2016 International Symposium on Nonlinear Theory and Its Applications,
NOLTA2016, Yugawara, Japan, November 27th-30th, 2016

Search for Discrete Breathers in Unstrained Graphene

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Abstract – Graphene is one atom thick carbon layer with unique combination of physical and mechanical properties promising for many applications. Nonlinear lattice dynamics of graphene has been addresses in recent theoretical and experimental works. In particular, several studies have been done on the possibility to excite discrete breathers (DBs), which are long-lived, spatially localized nonlinear vibrational modes. In the present work, based on the molecular dynamics simulations, we discuss the possibility to excite DBs in unstrained graphene. It is concluded that the results are strongly dependent on the interatomic potentials used in the simulations. Our study calls for additional studies based on *ab initio* calculations to prove or disprove the existence of DBs in unstrained graphene.

1. Introduction

Graphene attracts attention of many researchers because it is a promising material in a number of applications ranging from electronics and solar cells to supercapacitors and hydrogen storage devices [1]. Of great interest is the nonlinear dynamics of graphene lattice, in particular, the possibility to excite spatially localized nonlinear vibrational modes, called intrinsic localized modes or discrete breathers (DB), which have been studied experimentally [2] and theoretically [3-15]. DBs in graphene and carbon nanotubes have been studied by Japanese researchers [3-9]. To excite a DB in graphene, a complex procedure to find proper initial conditions has been used [3]. The DB had frequency above the gapless phonon spectrum and it was proved to be unstable. The gap in the phonon spectrum of graphene can be opened by applying homogeneous elastic deformation, allowing to easily excite highly localized gap DBs [10]. Clusters of such DBs were studied in [11] and the possibility of energy exchange between DBs in clusters was demonstrated. DBs can also be excited on the edge of a stretched graphene nanoribbons of the armchair orientation [12,13]. DB frequency lies in the gap of the phonon spectrum, resulting from the application of tensile elastic strain of the nanoribbon. There exist a review on DBs in carbon and hydrocarbon nanomaterials [14] and a more general review on DBs in crystals [15].

In the two very recent papers [16,17] the authors report on the excitation of DBs in unstrained graphene in frame of the molecular dynamics simulations. In [16], using the AIREBO potential, a DB with atomic vibrations normal to the graphene sheet has been excited. Our simulations confirm this result. Even though DB frequency lies in the phonon spectrum, it is outside the spectrum of the out-of-plane phonon modes. In graphene the in-plane and out-of-plane modes interact very weakly even at relatively large amplitudes, which allows for the out-of-plane DBs to have very long lifetime. In [17], in-plane DBs in free-standing graphene have been reported based on the Tersoff interatomic potential. We will discuss in this work that the vibrational mode excited in [17] cannot be called a DB but rather it is a defect mode.

It should be pointed out that the conclusions about properties and the very existence of DBs found in molecular dynamics simulations are very sensitive to the choice of the interatomic potentials.

In this work we use the Savin potentials [18] to check what kind of DBs can be excited in the unstrained flat graphene sheet. We use the assumption that a DB can be excited by application of a bell-shape function on a short-wavelength, zone-boundary mode, whose frequency at large amplitudes leaves the phonon spectrum. This approach has been successfully used earlier [19]. We thus focus on the study of the frequency-amplitude dependence of the short-wavelength extended vibrational modes.

2. Search for DB in unstrained graphene

2.1. Phonon DOS

Phonon density of states (DOS) calculated for unstrained graphene with the use of the Savin interatomic potentials [18] is plotted in Fig. 1 for (a) in-plane modes, (b) out-of-plane modes, (c) cumulative. Highest frequency for the in-plane modes is $\omega_{\max}^{xy} = 47.96$ THz, while that for the out-of-plane modes is $\omega_{\max}^{z} = 26.94$ THz. Symmetry of the graphene lattice precludes the appearance of a gap in the phonon DOS.

2.2. Frequencies of the in-plane short-wavelength extended modes as the functions of their amplitudes

In the work by Chechin with co-authors [20], with the use of the group-theoretical approach, four short-

wavelength vibrational modes depicted in Fig. 2 have been derived. These modes are the symmetry-dictated exact solutions to the atomic equations of motion, regardless the type of the interatomic potentials used in the simulations.

