The COMPASS force field: validation for carbon nanoribbons.

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The COMPASS force field has been successfully applied in a large number of materials simulations, including the analysis of structural, electrical, thermal, and mechanical properties of carbon nanoparticles. This force field has been parameterized using quantum mechanical data and is based on hundreds of molecules as a training set, but such analysis for graphene sheets was not carried out. The objective of the present study is the verification of how good the COMPASS force field parameters can accurately describe the frequency spectrum of atomic vibrations of graphene, graphane and fluorographene sheets. We showed that the COMPASS force field allows to describe with good accuracy the frequency spectrum of atomic vibrations of graphene and fluorographene sheets, whose honeycomb hexagonal lattice is formed by sp² hybridization. On the other hand, the force field doesn't describe very well the frequency spectrum of graphene sheet, whose planar hexagonal lattice is formed by sp² banding. In that case the frequency spectrum of out-of-plane vibrations differs greatly from the experimental data – bending stiffness of a graphene sheet is strongly over estimated. We present the correction of parameters of out-of-plane and torsional potentials of the force field, that allows to achieve the coincidence of vibration frequency with experimental data. After such corrections the COMPASS force field can be used to describe the dynamics of flat graphene sheets and carbon nanotubes.

I. INTRODUCTION

The obtaining of the monolayer graphene membrane with the unique physical properties [1] caused the unprecedented rise in research of single and multilayer graphene sheets, graphene nanoribbons and nanoscrolls, other graphene-based and functional graphene nanostructures [2–8]. The possibility of using such structures in electronics [9, 10], optics [11], and in many other industries has been much discussed recently [5, 7, 12–16]. The remarkable properties of graphene make it one of the key components in creating nanomaterials for energy storage [10, 17, 18, 20], polymer nanocomposites [2, 21] and for medicine [22, 23].

Experimental studies of these nanostructures are difficult because of their small size. So particular attention is paid to their computer simulation, where quantum mechanics (QM) equations, molecular dynamics (MD) or molecular mechanics (MM) equations are used. QM simulation allows to consider only small-sized molecular structures, but enables to justify empirical interatomic potentials in MM/MD modelling. However, the accuracy of MD simulations depends on parametrization of the empirical potentials that describe the atomic interactions. Both experimental data and results of QM calculation used for determination of these parameters. For MM/MD modelling carbon nanofoms a variety of carbon interatomic potentials have been used. Examples of the carbon potentials are reactive empirical bond-order potential REBO/AIREBO [24–27], reactive force field ReaxFF [28], long-range carbon bond order potential LCBOP [29], an analytical bond order potential (BOP) [30], environment dependent interatomic potential (EDIP) [31], the modified embedded atom method (MEAM) potential [32], the DREIDING force field [33], Morse force field [34, 35].

It is assumed that the force field parameters should reproduce the value of mechanical moduli and vibration spectrum of nanoparticles, but the standard parameter sets of the above-mentioned force fields have been received taking into account only in-plane frequency spectrum or/and in-plane molecular mechanics. Taking into account out-of-plane vibrations made it possible to significantly improve the matching of the bending rigidity modulus and dispersion curves calculated in MD with the available experimental data and QM simulation for force fields Morse [36, 37], MEAM [38] and DREIDING [39].

A condensed-phase optimised ab-initio COMPASS force field has been developed recently [40, 41] and has been successfully applied in a large number of soft materials simulations with carbon nanostructures (see [42–49] and references in them). The force field has been parameterized using hundreds of molecules as a training set including molecules with

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FIG. 1: Structures of nanoribbons (a) graphene (C_{12}H_{2}H_{12} (of size 29.9 × 13.4Å²) and (b) graphane (C_{12}H_{14}H_{12} (of size 29.1 × 11.7Å²).
sp<sup>3</sup>- and sp<sup>2</sup>-hybridized carbon atoms, but the parameterization and validation using planner monomolecular lattice structures as graphene sheets and its modifications have not been yet performed.

The purpose of article is to checking how well force field of the COMPASS reproduces a vibration range of three nanoribbons: graphene, graphane, and fluorographene. For this we calculated the frequency spectrum and dispersion curves of these nanoribbons using the COMPASS force field, and compared them with results of ab-initio data. It was found that the force field could give an accurate reproduction of experimental spectrum lattice of sp<sup>3</sup> hybridization, such as graphene or fluorographene. However, the obtained frequency spectrum of graphene turned out to be noticeably shifted to the high-frequency region with respect to the known theoretical and experimental data for out-of-plane vibrations of carbon. We made a correction of parameters of torsional potentials, what allowed to rectify that deficiency of the COMPASS force field.

II. A MODEL OF A GRAPHENE AND GRAPHANE NANORIBBONS

Molecular nanoribbon is a narrow, straight-edged strip, cut from a single-layered molecular plane. The simplest example of such molecular plane is a graphene sheet (isolated monolayer of carbon atoms of crystalline graphite) and its various chemical modifications: graphane (fully hydrogenated on both sides graphene sheet) and fluorographene (fluorinated graphene). As is known, graphene and its modifications are elastically isotropic materials, the longitudinal and flexural rigidity of which is weakly dependent on chirality of the structure. Therefore, for definiteness, we will consider nanoribbons with the zigzag structure shown in Fig. 1 and 2.

