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ENERGY EXCHANGE BETWEEN THE DISCRETE BREATHERS IN GRAPHANE

J. A. Baimova[1] and S. V. Dmitriev[1,2]

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Discrete breathers in graphane (fully hydrogenated graphene) are studied by the molecular dynamics method. It has previously been demonstrated that in graphane, there are discrete breathers in the form of single hydrogen atoms oscillating with the big amplitude in the direction perpendicular to the graphane plane with a frequency lying in the bandgap of the phonon spectrum. In this work, the possibility of the existence of long-lived clusters of discrete breathers of different configurations is shown, their properties are studied, and the possibility of energy exchange between the discrete breathers in the cluster is demonstrated. These results are important for the discussion of physical processes occurring during dehydrogenation of graphane at high temperatures, which, in turn, is of great importance for the development of the hydrogen storage and transport devices based on sp^2-carbon materials.

Keywords: graphane, a discrete breather, cluster, energy exchange, molecular dynamics.

INTRODUCTION

Graphene, whose physical, mechanical, electronic, and other properties are being actively investigated in the last decade, is one of the most chemically active materials. It has been shown that graphene readily reacts, e.g., with hydrogen, which results in a transition from a highly conductive material to the semiconductor. Fully hydrogenated graphene named "graphane" was first predicted theoretically [1, 2] and then, it was obtained experimentally [3]. In contrast to graphene, graphane is not a flat two-dimensional material, since the attachment of hydrogen atoms leads to the displacement of carbon atoms from the plane.

To each of the carbon atoms above and below of the graphene sheet, one hydrogen atom is attached, whereby hybridization of carbon atoms is changed from sp^2 to sp^3 [4–9], which, in turn, leads to significant changes in the material properties. Thus, full or partial hydrogenation is a promising method for the controlled variation of many properties of graphene. For example, hydrogenation can be used to control the electron transport [10] and gap width of the electron spectrum [11], to change electrochemical [12, 13] and magnetic properties [14] and thermal conductivity [6, 9]. Now, methods of hydrogenation of graphene are well known and widely used in practice [5, 10, 15, 16]. However, experimental determination of the morphology of hydrogenated graphene is a rather complicated task [10]. One of the most popular experimental methods to evaluate the degree of hydrogenation of graphene is Raman spectroscopy [3]. Theoretical studies of structure and properties of graphene were presented in [1, 9, 17, 18]. For example, the formation of clusters of hydrogen atoms and the graphene surface regions free of hydrogen atoms were investigated [4, 18].

In recent decades, considerable attention is attracted to the problem of storage and transportation of hydrogen due to the increasing requests for the creation of environmentally friendly and energy saving sources of energy.

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[1] Institute for Metals Superplasticity Problems of the Russian Academy of Sciences, Ufa, Russia, e-mail: julia.a.baimova@gmail.com; dmitriev.sergey.v@gmail.com; [2] National Research Tomsk State University, Tomsk, Russia. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 6, pp. 42–46, June, 2015. Original article submitted March 6, 2015.