It is interesting to find the relation between amplitude and frequency for these four modes. These relations were found with the use of the Savin potential [18] and the result is presented in Fig. 3 for the modes I to IV, shown in Fig. 2 (a) to (d), respectively. Horizontal dashed line in Fig. 3 shows the upper edge of the phonon spectrum.

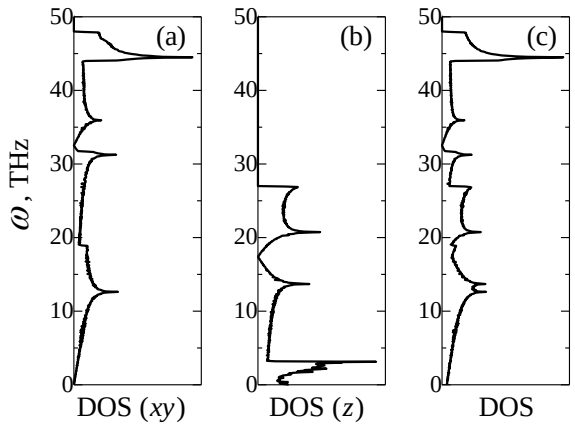

Fig. 1. Phonon density of states for unstrained graphene: (a) in-plane modes, (b) out-of-plane modes, (c) cumulative.

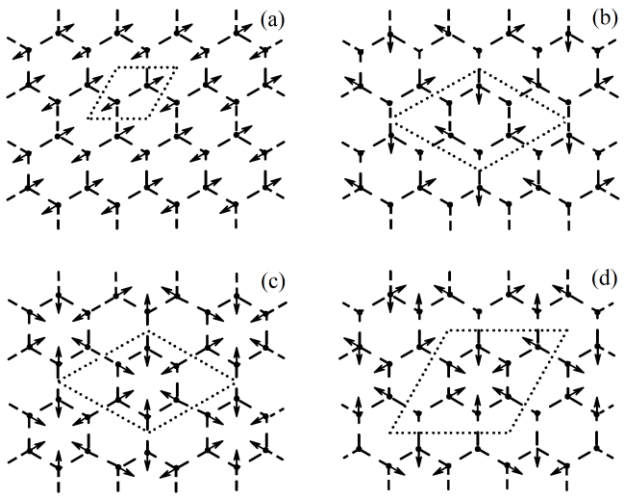

Fig. 2. Four symmetry dictated exact solutions to the equations of atomic motion regardless the type of interatomic potential and regardless the mode amplitude. The case of in-plane displacements of atoms. The modes in panels (a) to (d) are referred to as modes I, II, III, and IV, respectively.

As it can be seen from Fig. 3, at small amplitudes, mode I has the highest frequency which bifurcates from the upper edge of the phonon spectrum and decreases with the increase in the amplitude. Mode II also demonstrates soft type nonlinearity with the mode frequency decreasing with the amplitude. Modes III and IV show hard type nonlinearity, since their frequencies increase with the amplitude. Only mode III leaves the phonon spectrum but this happens at relatively large amplitudes, greater than 0.22 Å. Since frequencies of the modes I, II, and IV lie in the phonon band, they cannot produce a DB by applying a bell-shape function upon them. We have tried to apply a bell-shape function to the mode III at amplitudes greater than 0.25 Å, but we were unable to excite a long-lived DB. At large amplitudes the instability of DB develops too fast.

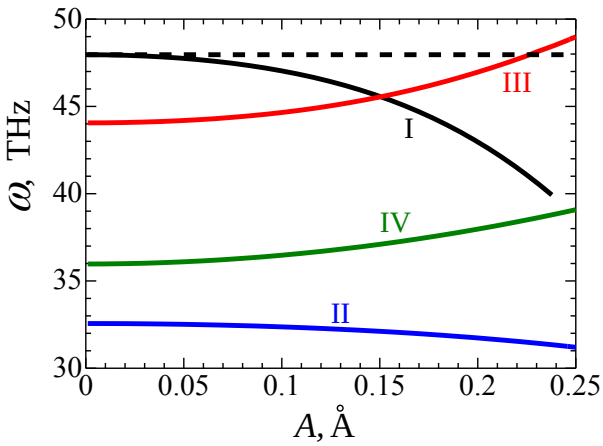

Fig. 3. Frequency as the function of amplitude for the four in-plane modes shown in Fig. 2. The modes I to IV correspond to the panels (a) to (d) of Fig. 2. Horizontal dashed line shows the upper edge of the phonon spectrum.