Let us consider a rectangular ribbon cut from a flat sheet of graphene [Fig. 1(a)] and graphane [Fig. 1(b)] in the zigzag directions. The nanoribbons structure can be obtained by longitudinal translation of a transverse unit cell consisting of \(N_e = N_C + N_H\) atoms (see Fig. 2). Number of the carbon atoms in the unit cell is always multiple of two, and number of hydrogen atoms \(N_H = 2\) for graphene nanoribbon and \(N_H = N_C + 2\) for graphane. Further we use the following notation (see Fig. 2): each atom is numbered with at two-component index \(\alpha = (n, k)\), where \(n = 0, \pm 1, \pm 2, \ldots\) defines the unit cell number and \(k = 1, \ldots, N_e\) numbers atoms in the unit cell.

For numerical simulation we will use COMPASS force-field functional form [40]:

\[
E_{total} = \sum_b [k_{b,2} (b - b_0)^2 + k_{b,3} (b - b_0)^3 + k_{b,4} (b - b_0)^4] \\
+ \sum_{\theta} [k_{\theta,2} (\theta - \theta_0)^2 + k_{\theta,3} (\theta - \theta_0)^3 + k_{\theta,4} (\theta - \theta_0)^4] \\
+ \sum_\phi [k_{\phi,1} (1 - \cos \phi) + k_{\phi,2} (1 - \cos 2\phi)] \\
+ \sum_x k_x x^2 + \sum_{b,b'} k_{bb'} (b - b_0) (b' - b_0') \\
+ \sum_{b,\theta} k_{b,\theta} (b - b_0) (\theta - \theta_0) + \sum_{\theta,\theta'} k_{\theta,\theta'} (\theta - \theta_0) (\theta' - \theta'_0) \\
+ \sum_{b,\phi} (b - b_0) [k_{b,\phi,1} \cos \phi + k_{b,\phi,2} \cos 2\phi + k_{b,\phi,3} \cos 3\phi] \\
+ \sum_{\theta,\phi} (\theta - \theta_0) [k_{\theta,\phi,1} \cos \phi + k_{\theta,\phi,2} \cos 2\phi + k_{\theta,\phi,3} \cos 3\phi] \\
+ \sum_{\theta,\theta',\phi} k_{\theta,\theta',\phi} (\theta - \theta_0) (\theta' - \theta'_0) \cos \phi \\
+ \sum_{i,j} q_i q_j / r_{ij} + \sum_{i,j} \epsilon_{ij} [2(r_{ij}^0 / r_{ij})^6 - 3(r_{ij}^0 / r_{ij})^2]. \tag{1}
\]

The functions could be divided into two categories: (1) valence terms including diagonal and off-diagonal cross-coupling terms and (2) nonbonded interactions terms. The valence terms represent internal coordinates of bond \(b\), angle \(\theta\), torsion angle \(\phi\), and out-of-plane angle \(x\), and the cross-coupling terms include combinations of two or three internal
TABLE I: Values of the parameters for valence bond potential $V_1(b) = k_{b,2}(b - b_0)^2 + k_{b,3}(b - b_0)^3 + k_{b,4}(b - b_0)^4$, angle potential $V_2(\theta) = k_{\theta,2}(\theta - \theta_0)^2 + k_{\theta,3}(\theta - \theta_0)^3 + k_{\theta,4}(\theta - \theta_0)^4$ and torsional potential $V_3(\phi) = k_{\phi,1}(1 - \cos \phi) + k_{\phi,2}(1 - \cos 2\phi) + k_{\phi,3}(1 - \cos 3\phi)$. 

| Bond (sp$^2$ atoms) | $b_0$ (Å) | $k_{b,2}$ (kcal/mol·Å$^2$) | $k_{b,3}$ (kcal/mol·Å$^3$) | $k_{b,4}$ (kcal/mol·Å$^4$) |
|---------------------|-----------|-----------------|-----------------|-----------------|
| CC (sp$^2$ atoms)   | 1.4170    | 470.8361        | -627.6179       | 1327.6345       |
| CH (sp$^2$ atoms)   | 1.0982    | 372.8251        | -803.4526       | 894.3173        |
| CC (sp$^3$ atoms)   | 1.530     | 299.670         | -501.77         | 679.81          |
| CH (sp$^3$ atoms)   | 1.101     | 345.000         | -691.89         | 844.60          |
| CF (sp$^3$ atoms)   | 1.390     | 403.032         | 0               | 0               |

| Angle (sp$^3$ atoms) | $\theta_0$ (deg) | $k_{\theta,2}$ (kcal/mol·rad$^2$) | $k_{\theta,3}$ (kcal/mol·rad$^3$) | $k_{\theta,4}$ (kcal/mol·rad$^4$) |
|----------------------|------------------|-----------------|----------------|----------------|
| CCC (sp$^3$ atoms)   | 118.90           | 61.0226         | -34.9931       | 0              |
| CCH (sp$^3$ atoms)   | 117.94           | 35.1558         | -12.4682       | 0              |
| CCC (sp$^3$ atoms)   | 112.67           | 39.5160         | -7.4430        | -9.5583        |
| CCH (sp$^3$ atoms)   | 110.77           | 41.4530         | -10.6040       | 5.1290         |
| HCH (sp$^3$ atoms)   | 107.66           | 39.6410         | -12.9210       | -2.4318        |
| CCF (sp$^3$ atoms)   | 109.20           | 68.3715         | 0              | 0              |
| FCF (sp$^3$ atoms)   | 109.10           | 71.9700         | 0              | 0              |

