Bushes of Nonlinear Normal Modes in Single-Layer Graphene

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Abstract
In-plane vibrations in uniformly stretched single-layer graphene (space group P6mm), which are described by the Rosenberg nonlinear normal modes (NNMs) and their bushes, are studied with the aid of group-theoretical methods developed by authors in some earlier papers. It was found that only 4 symmetry-determined NNMs (one-dimensional bushes), as well as 14 two-dimensional bushes are possible in graphene. They are exact solutions to the dynamical equations of this two-dimensional crystal. The verification of group-theoretical results with the aid of ab initio simulations based on density functional theory is discussed

Keywords
lattice dynamics, nonlinear normal modes, graphene, group-theoretical methods, ab initio simulations, density functional theory

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Introduction

Conventional linear normal modes are exact solutions to the dynamical equations of Hamiltonian system in the harmonic approximation. They turn out to be approximate solutions when we take into account small anharmonic terms in potential energy. On the other hand, there it can exist exact solutions beyond the harmonic approximation for nonlinear Hamiltonian systems with some specific types of potential energy. In [1], Rosenberg introduced the notion of nonlinear normal modes (NNMs). Detailed theory of these dynamical objects with different applications can be found in [2, 3].

According to definition, in the dynamical regime described by a given Rosenberg mode, all degrees of freedom, $x_i(t)$, vibrate as follows:

$$x_i(t) = a_i f(t), i = 1 \dots N \qquad (1)$$

Thus, all $x_i(t)$ at any moment t are proportional to the *same* time-dependent function $f(t)$. Actually, this means a separation of space and time variables.

Rosenberg found several classes of mechanical systems for which Eq. (1) is fulfilled. The most important class is formed by systems whose potential energy is a homogeneous function, of arbitrary degree, of all its arguments.

In [4-6], it was shown that the existence of Rosenberg NNMs can be a direct consequence of a certain discrete symmetry of the considered physical system and this existence does not depend on the concrete particle interactions. We refer to such modes as symmetry-determined NNMs (SD-NNMs). Hereafter, only this type of Rosenberg modes is considered.

As a rule, only a *finite* number of *individual* NNMs exist in given physical system with discrete symmetry, and they can be single out by some group-theoretical methods. In general, excitation of a nonlinear normal mode does not lead to its independent existence from other NNMs. This means, that the excitation transfers from the initially excited (primary) mode to some collection of other (secondary) modes. This collection forms the so-called *bush* of nonlinear normal modes.

Each bush represents an *exact* solution to equations of motion. As a consequence, the set of modes entering given bush is conserved in time, as well as it whole energy.

The number m of modes in the bush defines its dimension. One-dimensional bushes represent individual nonlinear normal modes by Rosenberg. Note that each Rosenberg NNM describes a *periodic* dynamical regime, while the m-dimensional bush ($m > 1$) describes *quasiperiodic* vibrations with m basis frequencies in its Fourier spectrum.

Every bush can be characterised by a certain symmetry group G which is a subgroup of the symmetry group G_0 of the considered system in equilibrium (or the group of its Hamiltonian).

Each NNM of a given bush possesses its own symmetry group. It is essential that energy transfer is possible only from the modes with lower symmetry to those with higher or equal symmetry but not vice versa. If we excite a given bush by placing energy only to one (primary) mode, this NNM must be of the lowest symmetry among all other modes of the bush[1].

The mathematical apparatus of the bush theory is based on the irreducible representations of the parent symmetry group G_0. Using this approach, the bushes of vibrational modes were studied in various nonlinear systems of different physical nature with some point and space symmetry groups [4-6, 9-11].

In [12], all one- and two-dimensional bushes of nonlinear normal modes were found in uniformly stretched single-layer graphene (space group *P6mm*) with the aid of group-theoretical methods. It is necessary to verify these results by natural experiments on graphene. However, experimental investigation of bushes of vibrational modes in microscopic systems is associated with great difficulties. In view of this, ab initio computer simulations, based on the density functional theory (DFT) [13], are very important for studying properties of these dynamical objects. In [11], DFT simulations were successfully applied for verification group-theoretical results of the bush theory for *SF₆* molecule.

In the present paper, we study nonlinear dynamics of low-dimensional bushes of nonlinear normal modes in uniformly stretched single-layer graphene (space group *P6mm*) in the framework of the density functional theory.

1. Group-theoretical results on nonlinear vibrations of the graphene lattice

We consider in-plane nonlinear vibrations in a single-layer graphene subjected to the uniform stretching. In equilibrium state, this graphene sheet possesses the space symmetry group $G_0 = P6mm$.