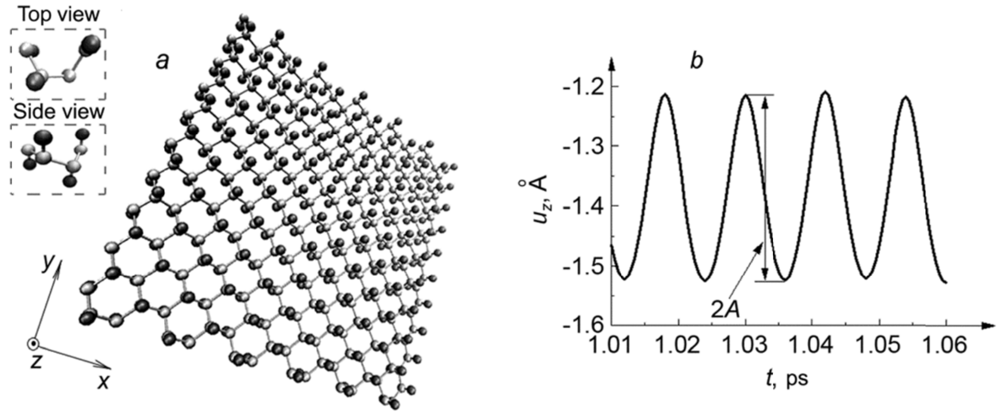

Fig. 1. Structure of graphane. Light circles show the carbon atoms and dark circles show the hydrogen atoms. The insert in the upper left corner of the figure shows the primitive cell of graphane (*a*). Time dependence of the displacement of the hydrogen atom along the *z*-axis in a single DB (*b*).

However, before applying such technologies in practice, it is necessary to solve a number of problems, main of which are the safe transportation and application of hydrogen.

Carbon materials with sp^2-hybridization including graphene are very promising for the hydrogen storage due to theirs light weight and high capacity [3, 19]. It has been shown that hydrogen can be easily absorbed by graphene at low temperatures and released at higher temperatures [3].

Therefore, the study of hydrogenated graphene is important for its use in electronics, spintronics, and hydrogen storage. Moreover, investigation of linear and nonlinear dynamics of the graphene lattice may shed light on the processes of its hydrogenation and dehydrogenation. The hydrogen atom is 12 times lighter than the carbon atom. Such a great difference in atomic masses of elements composing graphane provides the presence of the wide gap in the phonon spectrum of graphane. The presence of such a gap, in turn, is a necessary condition for the existence of the gap discrete breathers (DBs), or, in other words, the spatially localized non-linear vibrational modes [20]. DBs are the object of close attention of scientists in recent decades. They are studied both theoretically and experimentally in various materials [21–25] including graphene [26] and graphane [27, 28]. DBs can localize considerable energy and, presumably, play an important role in the dehydrogenation of graphane. Even more energy can be localized by the clusters of DBs. Therefore, the study of such objects is an interesting and urgent task.

In this paper, the possibility of existence of clusters of DBs in graphane, their behavior and, in particular, the energy exchange between the DBs in the cluster are studied by the method of molecular dynamics.

THE MODEL DESCRIPTION

The graphane structure is shown in Fig. 1*a*. The carbon atoms C shown with light circles form a planar hexagonal lattice, where the distance between the nearest atoms is 1.55 Å in equilibrium. The hydrogen atoms H shown with dark circles are regularly attached to the carbon atoms on both sides of the sheet. The length of the C-H bond is 1.1 Å. The graphane primitive translational cell contains two hydrogen atoms and two carbon atoms. In calculations, the rectangular cell containing the 2-fold more atoms, as shown in the inset in Fig. 1*a*, was used. In the plane of the graphene sheet, that is, along the *x* and *y* axes, periodic boundary conditions were imposed.

Simulation was performed using the software package LAMMPS [29] with an empirical set of interatomic potentials AIREBO [30]. This potential is well tested for modeling of various carbon structures including graphene, graphane, and carbon nanotubes [26, 31–34].

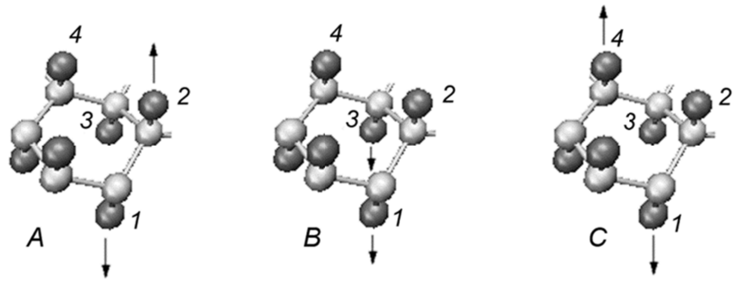

Fig. 2. Examples of clusters of two DBs in graphane. Arrows show one of the possible variants of setting the initial displacements of H atoms.