| Torsion (sp$^3$ atoms) | $k_{\phi,1}$ (kcal/mol) | $k_{\phi,2}$ (kcal/mol) | $k_{\phi,3}$ (kcal/mol) |
|------------------------|--------------------------|--------------------------|--------------------------|
| CCCC (sp$^3$ atoms)    | 8.3667                   | 1.2000                   | 0                         |
| CCH (sp$^3$ atoms)     | 0                        | 3.9661                   | 0                         |
| HCC (sp$^3$ atoms)     | 0                        | 3                      | 0                         |
| CCC (sp$^3$ atoms)     | 0                        | 0.0514                  | -0.1430                  |
| CCH (sp$^3$ atoms)     | 0                        | 0.0316                  | -0.1681                  |
| HCH (sp$^3$ atoms)     | 0                        | 0                      | 0.1500                   |
| FCF (sp$^3$ atoms)     | 0                        | 0.0617                  | -0.1530                  |
| FCC (sp$^3$ atoms)     | 0                        | 0                      | 0.1                     |

coordinates. The nonbond interactions include a LJ-9-6 potentials for the van der Waals (vdW) term and a Coulombic potential for an electrostatic interaction.

Graphene has a flat form due to the sp$^2$ hybridization of all valence bonds [Fig. 1 (a)]. Graphane (fully hydrogenated graphene) as a two-dimensional crystal was predicted in theoretical works [50, 51] and was confirmed by experimental data in [52]. Graphane is an analogue of graphene with the unique properties [53–56]. Graphane nanoribbon is a strip with a constant width cut from a two-sized hydrogenated graphene sheet [see Fig. 1 (b), 2 (b)]. Several conformations of the graphene sheet are existed, and we consider the most energy-efficient configuration armchair, where hydrogen atoms are connected from different sides to all adjacent carbon atoms. Substitution of hydrogen atoms for fluorine atoms leads to formation of the fluorographene sheet structure (fully fluorinated graphene). In comparison with graphene, graphane and fluorographane are not two-dimensional crystal structures, but corrugated sheets with sp$^3$ hybridized carbon atoms and with atoms of hydrogen or fluorine connected to the different sides of the sheet.

For graphene nanoribbon simulation the potentials (1) with the parameters of atom with sp$^2$ hybridization should be used, and for graphane and fluorographene nanoribbon simulation – potentials with the parameters of atom with sp$^3$ hybridization. There quired parameters for interatomic interaction potentials are shown in Tabl. I. Out-of-plane angle potential $V_3(\chi) = k_{\chi}\chi^2$ appears in the Hamiltonian only for graphene nanoribbons with planar sp$^2$ valence bands: for C–C–C–C atom group $k_{\chi} = 7.1794$ kcal/mol, for C–C–C–H atoms $k_{\chi} = 4.8912$ kcal/mol. Parameters for cross-coupling interactions potentials are shown in Tables II and III. Parameters for nonvalence interactions can be found in Table IV. Parameters values for C and H atoms are taken from [40], for fluorine atom the parameters values – from force field CFF91.

Taking into consideration the noncovalent interactions of atoms only from neighboring unit cells, the Hamiltonian of a nanoribbon can be written in the following form

$$H = \sum_{n=-\infty}^{+\infty} \left[ \frac{1}{2}(\mathbf{M}\mathbf{u}_n, \mathbf{u}_n) + P(\mathbf{u}_{n-1}, \mathbf{u}_n, \mathbf{u}_{n+1}) \right],$$

where $n$ – number of the unit cell, $\mathbf{u}_n = 3N_e$-dimensional vector defining coordinates of atoms in the unit cell, $\mathbf{M}$ – the diagonal matrix of cell atomic masses, $P(\mathbf{u}_{n-1}, \mathbf{u}_n, \mathbf{u}_{n+1})$ – of the cell atom’s interaction with each other and with atoms from neighboring cells.

In the ground state each nanoribbon unit cell is obtained from the previous one by shifting by the step $a$: $\mathbf{u}_{n} = \mathbf{u}_0 + an \mathbf{e}_x$, where the unit vector $\mathbf{e}_x = \{(1, 0, 0)^N_e\}_{k=1}^{N_e}$ (nanoribbon lies along the $x$ axes). To find the ground state (the period $a$ and the coordinate vector $\mathbf{u}_0$) we should solve the minimum problem:

$$P(\mathbf{u}_0 - ae_x, \mathbf{u}_0, \mathbf{u}_0 + ae_x) \rightarrow \min : \mathbf{u}_0, a.$$
TABLE II: Values of parameters for cross-coupling bond/bond potential \( V(b, b') = k_{bb'}(b - b_0)(b' - b_0') \), bond/angle potential \( V(b, \theta) = k_{b\theta}(b - b_0)(\theta - \theta_0) \) angle/angle potential, \( V(\theta, \theta') = k_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta_0') \) and angle/angle/torsional potential \( V(\theta, \theta', \phi) = k_{\theta\theta'\phi}(\theta - \theta_0)(\theta' - \theta_0') \cos \phi \) describing the displacement of atoms in the \( n \)-th cell from their equilibrium positions. Then the Hamiltonian (2) of a nanoribbon can be written in the following form:

\[
H = \sum_{n=-\infty}^{+\infty} \left[ \frac{1}{2} \mathbf{M} \mathbf{\dot{v}}_n + U(v_{n-1}, v_n, v_{n+1}) \right],
\]

where interaction potential

\[
U(v_1, v_2, v_3) = P(u^0 - a\mathbf{e}_x + v_1, u^0 + v_2, u^0 + a\mathbf{e}_x + v_3).
\]

