

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/258261393>

Discrete breathers in hydrogenated graphene

Article in *Journal of Physics D Applied Physics* · July 2013

DOI: 10.1088/0022-3727/46/30/305302

CITATIONS

56

READS

241

6 authors, including:



Bo Liu

Shaanxi Normal University

67 PUBLICATIONS 1,382 CITATIONS

SEE PROFILE



Yu. A. Baimova

Institute for Metals Superplasticity Problems of Russian Academy of Sciences

96 PUBLICATIONS 1,426 CITATIONS

SEE PROFILE



Sergey V. Dmitriev

Institute for Metals Superplasticity Problems of Russian Academy of Sciences

406 PUBLICATIONS 4,891 CITATIONS

SEE PROFILE



Xu Wang

East China University of Science and Technology

312 PUBLICATIONS 2,629 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Extreme values of elastic strain and energy in the collision of N kinks in the ϕ^6 model [View project](#)



Graphene and graphene-based structures as a hydrogen storage media [View project](#)

Discrete breathers in hydrogenated graphene

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2013 J. Phys. D: Appl. Phys. 46 305302

(<http://iopscience.iop.org/0022-3727/46/30/305302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 155.69.4.4

The article was downloaded on 05/07/2013 at 15:47

Please note that [terms and conditions apply](#).

Discrete breathers in hydrogenated graphene

Bo Liu¹, Julia A Baimova¹, Sergey V Dmitriev², Xu Wang³, Hongwei Zhu⁴ and Kun Zhou¹

¹ School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

² Institute for Metals Superplasticity Problems, Russian Academy of Sciences, Ufa 450001, Russia

³ School of Mechanical and Power Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China

⁴ School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

E-mail: kzhou@ntu.edu.sg (K Zhou)

Received 20 April 2013, in final form 4 June 2013

Published 5 July 2013

Online at stacks.iop.org/JPhysD/46/305302

Abstract

Discrete breathers (DBs) in graphane (fully hydrogenated graphene) are investigated using molecular dynamics simulations. It is found that the DB can be excited by applying an out-of-plane displacement on a single hydrogen atom of graphane. The vibration frequency of the DB lies either within the gap of the phonon spectrum of graphane or beyond its upper spectrum bound. Both soft and hard types of anharmonicity of the DB, which have not been found in the same system, are observed in graphane. The study shows that the DB is robust and its lifetime is affected by various factors including its anharmonicity type, its amplitude and frequency, and the force on the hydrogen atom that forms it, whose competition results in a complex mechanism for the lifetime determination. The investigation of the maximum kinetic energy of DBs reveals that they may function to activate or accelerate dehydrogenation of hydrogenated graphene at high temperatures.

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene, the two-dimensional allotrope of carbon, has been the subject of many recent investigations ever since its mechanical extraction from graphite [1], due to its novel mechanical and physical properties [2–9]. Although graphite is known as one of the most chemically inert materials, it was found that graphene can react with atomic hydrogen, which transforms this highly conductive zero-overlap semimetal into a semiconductor. The fully hydrogenated graphene, named graphane, was first theoretically predicted [10, 11] and then experimentally confirmed by Elias *et al* [12]. Unlike graphene, graphane is no longer planar but crumpled because hydrogen atoms are bonded to all the carbon atoms on both sides of the plane alternatively and the hybridization of carbon atoms is transformed from sp^2 to sp^3 [13–18].

Hydrogenation is a promising way to modify many physical properties of graphene in a controllable fashion. By

means of hydrogenation of graphene, it is possible to alter its electronic transport [19], tune its band gap [20], change its electrochemical properties [21, 22] and thermal conductivity [15, 18], and induce its room temperature ferromagnetism [23].

Hydrogenation of graphene can be achieved by various experimental techniques such as exposure to cold hydrogen plasmas [12, 19, 24–26], using a conditioning catalyst upstream [27], synchronized reduction and hydrogenation of graphene oxide in an aqueous suspension under gamma ray irradiation [21], applying an electric field as a catalyst [28] and electron irradiation of an adsorbate on graphene [14].

It is challenging to experimentally determine the hydrogen coverage and morphology of hydrogenated graphene [19]. Raman spectroscopy is one of the most popular methods for estimating hydrogen coverage by measuring the relative intensities of the D and D' bands, which are symmetry-forbidden in pristine graphene and appear in the Raman spectrum of defected graphene due to the defect-induced

symmetry breaking, in comparison with the G band that exists in pristine and hydrogenated graphene [12].

Theoretical studies on the structure and properties of graphene functionalized by means of hydrogenation have been reported [10, 18, 29–32]. Particularly, the tendency for clustering of hydrogenated and nonhydrogenated sites was observed [13, 30].

Recently, hydrogen storage technologies have attracted considerable attention due to increasing demands for cleaner and safer energy sources. However, several problems must be overcome before the practical implementation of such technologies becomes feasible. Portability and safety are critical issues regarding the utilization of hydrogen gas as fuel. Particularly, carbon materials, for example graphene, provide a fertile playground for hydrogen storage due to their lightweight structure and high performance potential [12, 33–37]. It was shown that graphene at low temperatures can easily absorb hydrogen and at high temperatures can easily desorb hydrogen [12].

The above-mentioned studies suggest that the study of hydrogenation and dehydrogenation of graphene is very important for possible applications in electronics, spintronics and hydrogen storage.

Interestingly, dehydrogenation kinetics during annealing turns out to be not as simple as expected. The thermal stability of adsorbed hydrogen can depend on the conditions of plasma treatment [26]. More interestingly, it was found that there are two types of dehydrogenation mechanisms with different dehydrogenation barriers [25]. It is challenging to find a theoretical explanation of this effect. For vacuum annealing, dehydrogenation starts at temperatures as low as 75–100 °C [25]. However, to achieve complete dehydrogenation within an annealing time on the order of 1 h, the annealing temperature should be increased up to 400–500 °C [25, 26]. The annealing temperature cannot be raised significantly higher than 500 °C because undesirable damage to graphene sheets by thermal fluctuation and/or by interaction with their substrate increases with temperature [12, 26]. An annealing time on the order of 1 h makes it impossible to apply molecular dynamics for direct simulation of dehydrogenation. Heating in nitrogen environment reduces the annealing time to minutes [19]; but this is still far beyond the capacity of molecular dynamics simulation.

