2D supracrystals as a promising materials for planar nanoacoustoelectronics

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Abstract. The elastic and acoustic properties of 2D carbon supracrystals are simulated within the scope of modified density functional theory. The central and non-central force constants of carbon atoms and the corresponding elastic moduli, have been calculated in order to determine the velocities of elastic wave propagation in 2D supracrystalline nanoallotropes. It is shown that in $sp^2$ nanoallotropes and graphene these velocities are approximately of the same value, and in $sp^3$ nanoallotropes they are much less than in graphene.

1. Introduction
The supracrystals are defined by us as the supra atomic periodic structures where the atoms in nodes of a structure are replaced by their symmetric complexes (Fig.1).

Fig. 1. 2D supracrystalline structures and the form of the corresponding supracrystalline cells. Here X is the symbol of the chemical element, and the order of the indexes behind the parentheses is following: the first index determines the type of supracell, the next indexes describe the cell’s of enclosing. At first, the numbers of sides of the nodal cell are shown, than the same are shown for the surrounding cells (if there are). Numbers in parentheses indicate the form of a polygon in the cell’s center.
The possibility of such structures existence is shown in [1]. Some of the structures and similar to them have been investigated in [2–11]. By a random structure searching Pickard and Needs [5] found many structures, one of which was the chiral framework structure (CFS). Note, that there are a certain relationship between CFS and \((X)_{664}\) structure. One of the framework structures consist of boron and nitrogen atoms at first synthesized in [8, 9] is our \((X)_{44}\) structure. Here we summarized these previous results in order to show the common character of 2D supracrystalline structures.

In this paper, the estimations for electric and energetic properties of 2D supracrystals consist of carbon, silicon, boron, nitrogen etc. atoms are also adduced. Our paper is devoted to the mechanical and acoustic properties of supracrystals. Note, that mechanical properties of nanoscale objects are studied worse than their electrical ones. Nevertheless, one can find the papers devoted to the mechanical properties of carbon systems [12–16]. In [16] the elastic constants of graphene are obtained using the Harris bond-orbital method. In our terms the graphene is a special case of 2D supracrystalline carbon \(sp^2\) nanoallotropes. Therefore, we have a right to use the checked but slightly modified scheme [15, 16] to study the mechanical and acoustic properties of carbon 2D supracrystals.

Moreover, using this scheme one can find the agreement between the numerical estimations of the diamond phonon frequencies made in [14] and the experimental data on Raman scattering [17–19] and lattice (phonon) thermal conductivity [20].

2. Calculation of the constants of central and non-central interaction for the carbon atoms in 2D supracrystals

The idea of approach is as follows: the constants of the central and non-central interactions are to express from the system energy per one atom which, in its turn, is to express from the metallic energy and the covalent energy [15, 16].

With the notations adopted in [15] the covalent energy

\[
V_2 = \eta_2 \frac{\hbar^2}{m_0 l^2},
\]

where \(\eta_2 = -3,26\) for \(sp^3\) hybridization and \(-3,22\) for \(sp^3\) hybridization of an electron wave function, \(\hbar\) is the reduced Planck constant, \(m_0\) is the free electron mass, \(l\) is the bond length. In [15] the metallic energy was calculated from the energy of \(s\)- and \(p\)-states but in the case of supracrystals we really do not have any simple way to find them. Therefore, the particularity of approach used here is that metallic energy was calculated from energy per one atom [15]:

\[
E_{atom} = -\frac{n_2}{3} V_2 \left[ 1 + \frac{10}{3} \left( \frac{V_1}{V_2} \right)^2 \right],
\]

where \(n_2\) is a number of nearest atoms in 2D structures. Knowing \(V_2\) and \(E_{atom}\) one can find \(V_1\) from (2) as

\[
|V_1| = \sqrt{\frac{3}{10n_2} \left[ \frac{1}{V_2} \left( 3\left|E_{atom}\right| - n_2 \right) \right]^\frac{1}{2}}.
\]

Using the software package Abinit-5.8.4 [21] within the scope of the density functional theory [22] in Hartree–Fock approximation the values of \(l\) and \(E_{atom}\) were calculated for the supracrystals considered. To generate \(k\)-points in Brillouin zone the Monkhorst–Pack algorithm [22] was used. As a mathematical approximation the Broyden method of iterations was used. The cutoff energy was chosen for \(k = 6\).

Defining \(l\), \(E_{atom}\) and calculating \(|V_1|, |V_2|\) from Eqs. (1), (3) we can find the constants of the central (\(\alpha\)) and the non-central (\(\beta\)) interactions [15] as
\[ \alpha = \frac{2}{l^2} |V_2| \left[ 1 - \frac{10}{3} \left( \frac{V_1}{V_2} \right)^2 \right] \]

(4)

\[ \beta = \frac{\lambda}{3} \alpha. \]

(5)

Here \( \lambda \) is the coefficient determined through the matrix elements of the covalent energy operator between the corresponding atomic wave function of \( s- \) and \( p- \) states \([14, 15, 23]\). For 2D structures of graphene type in \([14, 15]\) is adopted that \( \lambda = 0.66 \). In the case of 2D supracrystals we used the value of \( \lambda = 0.69 \) from \([23]\). The results of calculations are summarized in the Table 1.