The Hamiltonian (4) corresponds to the equations of motion

\[
-M\ddot{v}_n = U_{v1}(v_n, v_{n+1}, v_{n+2}) + U_{v2}(v_{n-1}, v_n, v_{n+1}) + U_{v3}(v_{n-2}, v_{n-1}, v_n),
\]

where the matrices \( \mathbf{B}_1 = U_{v1}, \mathbf{B}_2 = U_{v2}, \mathbf{B}_3 = U_{v3} \) and the matrices of partial derivatives are

\[
U_{v_i,v_j} = \frac{\partial^2 U}{\partial v_i \partial v_j}(0, 0, 0), \quad i, j = 1, 2, 3.
\]

The solution of the systems of linear equations (6) can be written in the standard form of the wave

\[
v_n = A\mathbf{w} \exp(i\omega t - i\omega t),
\]

where \( A \) – amplitude, \( \mathbf{w} \) – eigenvector, \( \omega \) is the phonon frequency with the dimensionless wave number \( q \in [0, \pi] \). Substituting Eq. (7) into Eq. (6), we obtain the eigenvalue problem

\[
\omega^2 \mathbf{M} \mathbf{w} = \mathbf{C}(q) \mathbf{w},
\]

where Hermitian matrix

\[
\mathbf{C}(q) = \mathbf{B}_1 + \mathbf{B}_2 e^{i q} + \mathbf{B}_2^* e^{-i q} + \mathbf{B}_3 e^{2i q} + \mathbf{B}_3^* e^{-2i q}.
\]

Using the substitution \( \mathbf{w} = \mathbf{M}^{-1/2} \mathbf{e} \), problem (8) can be rewritten in the form

\[
\omega^2 \mathbf{e} = \mathbf{M}^{-1/2} \mathbf{C}(q) \mathbf{M}^{-1/2} \mathbf{e},
\]

where \( \mathbf{e} \) is the normalized eigenvector, \( (\mathbf{e}, \mathbf{e}) = 1 \).

Thus, for obtaining the dispersion curves \( \omega_j(q) \), it is necessary to find the eigenvectors of the Hermitian matrix (9) of a size \( 3N_e \times 3N_e \) for each fixed wave number \( 0 \leq q \leq \pi \). As a result, we obtain \( 3N_e \) branches of the dispersion curve \( \{\omega_j(q)\}_{j=1}^{3N_e} \).

### III. DISPERSION EQUATION

Let us introduce a \( 3N_e \)-dimensional vector

\[
v_n = \{u_{n,k}^0 - u_{n,k}^0\}_{k=1}^{N_e} \]

The numerical solution shows that the ground state calculated by the COMPASS force field agrees well with the experimental values (the equilibrium values of bond lengths, valence angles and torsional angles are the same). Let us verify the coincidence of the of the nanoribbon frequency spectrum with the experimental data. To accomplish this, we find the dispersal curve of the nanoribbon.

The problem (3) is solved by the conjugate gradient method. The numerical solution shows that the ground state calculated by the COMPASS force field agrees well with the experimental values (the equilibrium values of bond lengths, valence angles and torsional angles are the same). Let us verify the coincidence of the of the nanoribbon frequency spectrum with the experimental data. To accomplish this, we find the dispersal curve of the nanoribbon.

\[
\text{bond/bond} \quad k_{bb'} \text{ (kcal/mol·Å²)}
\]

| bond/bond       | \( k_{bb'} \) (kcal/mol·Å²) |
|-----------------|-----------------------------|
| C–C/CC (first neighboring, sp³) | 68.2856 |
| C–C/CH (first neighboring, sp³) | 1.0795 |
| C–C/CC (second neighboring, sp³) | 53.0 |
| C–C/CH (second neighboring, sp³) | -6.2741 |
| CH/CH (first neighboring, sp³) | -1.7077 |
| CH/CH (second neighboring, sp³) | 3.3872 |
| CC/CH (first neighboring, sp³) | 5.3316 |

\[
\text{bond/angle} \quad k_{b\theta} \text{ (kcal/mol·Å·rad)}
\]

| angle/angle       | \( k_{b\theta} \) (kcal/mol·Å·rad²) |
|-------------------|----------------------------------|
| C–C–C–C–C (sp³ atoms) | 0 |
| C–C–C–C–H (sp² atoms) | 0 |
| H–C–C–C–H (sp² atoms) | 0 |
| C–C–C–C–C (sp³ atoms) | -0.1729 |
| C–C–C–C–H (sp³ atoms) | -1.3999 |
| H–C–C–C–H (sp³ atoms) | -0.4825 |

\[
\text{angle/angle/torsional} \quad k_{b\theta\phi} \text{ (kcal/mol·Å·rad³)}
\]

| angle/angle/torsional | \( k_{b\theta\phi} \) (kcal/mol·Å·rad³) |
|------------------------|-------------------------------------|
| C–C–C–C–C–C–C–C–C (sp³) | 0 |
| C–C–C–C–H–C–C–C–H (sp³) | 0 |
| H–C–C–C–H–C–C–H (sp³) | 0.3598 |
| C–C–C–C–C–C–C–C–C (sp³) | -2.2045 |
| C–C–C–C–H–C–C–C–H (sp³) | -1.6164 |
| H–C–C–C–C–H–C–C–C–H (sp³) | -12.564 |
TABLE III: Values of parameters for cross-coupling bond/torsion potential $V(b, \phi) = (b - b_0)[k_{b\theta,1} \cos \phi + k_{b\theta,2} \cos 2\phi + k_{b\theta,3} \cos 3\phi]$. and cross-coupling angle/torsion potential $V(\theta, \phi) = (\theta - \theta_0)[k_{\theta\phi,1} \cos \phi + k_{\theta\phi,2} \cos 2\phi + k_{\theta\phi,3} \cos 3\phi]$.