It is proved in the bush theory that all dynamical regimes in the physical system with discrete symmetry can be classified by subgroups of its parent group G_0. As a consequence, we must consider all subgroups G_j of the group G_0 for finding complete list of the bushes of NNMs. In this list there are bushes of different dimensions (m). Here, we restrict ourselves by studying one-dimensional bushes (they represent Rosenberg symmetry-determined modes) and two-dimensional bushes.

Displacement pattern corresponding to a given bush can be expressed as a sum of contributions from several irreducible representations (irreps) of the parent space group G_0. Every irrep is determined by two indices [14]: the wave vector in Brillouin zone and the number of irreducible representation of the symmetry group of this vector. As well as in the theory of structural phase transitions in crystals, we confine our consideration by the irreps corresponding to high-symmetry points in the Brillouin zone. As a consequence, the primitive cell of *vibrational state* is the integer times larger than that of the crystal in equilibrium. Thus, considering nonlinear oscillations of the crystal lattice, we deal with lowering of the symmetry from the group G_0 of the equilibrium state to the group G_j of vibrational state ($G_0 \rightarrow G_j$).

Group-theoretical studying of the bushes of NNMs involves two stages [15, 16]: a) construction of so-called invariant vectors of the irreps of the parent symmetry group G_0; b) construction of the basis vectors of the irreps entering mechanical representation of the group G_0.

Our group-theoretical analysis of the graphene lattice brought to the following results [12].

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[1] Note that there may be another ways for the bush excitation [7, 8].

There are three different high-symmetry points in the Brillouin zone of the graphene space group $P6mm$ [16]. They correspond to the wave vectors $k_{16} = (0,0)$, $k_{12} = \left(\frac{1}{2}, 0\right)$, and $k_{13} = \left(\frac{1}{3}, \frac{1}{3}\right)$. Four one-dimensional and two two-dimensional irreps correspond to the vector k_{16}, four three-dimensional irreps correspond to the vector k_{12}, two two-dimensional and one four-dimensional irreps are associated with the vector k_{13}.

There exist 37 different vibrational bushes corresponding to high-symmetry points in the Brillouin zone. There are 4 one-dimensional, 14 two-dimensional, 1 three-dimensional and 6 four-dimensional among them.

The atomic displacement patterns for one-dimensional bushes (they represent symmetry determined the Rosenberg nonlinear normal modes) were published in [12]. They are shown in Fig. 2-5 (the primitive cells of the vibrational states are depicted by dotted lines). Let us note that two *different* one-dimensional bushes possess the same group $P6mm$.
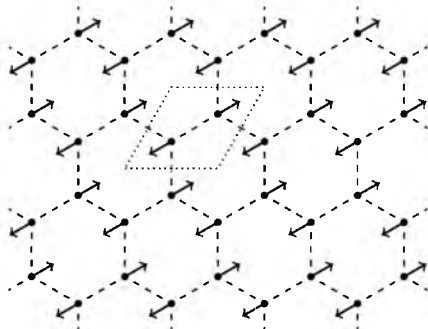

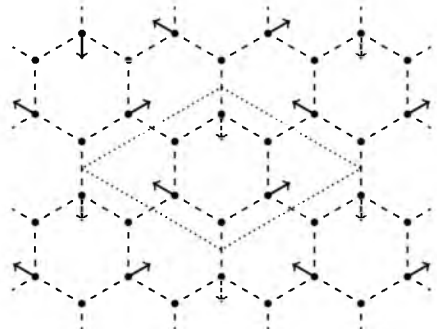**Figure 1.** One-dimensional bush with space group *Cmm2*

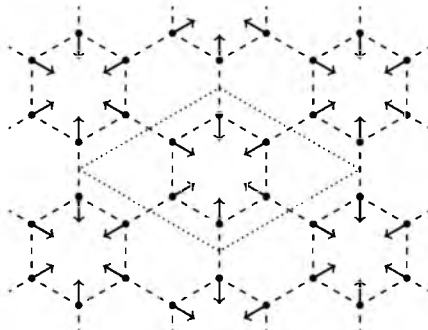**Figure 2.** One-dimensional bush with space group *P31m*

Figure 3. One-dimensional bush with space group *P6mm*
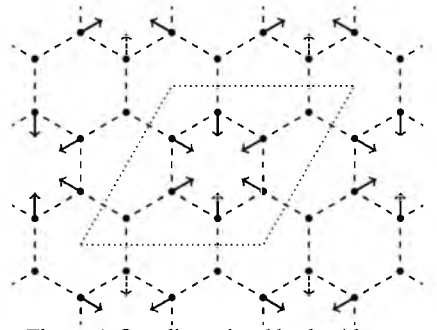

Figure 4. One-dimensional bush with space group *P6mm*

In [12], we also presented all possible in the graphene structure 14 two-dimensional bushes of NNMs.