The study of linear and nonlinear dynamics of graphene lattice can shed light on the basic physics of dehydrogenation. The hydrogen atom is 12 times lighter than the carbon atom. For such a large difference in their atomic weights, a wide gap in the phonon band can be expected and is a necessary condition for the existence of nonlinear excitations called gap discrete breathers (DBs) or intrinsic localized modes [38, 39], which are able to localize a large amount of energy so as to probably play an important role in overcoming the potential barrier of hydrogen desorption.

DBs are spatially localized vibrational modes of large amplitude in nonlinear defect-free lattices, described theoretically for the first time more than two decades ago [40]. Since then, the role of DBs has been extensively discussed in relation to many physical systems [39–41].

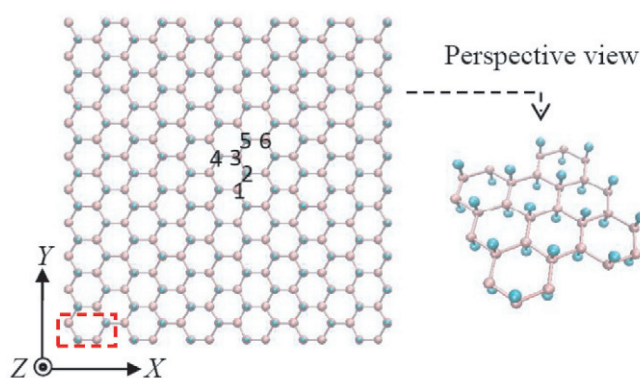


Figure 1. Schematic of a graphane sheet of which a unit cell is illustrated by a rectangular box. The H atom at the place marked by 1 will be displaced to form a DB, and the neighbouring places 2–6 are also marked for comparison.

The existence of stationary intrinsic localized modes has been proved experimentally in thermodynamic equilibrium in NaI crystals [42]. According to computer simulations, DBs can also be excited in graphene [43, 44]. Linear and nonlinear vibrational modes can exist at the edges of graphene nanoribbons [7, 45, 46] and in other carbon nano-polymorphs [47, 48]. To the best of our knowledge, no study has been conducted on the existence of DBs in graphane or other forms of hydrogenated graphene.

It is well known that DBs can exist only if it has a frequency above the phonon spectrum or in a spectrum gap if the gap exists. In graphene, there is no gap in the phonon spectrum, but there is a wide gap in graphane because of the presence of H atoms [49], which can be easily excited in the form of a DB. This paper studies the existence conditions of DBs in graphane and their properties and explores the role of DBs in thermally activated graphane dehydrogenation using molecular dynamic simulations.

2. The simulation model

In the simulation, the initial configuration of the graphane sheet is constructed by locating all the C atoms in a planar honeycomb lattice with the nearest neighbour distance $a = 1.55$ Å. The H atoms are bonded to the C atoms on both sides of the sheet alternatively with their distance, i.e. the C–H bond length, set as 1.1 Å. Figure 1 shows a graphane sheet consisting of 6 and 10 periodic unit cells along the X and Y directions. Each unit cell contains four C atoms (denoted by red points) and four H atoms (green points), as enclosed in the rectangular box.

The simulation is performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [50] with the adaptive intermolecular reactive empirical bond order (AREBO) potential [51] for description of interatomic interaction. The AREBO potential has been successfully used to study the thermal and mechanical properties of various carbon-based systems such as carbon nanotubes and graphene [32, 52–54]. In the potential, the

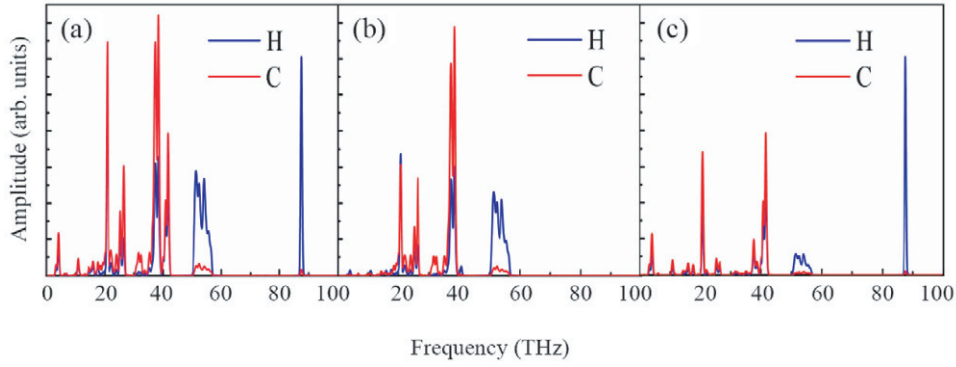


Figure 2. (a) Total phonon spectrum of a graphane sheet is projected on the C and H atoms with the modes of C atoms plotted in red lines and those of H atoms in blue; (b) the XY and (c) Z modes of the C (red) and H atoms (blue).

binding energy is given as summation over bonds:

$$E_b = \sum_i \sum_{j(j>i)} [V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij})], \quad (1)$$

where r_{ij} is the distance between atoms i and j , $\bar{B}_{ij}$ represents the empirical bond-order function and its definition can be found in [55], V_R and V_A are the repulsive and attractive pair terms, respectively. V_R and V_A are given by

$$V_R(r_{ij}) = \frac{D^{(e)}}{S-1} e^{-\sqrt{2S}\beta(r_{ij}-R^{(e)})} f_c(r_{ij}), \quad (2)$$

$$V_A(r_{ij}) = \frac{D^{(e)}S}{S-1} e^{-\sqrt{2S}\beta(r_{ij}-R^{(e)})} f_c(r_{ij}), \quad (3)$$

where the variables $D^{(e)}$, S , β and $R^{(e)}$ depend on the atom type (C or H) and their values refer to [55]. The function $f_c(r_{ij})$ is a smooth continuous cut-off function used to restrict the pair potential to the nearest neighbours and is given by

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} < R^{(1)} \\ \frac{1}{2} \left\{ 1 + \cos \left[\frac{\pi(r_{ij} - R^{(1)})}{R^{(2)} - R^{(1)}} \right] \right\}, & R^{(1)} < r_{ij} < R^{(2)} \\ 0, & r_{ij} > R^{(2)} \end{cases}, \quad (4)$$

where $R^{(1)}$ and $R^{(2)}$ are the cut-off constants for C–H binding interaction and we take $R^{(1)} = 1.3 \text{ \AA}$ and $R^{(2)} = 1.8 \text{ \AA}$ [55].