| Bond/torsion | $k_{b\theta,1}$ (kcal/mol-Å) | $k_{b\theta,2}$ (kcal/mol-Å) | $k_{b\theta,3}$ (kcal/mol-Å) |
|-------------|-----------------|-----------------|-----------------|
| C-C/C-C/C-C (sp² atoms, central bond) | 27.5989 | -2.3120 | 0 |
| C-C/C-C/C-H (sp² atoms, central bond) | 0 | -1.1521 | 0 |
| C-H/C-C/C-H (sp² atoms, central bond) | 0 | 4.8228 | 0 |
| C-C/C-C/C-C (sp² atoms, terminal bond) | -0.1185 | 6.3204 | 0 |
| C-C/C-C/C-H (sp² atoms, terminal bond) | 0 | -6.8958 | 0 |
| C-H/C-C/C-H (sp² atoms, terminal bond) | 0 | -0.4669 | 0 |
| C-H/C-C/C-H (sp² atoms, terminal bond) | 0 | -0.6890 | 0 |
| C-C/C-C/C-C (sp² atoms, central bond) | -17.787 | -7.1877 | 0 |
| C-C/C-C/C-H (sp² atoms, central bond) | -14.879 | -3.6581 | -0.3138 |
| C-C/C-C/C-H (sp² atoms, terminal bond) | -14.261 | -0.5322 | -0.4864 |
| C-C/C-C/C-C (sp³ atoms, central bond) | -0.0732 | 0 | 0 |
| C-C/C-C/C-H (sp³ atoms, central bond) | 0.2486 | 0.2422 | -0.0925 |
| C-H/C-C/C-H (sp³ atoms, terminal bond) | 0.0814 | 0.0591 | 0.2219 |
| C-H/C-C/C-H (sp³ atoms, terminal bond) | 0.2130 | 0.3120 | 0.0777 |

| Angle/torsion | $k_{\theta\phi,1}$ (kcal/mol-rad) | $k_{\theta\phi,2}$ (kcal/mol-rad) | $k_{\theta\phi,3}$ (kcal/mol-rad) |
|---------------|-----------------|-----------------|-----------------|
| C-C/C-C/C-C | 1.9767 | 1.0239 | 0 |
| C-C/C-C/C-H | 0 | 2.5014 | 0 |
| C-C/C-C/C-C | 0 | 2.7147 | 0 |
| H-C/C-H/C-C | 0 | 2.4501 | 0 |
| C-C/C-C/C-C | 0.3886 | -0.3139 | 0.1389 |
| C-C/C-C/C-H | -0.2454 | 0 | -0.1136 |
| C-C/C-C/C-C | 0.3113 | 0.4516 | -0.1988 |
| H-C/C-H/C-C | -0.8085 | 0.5569 | -0.2466 |

TABLE IV: Values of parameters for LJ-9-6 potential $V(r) = \epsilon[2(r_0/r)^9 - 3(r_0/r)^6]$ and charge valence bond increments $q_1, q_2$.

| atom atom | $\epsilon$ (kcal/mol) | $r_0$ (Å) |
|-----------|-----------------|-----------------|
| C C (sp² atoms) | 0.0680 | 3.9150 |
| C H (sp² atoms) | 0.0271 | 3.5741 |
| H H (sp² atoms) | 0.0182 | 2.7147 |
| C H (sp² atoms) | 0.0040 | 3.854 |
| H H (sp³ atoms) | 0.0230 | 2.878 |
| F F (sp² atoms) | 0.0598 | 3.200 |
| C H (sp³ atoms) | 0.0215 | 3.526 |
| C F (sp³ atoms) | 0.0422 | 3.600 |

| atom atom | $q_1$ (e) | $q_2$ (e) |
|-----------|-----------------|-----------------|
| C C (sp² atoms) | 0 | 0 |
| C H (sp² atoms) | -0.1268 | +0.1268 |
| C C (sp³ atoms) | 0 | 0 |
| C H (sp³ atoms) | -0.053 | +0.053 |
| C F (sp³ atoms) | +0.25 | -0.25 |

IV. GRAPHENE FREQUENCY SPECTRUM

Let us consider a wide nanoribbon (C$_{64}$H$_{2}$)$_{\infty}$ (the nanoribbon width $D = 68.79$Å, the period $a = 2.412$Å, the number of atoms in unit cell $N_c = 66$) to find the frequency spectrum of graphene sheet. Figure 3 shows the $3N_c$ dispersion curves of the nanoribbon. The plane structure of the nanoribbon allows to divide its vibrations into two classes: in-plane vibrations, when the atoms are always stayed in the plane of the nanoribbon and out-of-plane vibrations when the atoms are shifted orthogonal to the plane. Two third of the branches corresponds to the vibrations orthogonal to the plane (out-of-plane vibrations), whereas only one third corresponds to the vibrations orthogonal to the plane (out-of-plane vibrations), when the atoms are shifted along the axes $z$.

The nanoribbon frequency spectrum consists of two intervals $[0, 1911]$ and $[3086.6, 3099.2]$ cm$^{-1}$ (the second high-frequency interval corresponds to the edge vibrations of the valence bonds C–H). Discarding frequencies of the edge vibrations from the Figure 3, we can conclude that graphene sheet spectrum consists of the one frequency interval $[0, \omega_m]$ with the maximum frequency $\omega_m = 1911$ cm$^{-1}$. Spectrum of out-of-plane vibrations also consists of the one frequency interval $[0, \omega_o]$ with the maximum frequency $\omega_o = 1420$ cm$^{-1}$. The frequency spectrum of graphene sheet has been studied theoretically and experimentally in [57–60]. The maximum frequency of in-plane vibrations is $\omega_{m} = 1600$ cm$^{-1}$, the maximum frequency of out-of-plane vibrations is $\omega_{o} = 868$ cm$^{-1}$. Thus, the graphene frequency spectrum calculated
by the COMPASS force field does not coincide with experimental valuations. The frequency spectrum of in-plane vibrations is 1.2 times more and the frequency spectrum of out-of-plane vibrations is 1.6 times more than experimental valuations, i.e. the bending stiffness of the nanoribbon is 2.5 times more.