2. Ab initio results on nonlinear vibrations of the graphene lattice

In the present paper, we verify the group-theoretical results on bushes of vibrational nonlinear normal modes in uniformly stretched graphene with the aid of ab initio methods of the density functional theory realized in Quantum Espresso package [17].

In Fig.5, we present time evolution of the Rosenberg NNM with space symmetry group Cmm2 (see Fig.1) for several amplitudes (10% uniform stretch of graphene sheet). In Fig.6, for the same NNM, the frequency-amplitude characteristics are shown for some values of stretch. From these characteristics one can conclude, that *soft type of nonlinearity* takes place for NNM depicted in Fig. 1.
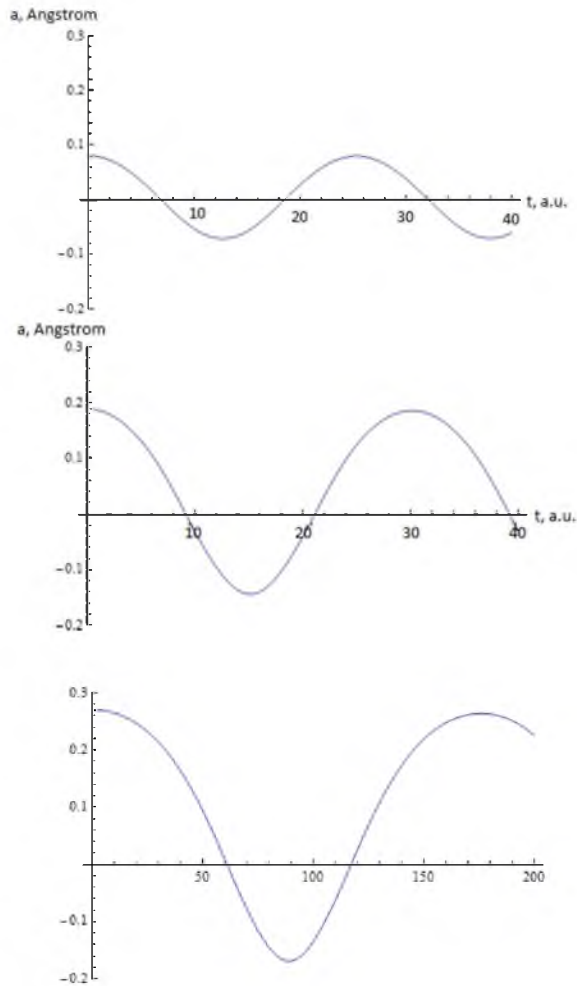
Figure 5. Time evolution of Rosenberg NNM with space symmetry group *Cmm2* for several amplitudes (10% uniform stretch of graphene sheet).
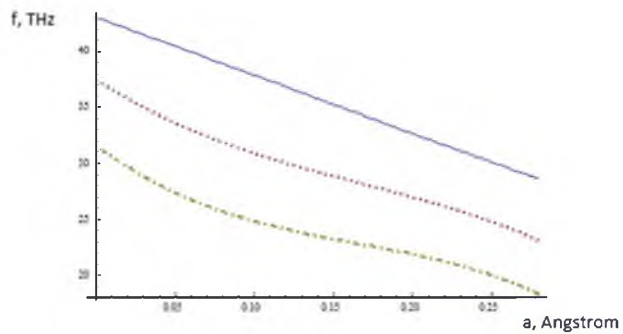

Figure 6. Amplitude-frequency characteristics of Rosenberg NNM with space symmetry group *Cmm2* for 5% (solid line), 10% (dotted line) and 15% (dot-dashed line) uniform stretch of graphene sheet

All our ab initio computer experiments confirm group-theoretical results. In particular, they show that the initial excitation of Rosenberg mode belonging to every one-dimensional bush *does not*

excite any other vibrational modes in graphene lattice. In the case of any two-dimensional bush, the initial excitation of its primary mode leads to the excitation of *only one*, predicted by group-theoretical analysis, secondary mode from the great number of all possible vibrational modes.