The initial temperature of the system was set 0 K. To achieve an equilibrium state, the relaxation of the system was carried out. It was shown that after relaxation, the C atoms are displaced from the plane by a distance of about 0.25 Å to the side of the attached hydrogen atom, which leads to some distortion of the graphene sheet. These changes in the positions of atoms are confirmed by the data represented in the literature.

For the excitation of a single DB in the center of the calculated cell after the structure relaxation, a hydrogen atom was selected, for which the initial displacement from the equilibrium position in the direction of the *z*-axis was set. The value of the initial displacement was varied in the range from 0.05 to 0.1 Å. All other atoms in the calculated cell had zero values of the initial displacements and velocities. Thus, a DB was excited that existed in the crystal for a long time radiating its energy very slowly.

The phonon state density of graphane is well known from the literature [27, 28]. In the spectrum, a wide gap in the frequency range from 56.92 to 87.83 THz is observed. The high-frequency optical phonon band (from 87.83 to 88.7 THz) is mainly determined by the vibrations of the hydrogen atoms. The low-frequency region of the spectrum (below 20 THz) is due to the vibrations of the carbon atoms.

The vibrational spectrum may also be divided according to the type of atoms. It has been shown that the vibrational modes of C and H atoms in the *xy* plane practically coincide, moreover, the frequencies of these vibrations are not higher than 60 THz, and the high-frequency vibrations correspond to the displacements from the plane of the sheet [28], which indirectly confirms that a hydrogen atom may easily create DB.

Figure 1*b* shows an example of the time dependence of the displacement of the H atom along the *z*-axis (perpendicular to the sheet of graphane) in a single DB. The figure shows that in graphane, the DB makes sustained oscillations of big amplitude. It has been found that the DB amplitude can be chosen in a fairly broad range [27, 28]. The figure shows an example with an average value of the oscillation amplitude.

RESULTS AND DISCUSSION

In this paper, main objects of study were the clusters of DBs, which have not previously been studied. Several types of DB clusters were examined, as shown in Fig. 2. Each of the clusters consisted of the two excited hydrogen atoms arranged within a single ring of six carbon atoms. The arrows indicate the possible direction, in which the initial displacement of the H atom in the cluster was set. In the examples shown in Fig. 2, DBs in the clusters A and C were excited in the opposite phase, while DBs in the cluster *B* were excited in the same phase.

The above example is not the only possible. For each type of the cluster, different initial displacements of the two excited hydrogen atoms were considered, that is, in some calculations, at the initial time, both the in-phase and anti-phase oscillations could be defined for the H atoms. Because of the symmetry of the system, within a hexatomic ring, all other variants of clusters consisting of a pair of H atoms will be equivalent to the one of the variants shown in Fig. 2.

In Fig. 3, the dependences of the amplitude *A* of both DBs in the cluster on the time *t* are shown with the solid and dashed lines for the clusters *A* and *B*, respectively. The figures show a representative period of time sufficient to