Periodic boundary conditions are applied on the graphane sheet along both X and Y directions. The initial temperature of the simulation system is set to be absolute zero temperature. The system is relaxed with the Nose–Hoover thermostat condition for 50 ps with a time step of 0.5 fs to reach the equilibrium state. It is found that upon equilibrium, the C atoms are pulled off the central plane by the H atoms for about 0.25 Å, resulting in a crumpled graphane sheet.

3. Phonon spectrum of a graphane sheet

The total phonon spectrum $P(\omega)$ of the graphane sheet upon equilibrium is calculated by performing the fast Fourier

transform on the velocity auto-correlation function [56]:

$$P(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{i\omega t} \left\langle \sum_{j=1}^N v_j(t) v_j(0) \right\rangle dt, \quad (5)$$

where ω and $v_j(t)$ denote the angular frequency and the atomic velocity at time t , respectively. The ensemble average in equation (5) is substituted by time averaging, which is performed over 50 ps after the realization of the equilibrium state. During the time averaging, the sample velocities are extracted from the simulation every 5 fs. The total phonon spectrum is projected on the C and H atoms, as shown in figure 2(a). A wide gap with the frequency range from 56.92 to 87.83 THz occurs in the projected spectra. The high-frequency optical phonon band (from 87.83 to 88.70 THz) is dominated by the modes of H atoms, while the low-frequency acoustic phonon band (below 20 THz) mainly consists of the modes of C atoms. The modes of the H and C atoms can be further classified into the modes along the X or Y direction (XY modes) and the modes along the Z direction (Z modes). As shown in figure 2(b), the XY modes of the C and H atoms are coupled with each other. Moreover, all the XY modes have frequencies no larger than 60 THz and the high-frequency optical phonon band consists of only the Z modes, as shown in figure 2(c).

4. Excitation of DBs

In this work, DBs are successfully excited in graphane by applying an initial out-of-plane displacement D_0 on one of the H atoms and then releasing it. For convenience, this H atom is chosen to be located at the centre of the sheet (position 1 in figure 1) and denoted by H1; its five neighbouring atoms at positions 2–6 are denoted by H2–H6 with distances a , $\sqrt{3}a$, $2a$, $\sqrt{7}a$ and $3a$, respectively. The displacement of a single H atom does not change the volume of the system and the energy of the system only transfers within the system and is not altered externally. Thus, the simulation is then performed under the constant volume and energy (NVE) ensemble for 10^7 time steps (5 ns). During the simulation, the displacements and kinetic energies of the six H atoms are recorded to investigate the properties of the DB. The Z -direction displacement u_z of H1 is used to determine the amplitude A and the oscillation

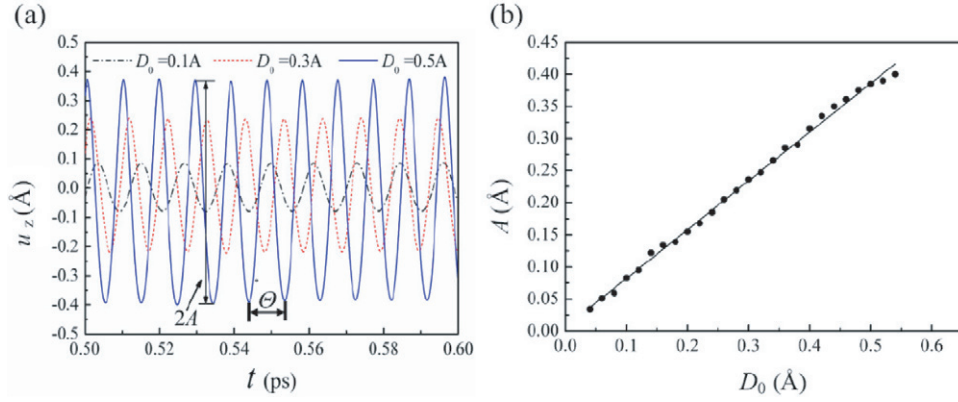


Figure 3. (a) Z-direction displacement u_z of H1 as a function of time t ; (b) linear relationship between the amplitude A of the DB and the initial displacement D_0 applied on H1.

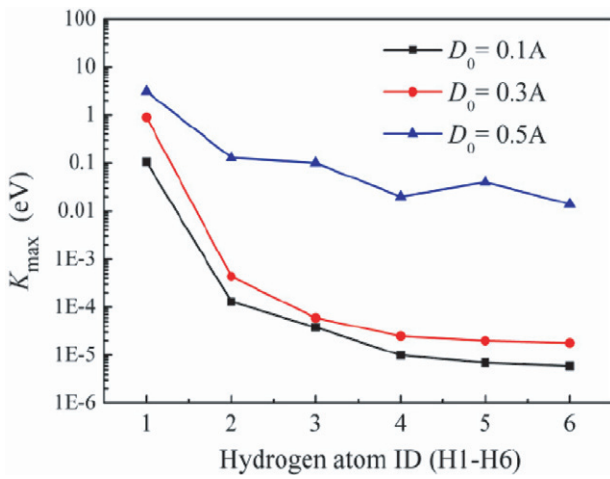


Figure 4. Maximum kinetic energies $K_{\max}$ of the atoms H1–H6 for three different initial displacements D_0 of H1.

period Θ of the DB. Figure 3(a) shows that H1 oscillates periodically after being released and its amplitude A exhibits a linear relationship with D_0 , i.e. $A = 0.76D_0$, as plotted in figure 3(b).

The DB has the intrinsic characteristic of highly localized energy. To demonstrate this characteristic, the energy localization is investigated by studying the maximum kinetic energy $K_{\max}$ of each of the six H atoms. Figure 4 plots $K_{\max}$ on the logarithmic scale for three different cases in which the initial displacement D_0 is taken to be 0.1 Å, 0.3 Å and 0.5 Å, respectively. It shows that $K_{\max}$ for the five neighbouring atoms (H2–H6) demonstrate an overall decrease trend as their distances to H1 increase. Specifically, for both $D_0 = 0.1$ and 0.3 Å, the $K_{\max}$ of H2 is smaller than that of H1 by almost three orders of magnitude, indicating that the energy of H1 is highly localized and barely transmitted to its neighbours. However, for $D_0 = 0.5$ Å, the $K_{\max}$ of H2 reaches about 2% that of H1 and is almost two orders of magnitude higher than those for $D_0 = 0.1$ and 0.3 Å. Thus, the energy localization effect of the DB is reduced when a large initial displacement is applied.