2.3. Frequency of the out-of-plane short-wavelength extended mode as the function of its amplitude

Our next step is to check if the Savin potentials allow for the existence of the DBs with the out-of plane vibrations of atoms similar to those described in [16] with the AIREBO interatomic potentials. For this we consider the out-of-plane extended vibrational mode in graphene shown in Fig. 4(a). Red and blue atoms vibrate out-of-phase in the direction normal to the graphene sheet with the amplitude *A*. We calculate the dependence of the mode frequency as the function of its amplitude and plot the result in Fig. 4(b), where the horizontal dashed line shows the upper edge of the phonon spectrum for the out-of-plane modes [see Fig. 1(b)]. It is clear that with the Savin potential this mode shows the soft nonlinearity type and thus, a DB with the out-of-plane atomic displacements cannot exist.

It is worth pointing out that the experimental discovery of carbon monoatomic chain [21] has inspired theoretical studies on DBs in the Fermi-Pasta-Ulam chain with atoms having three degrees of freedom [22]. The authors of the latter work have demonstrated that the well-studied longitudinal DBs become unstable in this generalized

model, but they were able to find transverse and rotational DBs and a region of the stretching force where rotational DBs are stable. Search of the transverse DBs in graphene can be regarded as a continuation of these works.

2.4. Localized mode in unstrained graphene modeled with the Tersoff interatomic potential

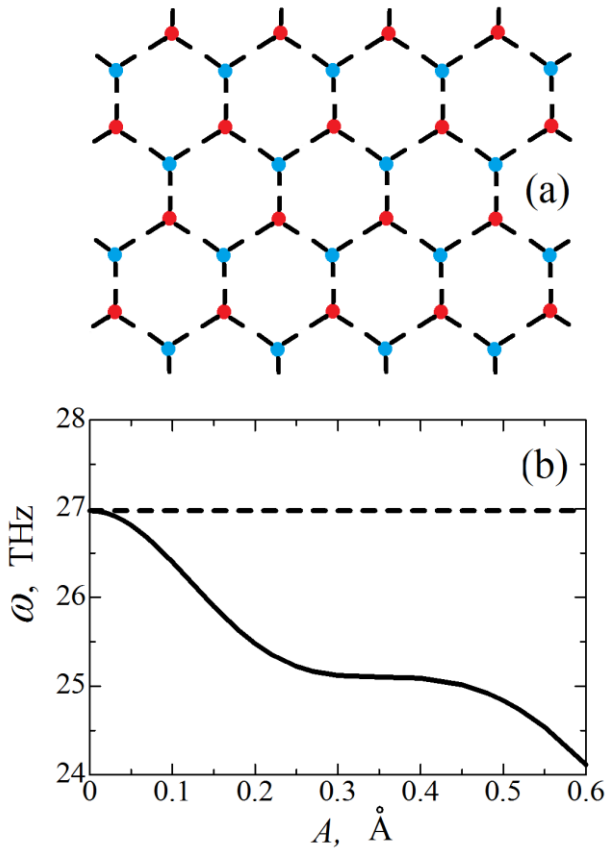

Fig. 4. (a) Out-of-plane vibrational mode in graphene. Red and blue atoms vibrate out-of-phase in the direction normal to the graphene sheet with the amplitude *A*. (b) Frequency as the function of amplitude for the mode shown in (a). Horizontal dashed line shows the upper edge of the phonon spectrum for the out-of-plane modes [see Fig. 1(b)].

We have revisited the results reported in [17], where the existence of DB was claimed in the free-standing graphene with the Tersoff potential. However, our simulations with the Tersoff potential have demonstrated the existence of a topological defect in graphene lattice, as shown in Fig. 5. Shown are the regular structure with translational symmetry (large black circles) and the defected structure with one valence bond, between atoms 1 and 2, longer than others (smaller gray circles). Pair of atoms 1 and 2 can vibrate out-of-phase in vertical direction with the frequency above the phonon spectrum near the defected equilibrium positions, but this mode cannot be classified as DB, because translational symmetry of the lattice is lost.