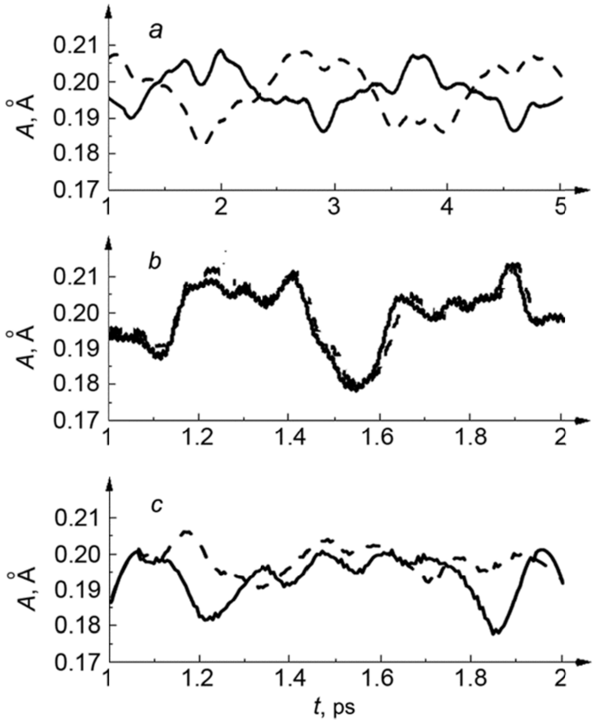

Fig. 3. Time dependences of amplitudes of the two DBs in the cluster for clusters *A* – DBs are excited in the same phase (*a*), *A* – DBs are excited in the anti-phase (*b*), and *B* – DBs are excited in the same phase (*c*).

manifest the behavior of each of the clusters. All types of clusters are quite stable, and the DBs exist in these clusters for a long period of time.

Figure 3 corresponds to the cluster *A*, where breathers were started in the same phase. In this case, a significant energy exchange between the DBs is observed, which is expressed in the fact that the amplitude of one of the DBs becomes (quasi) periodically greater or smaller, than the amplitude of another DB. Of interest is also the case shown in Fig. 3*b*, where in the same cluster, the DBs were started in the anti-phase. As a result, two identical breathers were obtained, whose vibrational amplitudes are completely similar. In so doing, if a small difference in the initial amplitudes of the two DBs in the cluster was set, stabilization of DBs in the cluster occurred after less than 1 ps and their amplitudes became equal to each other. As an example, Fig. 3*b* shows the case, where the two DBs have equal initial amplitudes.

Figure 3*c* shows the cluster *B* in case, where the breathers are started in the same phase. As can be seen from the figure, the energy exchange between the DBs in this cluster is less regular than that in the cluster *A*. Similar pattern is observed for the cluster *C*.

A detailed study of clusters with different initial conditions shows that the clusters *B* and *C* behave in the same way, if the DBs vibrate in the anti-phase. The initial value of the amplitude does not have any significant effect on the general form of the time dependence of amplitude. This demonstrates that the DBs in the clusters *B* and *C* less interact with each other than in the cluster *A* for all initial conditions.

It is interesting to note that the energy exchange between the DBs in the cluster *A* at an in-phase excitation of vibrations is observed only, if there is a difference in the initial amplitudes of DBs. In case shown in Fig. 3*a* this difference in amplitudes is 0.01 Å. As shown by simulation, an increase in the difference in the amplitudes worsens the energy exchange, i.e., the best condition for the energy exchange between the DBs is fulfilled at small difference in their initial amplitudes.

CONCLUSIONS

Thus, clusters composed of two discrete breathers in graphane were studied by the method of molecular dynamics. Each of the DBs in the cluster represents a hydrogen atom oscillating in the direction perpendicular to the plane of graphane. All types of clusters discussed in this paper have lifetimes of thousands of oscillation periods in the whole range of the studied initial amplitudes. Moreover, the DBs in the cluster may vibrate both in anti-phase and in phase. The change in the direction of initial oscillations usually does not result in the rapid decay of DBs. In clusters, energy exchange is observed between the DBs. The most favorable conditions for the sustainable energy exchange are realized, if two adjacent hydrogen atoms located on different sides of the graphene sheet (Fig. 3 *a*, the cluster *A*) are excited in phase and the initial difference of the DB amplitudes is small (about 0.01 Å).

We note that the energy of DB in graphane can reach several electron volts [27], that is, it is close to the energy of the hydrogen atom desorption. A couple of DBs is able to localize even more energy and greatly facilitate the desorption of hydrogen atoms from the graphane sheet due to the transfer of a part of energy from one DB to another. Thus, the DBs and their clusters may play an important role in dehydrogenation of graphane at higher temperatures. Investigation of the dehydrogenation of graphane is important, because this process is performed in devices of transportation and storage of hydrogen fuel based on sp^2-carbon materials. However, the dehydrogenation process requires more detailed studies. It is important to study the clusters consisting of more DBs, as well as the possibility of excitation of DBs in graphane by applying an external high-frequency field.

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