hydrogenation [35][36]. However, the larger dehydrogenation activation energy at temperatures above 200°C has not yet been well explained. The nonlinear nature of the DBs implies that they do not appear at relatively small temperatures and instead are excited at higher temperatures. The fact that DBs can be externally excited at temperatures near 0K indicates that they can also be spontaneously excited at a finite-temperature thermal equilibrium [27][44]. DBs spontaneously excited at finite temperatures may activate the dehydrogenation of hydrogenated graphene.

In conclusion, the existence of DBs in a crystal was demonstrated for the first time from \textit{ab initio} calcula-
tions. Graphane was chosen for this study because it supports highly localized gap DBs, treatable by DFT simulations, and also because it is promising for a number of applications.

DBs in graphane demonstrate the soft-type anharmonicity with frequency monotonously decreasing with increasing amplitude. On the other hand, molecular dynamics simulations based on the AIREBO potential [19] give an adequate description of the $\omega_{DB}(A)$ curve only for small $A$ and fail for large $A$.

The concept of DBs was used to explain basic physics behind the dehydrogenation kinetics of graphane at finite temperatures.

Finally, we note that DBs provide a very severe test of the interatomic potentials used in molecular dynamics simulations. The AIREBO potential is known to be applicable to many problems in the study of hydrocarbons but it fails to describe DBs in graphane. Thus, our study suggests the crucial importance of \textit{ab initio} simulations for the investigation of DBs in crystals.

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