The frequency ω_D of the DB depends on its amplitude, as presented in figure 5 where $\omega_D = 1/\Theta$. The lower (solid) and middle (dotted) horizontal lines delineate the lower

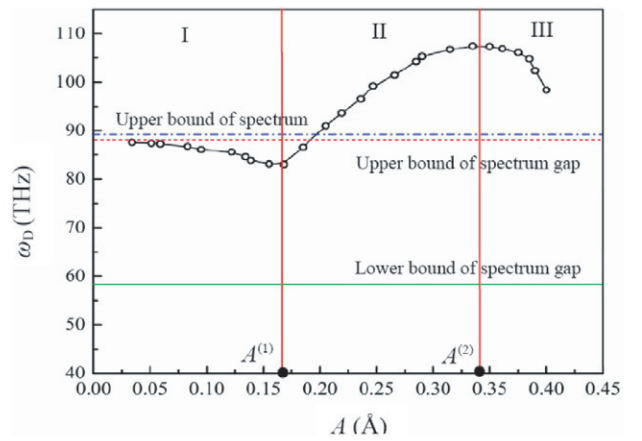


Figure 5. Dependence of the frequency ω_D of the DB on the amplitude A . The curve is divided into three regions where the DB exhibits different types of anharmonicity.

(56.92 THz) and upper (87.83 THz) bounds of the phonon spectrum gap, respectively, while the upper (dashed-dotted) line delineates the upper bound (88.70 THz) of the whole spectrum. Interestingly, the ω_D – A curve can be divided into three regions by two critical points at $A^{(1)} = 0.17$ Å and $A^{(2)} = 0.34$ Å. In region I, where A ranges from about 0.03 to 0.17 Å, ω_D bifurcates from the narrow high-frequency optical phonon band and then decreases as A increases, indicating a soft-type anharmonicity of the DB. In contrast, ω_D starts to dramatically increase in region II with 0.17 Å $< A < 0.34$ Å, showing a hard-type anharmonicity, which has rarely been observed in realistic crystal models. However, in region III with 0.34 Å $< A < 0.40$ Å, ω_D demonstrates a dramatic decrease again. In region I, the frequencies of the DBs lie within the gap of the phonon spectrum; in regions II and III, they are located below the upper bound of the whole phonon spectrum when 0.17 Å $< A < 0.20$ Å and above the upper bound when $A > 0.20$ Å.

Further study shows that the frequency ω_D of the DB is closely related to the force F on H1. The force F can be calculated by $F = -dE/dr$, where E is the potential energy of the graphane system and r is the distance between H1 and its covalently bonded C atom, named C1 hereafter. When H1 oscillates in the form of DB at a given amplitude

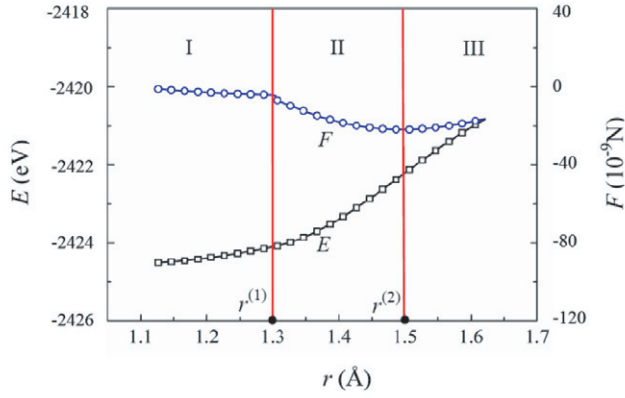


Figure 6. Force F on H1 and the potential energy E of the graphane sheet as a function of the distance r .

A , the distance r keeps changing and does not take a single value. In the calculation of E and F , the maximum value of r for a given A is used. Figure 6 presents the calculation results about E and F as a function of r . It shows that F is demonstrated to be an attractive force in the practical range of r , i.e. $1.13 \text{ Å} < r < 1.62 \text{ Å}$. The force F becomes zero at the equilibrium position of 1.1 Å . Two critical positions $r^{(1)} = 1.30 \text{ Å}$ and $r^{(2)} = 1.50 \text{ Å}$ divide the whole F - r curve into three regions. Specifically, as r increases, the force F experiences a slow increase in region I, a fast increase in region II, and finally a slow decrease in region III. The maximum amplitude of F is reached at $r = r^{(2)} = 1.50 \text{ Å}$. Moreover, it is found that when r takes $r^{(1)} = 1.30 \text{ Å}$, the oscillation amplitude A takes $A^{(1)} = 0.17 \text{ Å}$; when r takes $r^{(2)} = 1.50 \text{ Å}$, A takes $A^{(2)} = 0.34 \text{ Å}$. Thus, the three regions in the ω_D - A curve (figure 5) are well correlated with the three ones in the F - r curve (figure 6).

It is observed that in order to form a stable DB, the maximum distance r between C1 and H1 can only reach 1.62 Å , at which the amplitude A reaches the maximum value of 0.40 Å . As r increases from 1.62 Å to the cut-off distance $R^{(2)} = 1.8 \text{ Å}$, the force F between C1 and H1 approaches zero, as given in equation (4). The attempt to increase r beyond $r = 1.62 \text{ Å}$ by applying a larger D_0 would cause H1 to debond from C1 or the whole sheet after several oscillations. At $r = 1.62 \text{ Å}$, the total energy of the graphane system is found to increase by about 3.85 eV , compared with that of the system in which no DB is excited. This implies that H1 can be debonded or can escape from C1 if the provided energy is larger than 3.85 eV . Since DBs can be spontaneously excited in crystals at finite temperatures to localize a large amount of energy [42, 57–60], which can be utilized by hydrogen atoms to overcome the energy barrier of desorption from carbon atoms and thus may activate or accelerate dehydrogenation of hydrogenated graphene at high temperatures.

Figure 7 presents the dependence of the maximum kinetic energy $K_{\max}$ of H1 on its oscillation amplitude A . It shows that $K_{\max}$ increases monotonically with A . At the largest amplitude of $A = 0.40 \text{ Å}$, $K_{\max}$ takes 3.50 eV , a value close to the energy barrier of 3.85 eV for H1 to debond from C1. Another factor that could accelerate the desorption of H1 or help it to overcome the energy barrier is the vibration of C1 excited by H1, although this vibration is much smaller than that of H1.