Conclusions

Let us point out some ways of further research of nonlinear vibrations in graphene. It is necessary to investigate:

1. The stability properties of the individual symmetry-determined Rosenberg modes, as well as bushes of NNMs with dimension m>1.

2. The influence of temperature on the dynamics of the vibrational bushes in graphene.

3. Possible ways of excitation of bushes of nonlinear normal modes. It seems that this can be done by using radiation of two lasers with appropriate polarization at close frequencies with the aim at coincidence of their beat frequency with the frequency of the nonlinear oscillations in graphene (a similar study about the excitation of discrete breathers in crystal lattice one can see in [18]).

Acknowledgments

References

[1] R.M. Rosenberg. The normal modes of nonlinear n-degree-of-freedom systems. *J. Appl. Mech.*, 1962, Vol. 29(7), p. 7–14.
[2] A.F. Vakakis, L.I. Manevich, Yu.V. Mikhlin, V.N. Pilipchuk, A.A. Zevin. *Normal Modes and Localization in Nonlinear Systems*. New York: Wiley; 1996.
[3] Yu.V. Mikhlin, K.V. Avramov. *Nonlinear Dynamics of Elastic Systems*. Moscow-Izhevsk: Regular and Chaotic Dynamics; 2010 (in Russian).
[4] G.M. Chechin, N.V. Novikova, A.A. Abramenko. Bushes of vibrational modes for Fermi-Pasta-Ulam chain. *Physica D*, 2002, Vol. 166, p. 208–238.
[5] G.M. Chechin, D.S. Ryabov, K.G. Zhukov. Stability of low-dimensional bushes of vibrational modes in the Fermi–Pasta–Ulam chains. *Physica D*, 2005, Vol. 203(3), p. 121-166.
[6] G.M. Chechin, V.P. Sakhnenko, H.T. Stokes, A.D. Smith, D.M. Hatch. Nonlinear normal modes for systems with discrete symmetry. *Int. J. Non-Linear Mech.*, 2000, Vol. 35(3), p.497-513.
[7] G.M. Chechin, V.A. Koptsik. Relation between multidimensional representations of Fedorov groups and groups of color symmetry. *Comput. Math. Appl.*, 1988, Vol. 16, pp. 521–536.
[8] V.P. Sakhnenko, G.M. Chechin. Symmetry methods and space group representations in the theory of phase transitions. *Comput. Math. Appl., 1988.* Vol. 16 (5-8), pp.453-464.
[9] G.M. Chechin, A.V. Gnezdilov, M.Yu. Zekhtser. Existence and stability of bushes of vibrational modes for octahedral mechanical systems with Lennard-Jones potential. *Int.J.Non-Linear Mech.*, 2003, Vol. 38, p.1451-1472.
[10] G.M. Chechin, K.G. Zhukov. Stability analysis of dynamical regimes in nonlinear systems with discrete symmetries. *Physica Review E*, 2006, Vol. 73, p. 036216-17.
[11] G.M. Chechin, D.S. Ryabov, S.A. Shcherbinin. Nonlinear normal mode interactions in the SF 6 molecule studied with the aid of density functional theory. *Physical Review E*, 2015, Vol. 92(1), p. 012907.
[12] G.M. Chechin, D.S. Ryabov, S.A. Shcherbinin. Nonlinear vibrational modes in graphene: group-theoretical results. *Letters on materials*, 2016, Vol. 6 (1), p. 9-15
[13] W. Kohn. Nobel Lecture: Electronic structure of matter—wave functions and density functional. *Rev. Mod. Phys.*, 1999, Vol. **71**, p. 1253-1266.
[14] O.V. Kovalev. *Representations of the Crystallographic Space Groups: Irreducible Representations, Induced Representations and Corepresentations*. Amsterdam: Gordon and Breach, Amsterdam; 1993.

[15] G.M. Chechin, V.P. Sakhnenko. Interactions between normal modes in nonlinear dynamical systems with discrete symmetry. Exact results. *Physica D*, 1998, Vol. 117(1-4), p. 43-76.

[16] G.M. Chechin. Computers and group-theoretical methods for studying structural phase transitions. *Comput. Math. Appl.*, 1989, Vol. 16(1-3), p. 255-278.

[17] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter*, 2009, Vol. 21, 395502.

[18] P.L. Hagelstein, D. Letts, D. Cravens. Terahertz difference frequency response of pdd in two-laser experiments. *J. Condensed Matter Nucl. Sci.*, 2010 Vol. 3, p. 59-76.