V. GRAPHANE AND FLUOROGRAPHENE FREQUENCY SPECTRUM

Let us consider a wide nanoribbon \((C_{64}H_{66})_\infty\) (nanoribbon width \(D = 68.4\,\text{Å}\), period \(a = 2.522\,\text{Å}\), number of atoms in unit cell \(N_e = 130\)) to find the frequency spectrum of graphane sheet. Figure 4 shows the dispersion curves of the nanoribbon. As can be seen from the figure, the nanoribbon frequency spectrum consists of three intervals: low-frequency interval \([0, 757.8]\), middle-frequency interval \([987.5, 1543.6]\) and narrow high-frequency interval \([2921.8, 2966.6]\) cm\(^{-1}\). On average, carbon atoms account for 79.5% of the vibration energy in the first frequency interval, for 48.1% in the second frequency interval and only for 8.4% in the third. It enables us to say that the low-frequency spectrum corresponds to the vibrations, in which the valence bond C–H and the valence angles C–C–H remain nearly unchanged, the middle interval corresponds to the vibrations, in which the valence corners C–C–H begin to take part in the vibration, and the third interval corresponds to the vibrations of the hard valence bonds C–H (the number of such modes always coincide with the number of hydrogen atoms).

Since we have considered as sufficiently broad nanoribbon, the analysis of its dispersal curves suggests that the frequency spectrum of linear vibrations of the endless graphene sheet \((CH)_\infty\) consists of three continuous intervals \([0, 756], [987, 1544]\) and \([2922, 2967]\) cm\(^{-1}\). Thus, the graphene sheet has two gaps in the frequency spectrum: narrow low-frequency \([756, 987]\) and wide high-frequency \([1544, 2922]\) cm\(^{-1}\). Such structure of the frequency spectrum is in good agreement with the results of first-principles calculations. Quantum calculations suggest the high-frequency spectrum intervals \([0, 806], [950, 1350]\) and \([2733, 2783]\) cm\(^{-1}\) [61].

If the hydrogen atoms H change to the heavier deuterium atoms D, the three-zoned structure of the frequency spectrum will remain, but all the frequencies will shift down. The frequency spectrum of graphene sheet \((CD)_\infty\) also consists of three intervals \([0, 620], [813, 1503], [2130, 2200]\) cm\(^{-1}\) (the high-frequency interval most strongly shifts down). The stronger increase in the weight of the connected atoms, the change of hydrogen atoms for fluorine atoms, causes the stronger frequency shift and the closure of the gaps.
Figure 5 shows the dispersion curves for fluorographene nanoribbon (C_{64}F_{66})_∞. The thick red curves correspond to oscillations localized at the nanoribbon edges.

Figure 5 shows the dispersion curves for fluorographene nanoribbon (C_{64}F_{66})_∞. The figure clearly shows that the nanoribbon frequency spectrum of linear vibrations consists of two intervals: [0, 1183.6] and [1252.0, 1589.3] cm^{-1}. The analysis of the dispersion curves suggests that the frequency spectrum of linear vibrations of the endless fluorographene sheet (CF)_∞ consists of two continuous intervals [0, 1184] and [1252, 1589] cm^{-1} with the narrow gap between them. Such structure of the frequency spectrum is also in good agreement with the results of quantum chemical calculations [61]. Quantum calculations suggest the frequency spectrum intervals [0, 1039] and [1106, 1312] cm^{-1}.

The structure of the frequency spectrum can be obtained also from the analysis of the frequency spectrum density of atomic thermal vibrations of finite length nanoribbon. Let us consider the graphene nanoribbon (C_{12}H_{14})_{99}C_{10}H_{22} with size 25.09 x 1.17 nm², consisted of N = 100 unit cells.

The dynamics of the thermalized nanoribbon is described by the system of Langevin equations

\[
M_{n,k} \ddot{u}_{n,k} = -\frac{\partial H}{\partial u_{n,k}} - \Gamma M_{n,k} + \xi_{n,k}, \quad n = 1, 2, ..., N, \quad k = 1, 2, ..., N_c, \quad (10)
\]

where \( H \) – Hamiltonian of the nanoribbon, created by the COMPASS force field, \( u_{n,k} = (u_{n,k,1}, u_{n,k,2}, u_{n,k,3}) \) – 3D coordinate vector of atom \((n, k)\), \( M_{n,k} \) – mass of this atom, \( \Gamma = 1/t_r \) – damping coefficient (relaxation time \( t_r = 0.4 \) ps). Normally distributed random forces \( \xi_{n,k} = (\xi_{n,k,1}, \xi_{n,k,2}, \xi_{n,k,3}) \) normalized by conditions

\[
\langle \xi_{n,k,i}(t_1)\xi_{m,l,j}(t_2) \rangle = 2M_{n,k}\Gamma k_B T \delta_{nm}\delta_{kl}\delta_{ij}\delta(t_1 - t_2),
\]

where \( k_B \) – Boltzmann’s constant, \( T \) – thermostat temperature.