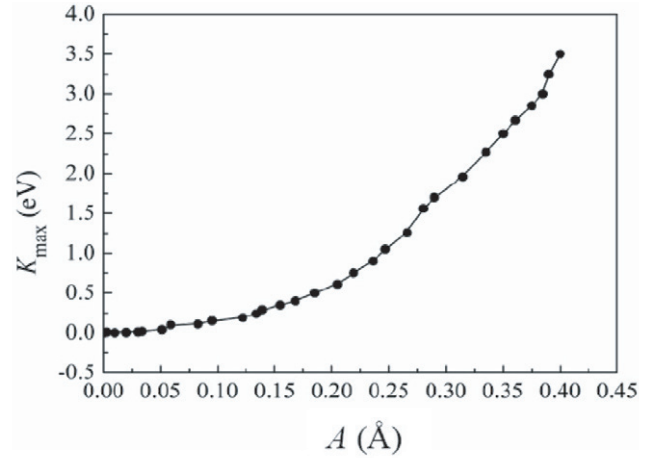


Figure 7. Maximum kinetic energy $K_{\max}$ of H1 versus its oscillation amplitude A .

5. Stability

When H1 is released from its initial displacement D_0 , most of the system energy is localized in the form of a DB, while the rest of the energy is transferred to the other atoms of the graphane sheet (background atoms) through C1, the first atom excited by H1, resulting in their vibrations or the so-called ‘background vibrations’. The background vibrations would disturb the DB and affect its stability or lifetime.

The disturbance is caused mainly by the interaction between the XY modes of H1 and the background atoms. As shown in figure 2(b), the phonon spectrum of the XY modes of the C atoms overlaps with that of the H atoms in a wide frequency range, which leads to the fact that the vibrations of H1 along the X or Y direction (XY vibrations) can be induced and affected by the background atoms. On the other hand, the XY vibrations of H1 would also perturb its vibration along the Z direction (Z vibration), particularly when they have large amplitudes.

The other reason for disturbance is that both C and H atoms possess the Z modes in the high-frequency optical phonon band. This makes the interaction between the Z modes of H1 and the background atoms possible. Nevertheless, since the high-frequency optical phonon band is narrow and the phonon spectrum of the Z modes of the C atoms is weak, the Z mode interaction does not happen frequently.

The stability of the DB is studied by investigating the decay of the vibration displacement of H1. Figures 8(a) and (b) plot the three displacement components u_x , u_y and u_z of H1 as a function of dimensionless time t/Θ for $D_0 = 0.10 \text{ Å}$ and $D_0 = 0.50 \text{ Å}$, respectively. Both cases demonstrate similar variation trends in the three displacement components. Specifically, the amplitude of u_z , i.e. the amplitude A of the DB, first undergoes a stable stage during which u_x and u_y stay almost zero. Afterwards, A gradually decays while the amplitudes of u_x and u_y increase up to the same order of A , indicating that the energy of the DB is transferred to the background atoms due to the XY mode interaction. Interestingly, u_y responses always later than u_x , which may be caused by the difference in chirality along the X and Y directions of the graphane sheet.

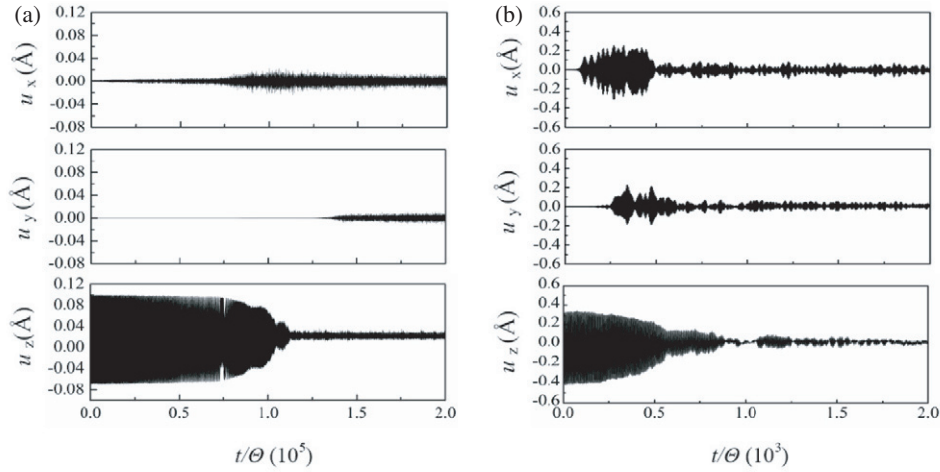


Figure 8. Displacements u_x , u_y and u_z of H1 for (a) $D_0 = 0.1 \text{ Å}$ and (b) $D_0 = 0.50 \text{ Å}$.

It is noted that the initial amplitude of u_z at $t = 0$ equals D_0 . However, due to the energy loss of H1 upon release from D_0 , the amplitude of u_z experiences a sharp decay before it reaches the stable state. Such a decay takes about one period and thus is not noticeable in figure 8.

After the stable stage, A gradually damps when $D_0 = 0.50 \text{ Å}$, but drastically damps when $D_0 = 0.1 \text{ Å}$. This is because the DB excited at $D_0 = 0.1 \text{ Å}$ has a frequency very close to the optical phonon band and thus excites its phonons, which take away the energy of the DB. Upon the decrease of amplitude, the frequency of the DB gets closer to the phonon band (figure 5) and the excitation of such phonons increases. Eventually, the frequency of the DB falls within the phonon band, leading to its immediate dying. For the DB excited at $D_0 = 0.50 \text{ Å}$, its frequency is far away from the phonon band (figure 5). In an infinite system, DBs with such frequencies do not interact with the phonons and can preserve the energy. However, due to the periodic boundary conditions used in the simulation, background vibrations are excited, which disturbs the DBs. Moreover, the larger the value of D_0 , the larger the energy transferred to the background atoms during the excitation of the DBs, and thus, the larger the amplitude of the background vibrations, leading to intensive disturbance to the DBs as well as further dissipation of their energy. Therefore, at large $D_0 = 0.50 \text{ Å}$, gradual dumping in A is observed.

The lifetime of the DB can be considered as lasting until its amplitude decays to be less than 10% of its initial value. The DB with $D_0 = 0.50 \text{ Å}$ has a lifetime of about 8.0×10^2 periods, which is two orders of magnitude shorter than the 1.03×10^5 period lifetime of the DB with $D_0 = 0.10 \text{ Å}$ (figure 8). This shows that the lifetime of the DB is strongly affected by the initial displacement D_0 of H1. Further studies also show that the maximum amplitude of each displacement component increase as D_0 increases.

Figure 9 shows that the lifetime of the DB ranges from 1.2×10^2 to 1.1×10^5 periods when A varies from 0.03 to 0.40 Å . A non-monotonic dependence of the lifetime on A is found, which can be categorized into three distinctive regions corresponding to those in the ω_D - A curve (figure 5) and in the F - r curve (figure 6). The lifetime decreases monotonically in region I, but fluctuates in regions II and III.