3. Conclusions

From the results presented in this work in comparison with the existing results on DBs in graphene it is clear that the effect of the interatomic potentials on the existence and properties of DBs is crucial. 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.

There exist a few studies on DBs in graphane (fully hydrogenated graphene) and strained graphene carried out in frame of the density functional theory (DFT) that takes into account electron structure of solids and does not use phenomenological interatomic potentials [23-26]. We understand that it is very important and timely to continue the DFT simulations to check the result presented in this study, particularly those for the short-wavelength modes, presented in Fig. 3 and Fig. 4. These studies are in progress and the results will be reported elsewhere.

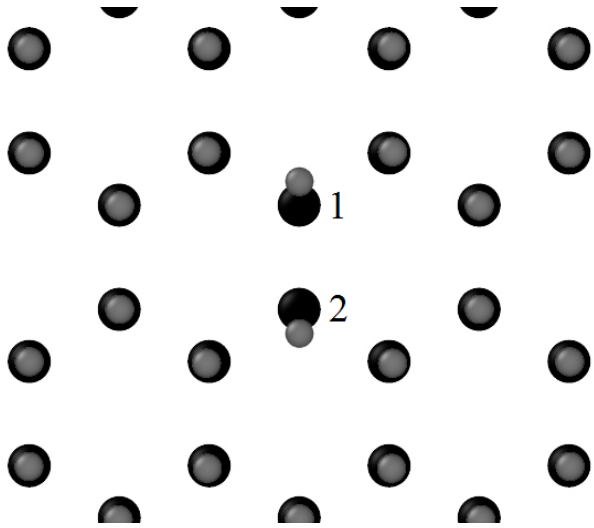

Fig. 5. Two equilibrium configurations of graphene sheet modeled with the use of the Tersoff potential. Regular structure with translational symmetry is shown by large black circles, while smaller gray circles present a defected structure with one valence bond (between atoms 1 and 2) longer than others. Atoms neighboring to the atoms 1 and 2 have much smaller displacements from the regular lattice positions.

Acknowledgments

The authors would like to thank NOLTA2016 organizing committee members for their fruitful suggestions and comments. Financial support from the Russian Science Foundation, grant 16-12-10175, is acknowledged with thanks by S.V.D. I.P.L. thanks the grant of President of Russian Federation for Young Researchers RF MK-5283.2015.2. E.A.K. is grateful for the financial support provided by the Russian Foundation for Basic Research, grant 14-02-97029 p_povolzhie_a.

References

[1] A. K. Geim, K. S. Novoselov, "The rise of graphene", *Nat. Mater.*, vol. 6, pp. 183-191, 2007.

[2] W. Liang, G. M. Vanacore, A. H. Zewail, "Observing (non)linear lattice dynamics in graphite by ultrafast Kikuchi diffraction", *Proc. Natl. Acad. Sci. USA*, vol. 111, p. 5491, 2014.

[3] Y. Yamayose, Y. Kinoshita, Y. Doi, A. Nakatani, T. Kitamura, "Excitation of intrinsic localized modes in a graphene sheet", *Europhys. Lett.*, vol. 80, p. 40008 (2007).

[4] T. Shimada, D. Shirasaki, T. Kitamura, "Stone-Wales transformations triggered by intrinsic localized modes in carbon nanotubes", *Phys. Rev.* B, vol. 81, p. 035401, 2010.

[5] T. Shimada, D. Shirasaki, Y. Kinoshita, Y. Doi, A. Nakatani, T. Kitamura, "Influence of nonlinear atomic interaction on excitation of intrinsic localized modes in carbon nanotubes", *Physica* D, vol. 239, pp. 407-413, 2010.

[6] Y. Kinoshita, Y. Yamayose, Y. Doi, A. Nakatani, T. Kitamura, "Selective excitations of intrinsic localized modes of atomic scales in carbon nanotubes", *Phys. Rev.* B vol. 77, p. 024307, 2008.

[7] Y. Doi, A. Nakatani, "Numerical study on unstable perturbation of intrinsic localized modes in graphene", *Journal of Solid Mechanics and Materials Engineering*, vol. 6, pp. 71-80, 2012.