The system of equations of motion (10) was integrated numerically during the time \( t = 10 \) ps (the stationary state of the plane nanoribbon serves as a starting point). During this time, the nanoribbon and the thermostat came to balance. Then its interaction with the thermostat was switched off and the dynamics of isolated thermalized nanoribbon was considered. The density of the frequency spectrum of atomic vibrations \( p(\omega) \) was calculated via fast Fourier transform.

The density of the frequency spectrum of atomic vibrations of the graphene and fluorographene nanoribbons at \( T = 300 \) K is presented in Fig. 6. The figure clearly shows that the profile of density \( p(\omega) \) coincides well with the forms of the dispersal curves. The low-frequency gap is clearly visible for the graphene nanoribbon, and the narrow gap in the frequency spectrum is clearly visible for the fluorographene nanoribbon.

VI. CORRECTIONS OF THE COMPASS FORCE FIELD FOR GRAPHENE SHEET

The simulation shows that the COMPASS force field does not describe well the frequency spectrum of graphene sheet. The frequency spectrum of out-of-plane vibrations differs strongly from the experimental values.
of valence angles, the third potential \( V_3(\chi) = k_\chi \chi^2 \) – out-of-plane deformations. The potentials of dihedral angles \( V_4 \) and \( V_5 \) are described by a single potential of the torsional angle \( V_i(\phi) = k_{\phi,1}(1-\cos \phi) + k_{\phi,2}(1-\cos 2\phi) + k_{\phi,3}(1-\cos 3\phi) \).

The specific value of the parameter \( k_\chi = 5.7537 \text{ kcal/mol} \) can be found from the frequency spectrum of small-amplitude oscillations of a sheet of graphite [62]. For the potentials of dihedral angles \( V_4 = c_4(\phi - \pi)^2 \) and \( V_5 = c_5(\phi^3 \) according to the results of Ref. [63] coefficient \( c_4 \) is close to \( k_\chi \), whereas \( c_5 \ll c_4 \). So for the second derivative of the torsion potential we have

\[
V''_i(\phi) = k_{\phi,1} + 4k_{\phi,2} - V''_5(\phi) = 0, \\
V''_i(\pi) = -k_{\phi,1} + 4k_{\phi,2} = V''_5(\phi) = 2c_4 = 2k_\chi,
\]

therefore coefficients \( k_{\phi,2} = k_\chi / 4 = 1.4384 \text{ kcal/mol}, \) \( k_{\phi,1} = -4k_{\phi,2} = -5.7537 \text{ kcal/mol} \).

Now let us consider the COMPASS force field with the new parameters values

\[
k_\chi = -k_{\phi,1} = 5.7537, \quad k_{\phi,2} = 1.4384 \text{ kcal/mol}. \quad (12)
\]

Since all the parameters for the off-diagonal interactions bond/torsion, angle/torsion and angle/angle/torsion have become undefined after such a modification, remove them away from the force field. Then we find the frequency value of the graphene sheet via that modification of the force field.

Figure 8 shows the dispersal curves of the graphene nanoribbon \((C_6H_{12})_{\infty}\) calculated via the modified COMPASS force field. From figure, we can conclude that now the spectrum of the graphene sheet consists of the frequency interval of in-plane vibrations [0, 1823] and the frequency interval of out-of-plane vibrations [0, 876] cm\(^{-1}\), that is in good agreement with the results described in [57–60]. Thus, modification (12) of the COMPASS force field allows to take into account the flexural mobility of graphene sheet (the initial set of parameters led to an over estimation of the bending stiffness)

VII. CONCLUSION

The study shows that the COMPASS force field allows to describe with good accuracy the frequency spectrum of atomic vibrations of graphene and fluorographene sheets, whose honeycomb hexagonal lattice is formed by sp\(^3\) valence bands. On the other hand, the force field doesn’t describe very well the frequency spectrum of graphene sheet, whose planar hexagonal lattice is formed by sp\(^2\) valence bands. In that case the frequency spectrum of out-of-plane vibrations differs greatly from the experimental data (bending stiffness of a graphene sheet is strongly overestimated). The correction (12) of parameters of out-of-plane and torsional potentials of the force field was made, and that allows to achieve the coincidence of vibration frequency with experimental data. After such corrections the COMPASS force field can be used to describe the dynamics of flat graphene sheets and carbon nanotubes.
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[1] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Electric field effect in atomically thin carbon films. Science 306:666-669. https://doi.org/10.1126/science.1102896

[2] Mohan VB, Lau K, Hui D, Bhattacharyya D (2018) Graphene-based materials and their composites: A review on production, applications and product limitations. Composites B 142:200-220. https://doi.org/10.1016/j.compositesb.2018.01.013

[3] Akinwande D, Brennan CJ, Bunch JS et al (2017) A review on mechanics and mechanical properties of 2D materials-Graphene and beyond. Extreme Mechanics Letters 13:42-77. http://dx.doi.org/10.1016/j.eml.2017.01.008

[4] Harik V (2018) Mechanics of Carbon Nanotubes. Fundamentals, Modelling and Safety. Academic Press. https://doi.org/10.1016/C2016-0-00799-4

[5] Feng W, Long P, Feng Y, Li Y (2016) Two-Dimensional Fluorinated Graphene: Synthesis, Structures, Properties and Applications. Adv. Sci. 3, 1500413.