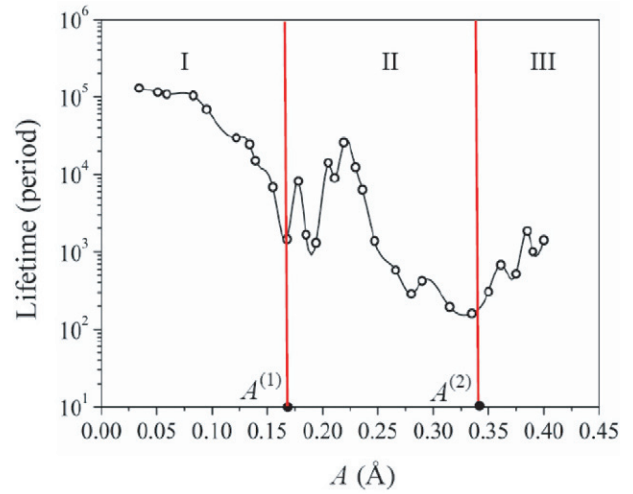


Figure 9. Lifetime of the DB at different A . The curve is divided into three sections by two red vertical lines at $A^{(1)} = 0.17 \text{ Å}$ and $A^{(2)} = 0.34 \text{ Å}$.

The decrease in the lifetime in region I is because the energy transferred to the background atoms upon the release of H1 increases with A , leading to enhanced XY vibrations for both the background atoms and H1. Accordingly, the interactions of their XY modes become strong. On the other hand, the attractive force F between C1 and H1 also slowly increases with A (figure 6), which further intensifies these XY mode interactions. As a result, the energy of the DB is increasingly transferred to the background atoms, thus causing its rapid decay. Here, the interactions of their Z modes do not happen because they do not vibrate in the same frequency range, as shown in figure 5.

In region II, the lifetime first has an overall increase trend for $0.17 \text{ Å} < A < 0.22 \text{ Å}$ with local valleys and then an overall decrease for $0.22 \text{ Å} < A < 0.34 \text{ Å}$ with local peaks. The initial overall increase might be due to the fact that the DB changes to the hard-type anharmonicity from the soft-type anharmonicity in region I. This characteristic change seems to affect the lifetime of the DB more dominantly at this stage than the interactions of the XY modes aforementioned.

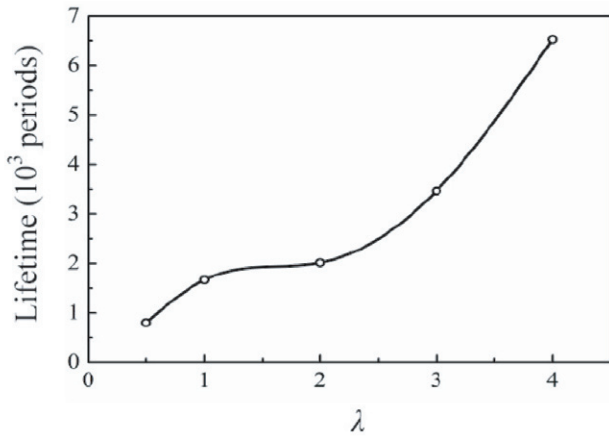


Figure 10. Dependence of the lifetime of the DB with $A = 0.24 \text{ \AA}$ on the size of the graphene sheet.

Nevertheless, an interesting finding is that there exists a dramatic decrease in the lifetime for $0.18 \text{ \AA} < A < 0.20 \text{ \AA}$ where the frequency of the DB falls in the high-frequency optic phonon band between 87.83 and 88.70 THz (figure 5), leading to the interaction between the Z modes of H1 and the background atoms and thus the reduced lifetime. The lifetime reaches the maxima at $A = 0.22 \text{ \AA}$ and then shows an overall decreasing trend because these XY mode interactions become dominant again at this stage.

In region III, the lifetime demonstrates an overall increase again because the attractive force between C1 and H1 decreases with A (figure 6), thus directly weakening the XY mode interactions of H1 and the background atoms. When the XY mode interactions become weak, the energy of the DB transferred to the background atoms decreases and leads to a longer lifetime.

In both regions II and III, local fluctuations of the lifetime are observed. Most likely, this fluctuation results from the interaction of H1 with the background atoms through their XY vibration modes. Since these modes are not periodic in time as the DBs and have random amplitudes, the frequency and intensity of this interaction have a probabilistic nature, which thus results in the local lifetime fluctuations. However, the sharp valley appearing in the range $0.18 \text{ \AA} < A < 0.20 \text{ \AA}$ is reproducible and originates from the intrinsic property of DBs as discussed above.

The above analyses reveal that the lifetime of the DB is affected by various factors including the anharmonicity type of the DB, its amplitude and frequency, and the force between H1 and C1. The competition of these factors gives rise to a complex determination mechanism for the lifetime.

In the simulation, periodic boundary conditions are applied on the graphene sheet. In fact, the size of the graphene sheet also affects the lifetime of the DB. A multiplier λ for both length and width of the graphene sheet illustrated in figure 1 is used to define the sheet size. It is found that the lifetime of the DB dramatically increases with λ , as exemplified for the DB with $A = 0.24 \text{ \AA}$ in figure 10. As the graphene sheet increases, the per-atom energy of the background atoms decreases and thus the effect of the background vibrations on the stability of the DB is reduced.

It is noted that the AREBO potential used in this study is a semi-empirical potential and the interatomic forces are cut off beyond a certain distance. Thus, the results obtained in this study may not be applicable to DBs with very large amplitudes where the AREBO potential does not work. Nevertheless, the simulation results do prove the existence of DBs in graphane. Experimental works are required to detect the existence and the type of anharmonicity of DBs in graphane, based on which the AREBO potential can be tested and, if necessary, improved.

6. Conclusions

This study shows that a DB can be excited in graphane by displacing a single hydrogen atom along the out-of-plane direction. The frequency of the DB lies either in the phonon spectrum gap of the graphane or beyond its upper spectrum bound. Both soft and hard types of anharmonicity of the DB, which have not been found in the same system, are observed in graphane. The anharmonicity of the DB depends on the amplitude of the DB and changes from the soft to the hard type and then to the soft type again as the amplitude increases. The DB is found to be robust under the disturbance of background vibrations, and its lifetime is affected by its anharmonicity type, its amplitude and frequency, and the force on the hydrogen atom that forms it. The competition of these affecting factors results in a complex determination mechanism for the lifetime of the DB.