[8] Y. Doi, A. Nakatani, "Structure and stability of discrete breather in zigzag and armchair carbon nanotubes", *Letters on Materials*, vol. 6, pp. 49-53, 2016.

[9] Y. Doi, A. Nakatani, "Structure and stability of nonlinear vibration mode in graphene sheet", *Procedia Engineering*, vol. 10, pp. 3393-3398, 2011.

[10] L. Z. Khadeeva, S. V. Dmitriev, Yu. S. Kivshar, "Discrete breathers in deformed graphene", *JETP Lett.*, vol. 94, p. 539, 2011.

[11] J. A. Baimova, S. V. Dmitriev, K. Zhou, "Discrete breather clusters in strained graphene", *Europhys. Lett.*, vol. 100, p. 36005, 2012.

[12] E. A. Korznikova, J. A. Baimova, S. V. Dmitriev, "Effect of strain on gap discrete breathers at the edge of armchair graphene nanoribbons", *Europhys. Lett.*, vol. 102, p. 60004, 2013.

[13] E.A. Korznikova, A.V. Savin, Y.A. Baimova, S.V. Dmitriev, R.R. Mulyukov, "Discrete breather on the edge of the graphene sheet with the armchair orientation", *JETP Lett.*, vol. 99, pp. 222-226, 2012.

[14] J.A. Baimova, E.A. Korznikova, I.P. Lobzenko, S.V. Dmitriev, "Discrete breathers in carbon and hydrocarbon nanostructures", *Rev. Adv. Mater. Sci.*, vol. 42, pp. 68-82, 2015.

[15] S. V. Dmitriev, E. A. Korznikova, J. A. Baimova, M. G. Velarde, "Discrete breathers in crystals", *Phys. Usp*. vol. 59, issue 5, 2016 (in press). DOI: 10.3367/UFNe.2016.02.037729

[16] V. Hizhnyakov, M. Klopov, A. Shelkan, "Transverse intrinsic localized modes in monatomic chain and in graphene", *Phys. Lett. A*, vol. 380, pp. 1075-1081, 2016.

[17] A. Fraile, E.N. Koukaras, K. Papagelis, N. Lazarides, G.P. Tsironis, "Long-lived discrete breathers in free-standing graphene", *Chaos, Solitons and Fractals*, vol. 87, pp. 262-267, 2016.

[18] A. V. Savin, Y. S. Kivshar, B. Hu, "Suppression of thermal conductivity in graphene nanoribbons with rough edges," *Phys. Rev. B*, vol. 82, p. 195422, 2010.

[19] E. A. Korznikova, S. Yu. Fomin, E. G. Soboleva, S. V. Dmitriev, "Highly symmetric discrete breather in a two-dimensional Morse crystal", *JETP Letters*, vol. 103, No. 4, pp. 277–281, 2016.

[20] G. Chechin, D. Ryabov, S. Shcherbinin, "Nonlinear vibrational modes in graphene: group-theoretical results", *Letters on Materials*, vol. 6, pp. 9-15, 2016.

[21] C. Jin, H. Lan, L. Peng, K. Suenaga, S. Iijima, "Deriving carbon atomic chains from graphene", *Phys. Rev. Lett*. 102, 205501 (2009).

[22] M. Kimura, A. Mitani, S. Doi, "Existence and stability of intrinsic localized modes in a finite FPU chain placed in three-dimensional space," *Letters on Materials*, vol. 6, pp. 22-26, 2016.

[23] G. M. Chechin, S. V. Dmitriev, I. P. Lobzenko, D. S. Ryabov, "Properties of discrete breathers in graphane from ab initio simulations", *Phys. Rev.* B, vol. 90, p. 045432, 2014.

[24] G. M. Chechin, I. P. Lobzenko, "Ab initio refining of quasibreathers in graphane", *Letters on Materials*, vol. 4, pp. 226-229, 2014.

[25] I. P. Lobzenko, "Discrete breathers properties obtained from ab initio calculations in graphene and graphane", *Letters on Materials*, vol. 6, pp. 73-76, 2016.

[26] I. P. Lobzenko, G. M. Chechin, G. S. Bezuglova, Yu. A. Baimova, E. A. Korznikova, S. V. Dmitriev, "Ab initio simulation of gap discrete breathers in strained graphene", *Phys. Solid State*, vol. 58, pp. 633–639, 2016.