[6] Chen T, Cheung R (2016) Mechanical properties of graphene. In: Aliofkhazraei M, Ali N, Milne WI, Ozkan CS, Mitura S, Gervasoni JL (eds.) Graphene Science Handbook: Mechanical and Chemical Properties. CRC Press, London. pp. 3-15

[7] Bhimamanapati GR, Lin Z, Meunieret V et al (2015) Recent advances in two-dimensional materials beyond graphene. ACS Nano 9:11509-115399. https://doi.org/10.1021/acsnano.5b05556

[8] Cao G (2014) Atomistic Studies of Mechanical Properties of Graphene. Review. Polymer 6:2404-2432. https://doi.org/10.3390/polymer6092404

[9] Li X, Tao L, Chen Z, Fang H, Li X, Wang X, Xu J-B, Zhu H (2017) Graphene and related two-dimensional materials: Structure-property relationships for electronics and optoelectronics. Appl. Phys. Rev. 4, 021306 (2017). http://dx.doi.org/10.1063/1.4983646

[10] Geim AK, Novoselov KS (2007) The rise of graphene. Nat. Mater. 6:183-191. https://doi.org/10.1038/nmat1849

[11] Brar VW, Sherrott MC, Jarivala D (2018) Emerging photonic architectures in two-dimensional opto-electronics. Chem. Soc. Rev. 47:6824-6844. https://doi.org/10.1039/c8cs00206a

[12] Khan ME, Khan MM, Cho MH (2018) Recent Progress of Metal-Graphene Nanostructures in Photocatalysis. Nanoscale 10: 9427-9440. https://doi.org/10.1039/C8NR03500H

[13] Ferrari AC, Bonaccorso F, Fal’ko V, et al (2015) Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. Nanoscale 7:4598-5062. https://doi.org/10.1039/c4nr05600a

[14] Xiang Q, Cheng B, Yu J (2015) Graphene-Based Photocatalysts for Solar-Fuel Generation. Angew. Chem., Int. Ed. 54:11350-11366. https://doi.org/10.1002/anie.201411096

[15] Ryu J, Lee E, Lee K, Jang J (2015) A Graphene Quantum Dots Based Fluorescent Sensor for Anthrax Biomarker Detection and Its Size Dependence. J. Mater. Chem. B 3:4865-4870 https://doi.org/10.1039/CSTB00585J

[16] Soldano C, Mahmoud A, Dujardin E (2010) Production, properties and potential of graphene. Carbon 48:2127-2150. https://doi.org/10.1016/j.carbon.2010.01.058

[17] Li X, Zhi L (2018) Graphene hybridization for energy storage applications. Chem. Soc. Rev. 47:3189-3216. https://doi.org/10.1039/C7CS00871F

[18] Siahlo AI, Poklonski NA, Lebedev AV, Lebedeva IV, Popov AM, Vycko SA, Knizhnik AA, Lazovik YE (2018) Structure and energetics of carbon, hexagonal boron nitride, and carbon/hexagonal boron nitride single-layer and bilayer nanoscrolls. Phys. Rev. Mater. 2, 036001. https://doi.org/10.1103/PhysRevMaterials.2.036001

[19] Azadmanjiri J, Srivastava VK, Kumar P, Nikzad M, Wang J, Yu A (2018) Two- and three-dimensional graphene-based hybrid composites for advanced energy storage and conversion devices. J. Mater. Chem. A 6, 702-734. https://doi.org/10.1039/C7TA08748A

[20] Sunnardikanto GK, Maruyama I, Kusakabe K (2017) Storing-hydrogen processes on graphene activated by atomic-vacancies. International Journal of Hydrogen Energy 42:23691-23697. https://doi.org/10.1016/j.ijhydene.2017.01.115

[21] Stankovich S, Dikin DA, Dommett GH, Kohlhaas KM, Zimney KM, Stach EA, Piner RD, Nguyen ST, Ruoff RS (2006) Graphene-based composite materials. Nature 442:282-286. https://doi.org/10.1038/nature04969

[22] Tan KH, Sattari S, Donskyi IS, Cuellar-Camacho JL, Cheng C, Schwibbert K, Lippitz A, Unger WES, Gorbushina A, Adeli M, Haag R (2018) Functionalized 2D nanomaterials with switchable binding to investigate graphene-bacteria interactions. Nanoscale 10:9525-9537. https://doi.org/10.1039/c8nr01347k

[23] Cheng C, Li S, Thomas A, Kotov NA, Haag R (2017) Functional Graphene Nanomaterials Based Architectures: Biointeractions, Fabrications, and Emerging Biological Applications. Chem. Rev. 117:1826-9537. https://doi.org/10.1021/acschemrev.1c00347k

[24] Brenner DW (1990) Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films. Phys. Rev. B 42:9458-9471. https://doi.org/10.1103/PhysRevB.42.9458

[25] Stuart SJ, Tutein AB, Harrison JA (2000) A reactive potential for hydrocarbons with intermolecular interactions. J. Chem. Phys. 112:4672. https://doi.org/10.1063/1.481208

[26] Brenner DW, Shenderova OA, Harrison JA, Stuart SJ, Ni B, Sinnott SB (2002) A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. J. Phys.: Condens. Matter 14:783-802. https://doi.org/10.1088/0953-8984/14/4/312

[27] Lindsay L, Briodo DA (2010) Optimized Tersoff and Brenner empirical potential parameters for lattice dynamics and phonon thermal transport in carbon nanotubes and graphene. Phys. Rev. B 81:205441. https://doi.org/10.1103/PhysRevB.81.205441

[28] Senfile TP, Hong S, Islam MM and et al (2016) The ReaxFF reactive force-field: Development, applications and future Directions. npj Comput. Mater. 2:15011 (2016). https://doi.org/10.1038/njpcompumat.2015.11

[29] Los JH, Ghiringhelli LM, Meijer EJ, Fasolino A (2005)