Note that DBs are the excitations of defect-free lattices. Evidence for hydrogen clustering at relatively high hydrogen coverage was found experimentally [22]. Thus, a natural question arises as to whether DBs are possible in partially hydrogenated graphene. This study shows that DBs in graphane are highly localized so that even relatively small hydrogenated islands can host DBs.

Reportedly, there are two activation energies of dehydrogenation with the transition temperature at about 200°C [25]. The smaller dehydrogenation activation energy at temperatures below 200°C observed in [19, 25] can be understood by the metastable attachment of the energetic ions to the graphene sheet during plasma hydrogenation. 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 near 0 K indicates that they can also be spontaneously excited at a finite-temperature thermal equilibrium [58–60]. The maximum kinetic energy of the externally excited DBs in this study is found to be very close to the energy barrier for hydrogen desorption, implying that the spontaneously excited DBs in graphane at finite temperatures may play a role in activating or accelerating the dehydrogenation of hydrogenated graphene, which therefore becomes the focus of a future study.

Acknowledgments

The authors acknowledge the Academic Research Fund Tier 1 from the Ministry of Education, Singapore

(Grant No M401050000). SVD acknowledges financial support from the Russian Foundation for Basic Research (Grant No 11-08-97057-p-povolzhie-a). XW thanks the National Natural Science Foundation of China (Grant No 11272121). HWZ thanks the National Program on Key Basic Research Project (Grant No 2011CB013000) and the Beijing Natural Science Foundation (Grant No 2122027).

References

- [1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films *Science* **306** 666–9
- [2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Two-dimensional gas of massless Dirac fermions in graphene *Nature* **438** 197–200
- [3] Chien S K, Yang Y T and Chen C K 2012 Influence of chemisorption on the thermal conductivity of graphene nanoribbons *Carbon* **50** 421–8
- [4] Soldano C S C, Mahmood A and Dujardin E 2010 Production, properties and potential of graphene *Carbon* **48** 2127–50
- [5] Li X, Sun P Z, Fan L L, Zhu M, Wang K L, Zhong M L, Wei J Q, Wu D H, Cheng Y and Zhu H W 2012 Multifunctional graphene woven fabrics *Sci. Rep.* **2** 395
- [6] Jhon Y I, Zhu S E, Ahn J H and Jhon M S 2012 The mechanical responses of tilted and non-tilted grain boundaries in graphene *Carbon* **50** 3708–16
- [7] Korznikova E A, Savin A V, Baimova Y A, Dmitriev S V and Mulyukov R R 2012 Discrete breather on the edge of the graphene sheet with the armchair orientation *JETP Lett.* **96** 222–6
- [8] Baimova J A, Dmitriev S V, Zhou K and Savin V 2012 Unidirectional ripples in strained graphene nanoribbons with clamped edges at zero and finite temperatures *Phys. Rev. B* **86** 035427
- [9] Li X M, Zhu H W, Wang K L, Cao A Y, Wei J Q, Li C Y, Jia Y, Li Z, Li X and Wu D H 2010 Graphene-on-silicon Schottky junction solar cells *Adv. Mater.* **22** 2743–8
- [10] Sluiter M H F and Kawazoe Y 2003 Cluster expansion method for adsorption: application to hydrogen chemisorption on graphene *Phys. Rev. B* **68** 085410
- [11] Sofo J O, Chaudhari A S and Barber G D 2007 Graphane: a two-dimensional hydrocarbon *Phys. Rev. B* **75** 153401
- [12] Elias D C *et al* 2009 Control of graphene's properties by reversible hydrogenation: evidence for graphane *Science* **323** 610–3
- [13] Roman T, Dino W A, Nakanishi H, Kasai H, Sugimoto T and Tange K 2007 Hydrogen pairing on graphene *Carbon* **45** 218–20
- [14] Jones J D, Mahajan K K, Williams W H, Ecton P A, Mo Y and Perez J M 2010 Formation of graphane and partially hydrogenated graphene by electron irradiation of adsorbates on graphene *Carbon* **48** 2335–40
- [15] Pei Q X, Sha Z D and Zhang Y W 2011 A theoretical analysis of the thermal conductivity of hydrogenated graphene *Carbon* **49** 4752–9
- [16] Dzhurakhalov A A and Peeters F M 2011 Structure and energetics of hydrogen chemisorbed on a single graphene layer to produce graphane *Carbon* **49** 3258–66
- [17] Sahin H, Ataca C and Ciraci S 2010 Electronic and magnetic properties of graphane nanoribbons *Phys. Rev. B* **81** 205417
- [18] Liu B, Reddy C D, Jiang J W, Baimova J A, Dmitriev S V, Nazarov A A and Zhou K 2012 Morphology and in-plane thermal conductivity of hybrid graphene sheets *Appl. Phys. Lett.* **101** 211909
- [19] Wojtaszek M, Tombros N, Caretta A, Van Loosdrecht P H M and Van Wees B J 2011 A road to hydrogenating graphene by a reactive ion etching plasma *J. Appl. Phys.* **110** 063715
- [20] Gao H L, Wang L, Zhao J J, Ding F and Lu J P 2011 Band gap tuning of hydrogenated graphene: H coverage and configuration dependence *J. Phys. Chem. C* **115** 3236–42
- [21] Chen W F, Zhu Z Y, Li S R, Chen C H and Yan L F 2012 Efficient preparation of highly hydrogenated graphene and its application as a high-performance anode material for lithium ion batteries *Nanoscale* **4** 2124–9
- [22] Luo Z Q, Yu T, Ni Z H, Lim S H, Hu H L, Shang J Z, Liu L, Shen Z X and Lin J Y 2011 Electronic structures and structural evolution of hydrogenated graphene probed by Raman spectroscopy *J. Phys. Chem. C* **115** 1422–7
- [23] Xie L F *et al* 2011 Room temperature ferromagnetism in partially hydrogenated epitaxial graphene *Appl. Phys. Lett.* **98** 193113
- [24] Burgess J S, Matis B R, Robinson J T, Bulat F A, Perkins F K, Houston B H and Baldwin J W 2011 Tuning the electronic properties of graphene by hydrogenation in a plasma enhanced chemical vapor deposition reactor *Carbon* **49** 4420–6
- [25] Luo Z Q, Yu T, Kim K L, Ni Z H, You Y M, Lim S, Shen Z X, Wang S Z and Lin J Y 2009 Thickness-dependent reversible hydrogenation of graphene layers *ACS Nano* **3** 1781–8
- [26] Jones J D, Hoffmann W D, Jesse A V, Morris C J, Verbeck G F and Perez J M 2010 On the mechanism for plasma hydrogenation of graphene *Appl. Phys. Lett.* **97** 233104
- [27] Zheng L, Li Z, Bourdo S, Watanabe F, Ryerson C C and Biris A S 2011 Catalytic hydrogenation of graphene films *Chem. Commun.* **47** 1213–5
- [28] Ao Z M and Peeters F M 2010 Electric field: a catalyst for hydrogenation of graphene *Appl. Phys. Lett.* **96** 253106
- [29] Lamari F D and Levesque D 2011 Hydrogen adsorption on functionalized graphene *Carbon* **49** 5196–200
- [30] Muniz A R and Maroudas D 2010 Hydrogenation effects on the structure and morphology of graphene and single-walled carbon nanotubes *J. Appl. Phys.* **108** 113532
- [31] Mapasha R E, Ukpong A M and Chetty N 2012 *Ab initio* studies of hydrogen adatoms on bilayer graphene *Phys. Rev. B* **85** 205402
- [32] Pei Q X, Zhang Y W and Shenoy V B 2010 A molecular dynamics study of the mechanical properties of hydrogen functionalized graphene *Carbon* **48** 898–904
- [33] Dillon A C, Jones K M, Bekkedahl T A, Kiang C H, Bethune D S and Heben M J 1997 Storage of hydrogen in single-walled carbon nanotubes *Nature* **386** 377–9
- [34] Liu C, Fan Y Y, Liu M, Cong H T, Cheng H M and Dresselhaus M S 1999 Hydrogen storage in single-walled carbon nanotubes at room temperature *Science* **286** 1127–9
- [35] Strobel R, Jorissen L, Schliermann T, Trapp V, Schutz W, Bohmhammel K, Wolf G and Garcke J 1999 Hydrogen adsorption on carbon materials *J. Power Sources* **84** 221–4
- [36] Yang R T 2000 Hydrogen storage by alkali-doped carbon nanotubes—revisited *Carbon* **38** 623–6
- [37] Xu W C, Takahashi K, Matsuo Y, Hattori Y, Kumagai M, Ishiyama S, Kaneko K and Iijima S 2007 Investigation of hydrogen storage capacity of various carbon materials *Int. J. Hydrogen Energy* **32** 2504–12
- [38] Flach S and Willis C R 1998 Discrete breathers *Phys. Rep.* **295** 181–264
- [39] Flach S and Gorbach A V 2008 Discrete breathers—advances in theory and applications *Phys. Rep.* **467** 1–116
- [40] Sievers A J and Takeno S 1988 Intrinsic localized modes in anharmonic crystals *Phys. Rev. Lett.* **61** 970–3
- [41] Campbell D K, Flach S and Kivshar Y S 2004 Localizing energy through nonlinearity and discreteness *Phys. Today* **57** 43–9

- [42] Manley M E, Sievers A J, Lynn J W, Kiselev S A, Agladze N I, Chen Y, Llobet A and Alatas A 2009 Intrinsic localized modes observed in the high-temperature vibrational spectrum of NaI *Phys. Rev. B* **79** 134304
- [43] Yamayose Y, Kinoshita Y, Doi Y, Nakatani A and Kitamura T 2007 Excitation of intrinsic localized modes in a graphene sheet *Europhys. Lett.* **80** 4008
- [44] Baimova J A, Dmitriev S V and Zhou K 2012 Discrete breather clusters in strained graphene *Europhys. Lett.* **100** 36005
- [45] Savin A V and Kivshar Y S 2010 Surface solitons at the edges of graphene nanoribbons *Europhys. Lett.* **89** 46001
- [46] Savin A V and Kivshar Y S 2010 Vibrational Tamm states at the edges of graphene nanoribbons *Phys. Rev. B* **81** 165418
- [47] Shimada T, Shirasaki D and Kitamura T 2010 Stone–Wales transformations triggered by intrinsic localized modes in carbon nanotubes *Phys. Rev. B* **81** 035401
- [48] Savin A V and Kivshar Y S 2012 Nonlinear breatherlike localized modes in C-60 nanocrystals *Phys. Rev. B* **85** 125427
- [49] Peelaers H, Hernandez-Nieves A D, Leenaerts O, Partoens B and Peeters F M 2011 Vibrational properties of graphene fluoride and graphane *Appl. Phys. Lett.* **98** 051914
- [50] Plimpton S 1995 Fast parallel algorithms for short-range molecular-dynamics *J. Comput. Phys.* **117** 1–19
- [51] Stuart S J, Tutein A B and Harrison J A 2000 A reactive potential for hydrocarbons with intermolecular interactions *J. Chem. Phys.* **112** 6472–86
- [52] Varshney V, Patnaik S S, Roy A K, Froudakis G and Farmer B L 2010 Modeling of thermal transport in pillared-graphene architectures *ACS Nano* **4** 1153–61
- [53] Wei N, Xu L Q, Wang H Q and Zheng J C 2011 Strain engineering of thermal conductivity in graphene sheets and nanoribbons: a demonstration of magic flexibility *Nanotechnology* **22** 105705
- [54] Xu Z P and Buehler M J 2009 Nanoengineering heat transfer performance at carbon nanotube interfaces *ACS Nano* **3** 2767–75
- [55] Brenner D W 1990 Empirical potential for hydrocarbons for use in simulating the chemical vapor-deposition of diamond films *Phys. Rev. B* **42** 9458–71
- [56] Alaghemandi M, Leroy F, Muller-Plathe F and Bohm M C 2010 Thermal rectification in nanosized model systems: a molecular dynamics approach *Phys. Rev. B* **81** 125410
- [57] Manley M E, Abernathy D L, Agladze N I and Sievers A J 2011 Symmetry-breaking dynamical pattern and localization observed in the equilibrium vibrational spectrum of NaI *Sci. Rep.* **1** 110614
- [58] Khadeeva L Z and Dmitriev S V 2011 Lifetime of gap discrete breathers in diatomic crystals at thermal equilibrium *Phys. Rev. B* **84** 144304
- [59] Ivanchenko M V, Kanakov O I, Shalfeev V D and Flach S 2004 Discrete breathers in transient processes and thermal equilibrium *Physica D* **198** 120–35
- [60] Eleftheriou M and Flach S 2008 Interaction of discrete breathers with thermal fluctuations *Low Temp. Phys.* **34** 554–8