**Table 1. Parameters and the results of the calculations for graphene and carbon 2D supracrystals**

| Parameter       | (C)\(_{6}\) graphene | (C)\(_{44}\) | (C)\(_{63(6)}\) | (C)\(_{63(12)}\) | (C)\(_{664}\) | (C)\(_{634}\) |
|-----------------|------------------------|-------------|-----------------|-----------------|-------------|-------------|
| Hybridization   | \( sp^2 \)             | \( sp^2 \)  | \( sp^3 \)      | \( sp^2 \)      | \( sp^2 \)  | \( sp^3 \)  |
| \( n_2 \)       | 3                      | 3           | 4               | 3               | 3           | 4           |
| \( l, \text{Å} \) | 1.42                   | 1.43        | 1.86            | 1.71            | 1.56        | 2.17        |
| \( |E_{\text{atom}}|, \text{eV} \) | 13.5        | 12.9          | 14.2            | 14.7            | 11.3        | 13.3        |
| \( |V_2|, \text{eV} \)  | 12.3                   | 12.1        | 7.10            | 8.50            | 10.2        | 5.20        |
| \( |V_1|, \text{eV} \)  | 2.08                   | 1.70        | 2.75            | 3.98            | 1.83        | 2.73        |
| \( \alpha, \text{N/m} \) | 177                    | 177         | 3.27            | 25.1            | 120         | 3.47        |
| \( \beta, \text{N/m} \) | 38.9                   | 40.8        | 0.75            | 5.80            | 27.6        | 0.80        |

Note: The results of calculations for graphene (C)\(_{6}\) are cited from \([15]\).

3. **Calculation of the elastic moduli for carbon 2D supracrystals**

The expressions for elastic moduli of 2D crystalline structure of 6mm symmetry class (graphene-like system) versus the constants of the central and non-central interactions have been obtained in \([16]\) and are of the form

\[
\begin{align*}
    c_{11} &= \frac{1}{\sqrt{3}} \left( 4\alpha + \beta + 18 \frac{\alpha \beta}{4\alpha + \beta} \right), \\
    c_{12} &= \frac{1}{\sqrt{3}} \left( 4\alpha + \beta - 18 \frac{\alpha \beta}{4\alpha + \beta} \right).
\end{align*}
\]

(6)

Obtain the corresponding expressions for (X)\(_{44}\) supracrystalline structure of 4mm symmetry class (Fig. 2).
Let the origin of coordinates is placed in “zeroth” atomic complex. Then the expressions for the energy of central $W_C$ and non-central $W_{NC}$ interactions take the form [16]

$$W_C = \frac{a}{d^2} \sum_{i=1}^{4} \left( R_{0i}^2 - r_{0i}^2 \right)^2,$$

$$W_{NC} = \frac{\beta}{d^2} \sum_{i,j>1} \left( R_{0i} R_{0j} - r_{0i} r_{0j} \right)^2.$$

Here $d$ is the length of supracell rib (it may be expressed via the bond length), where $R_{0i} = r_{0i} + \delta r_{0i}, \delta r_{0i} = u_0^i d + v_{0j}$ is the displacement of the $i$-th atomic complex under the lattice deformation. The coordinates of displacement radius-vector end $u_{0i}$ and $v_{0i}$ along $x_1$ and $x_2$ axes accordingly are of the form

$$u_{01} = u' - \frac{\sqrt{2}}{2} d e_{xx} + \frac{\sqrt{2}}{4} d e_{xy},$$

$$u_{02} = u' + \frac{\sqrt{2}}{2} d e_{xx} + \frac{\sqrt{2}}{4} d e_{xy},$$

$$u_{03} = u' + \frac{\sqrt{2}}{2} d e_{xx} - \frac{\sqrt{2}}{4} d e_{xy},$$

$$u_{04} = u' - \frac{\sqrt{2}}{2} d e_{xx} - \frac{\sqrt{2}}{4} d e_{xy},$$

$$v_{01} = v' + \frac{\sqrt{2}}{2} d e_{yy} - \frac{\sqrt{2}}{4} d e_{xy},$$

$$v_{02} = v' - \frac{\sqrt{2}}{2} d e_{yy} + \frac{\sqrt{2}}{4} d e_{xy},$$

$$v_{03} = v' - \frac{\sqrt{2}}{2} d e_{yy} + \frac{\sqrt{2}}{4} d e_{xy},$$

$$v_{04} = v' - \frac{\sqrt{2}}{2} d e_{yy} - \frac{\sqrt{2}}{4} d e_{xy},$$

where $u'$ and $v'$ are the inner displacements, $e_{xx}, e_{yy}, e_{xy}$ are the components of the strain tensor.
Taking into account (8) we’ll expend Eq. (7) in powers of \(u_0\) and \(v_0\) neglecting terms above the second order. Then we’ll minimize the elastic energy \(W = W_C + W_{NC}\) with respect to inner displacements considering that \(\partial W/\partial u' = \partial W/\partial v' = 0\). It allows us to get the expression for the elastic energy density \(w = W/S\) as a function of \(\alpha, \beta, e_{xx}, e_{yy}, e_{xy}\) where \(S = d^2\) is an area per one supracell. This expression may be compared with the corresponding expression for two-dimensional structure of 4mm symmetry class [24]:

\[
w = \frac{1}{2} \lambda_{xxyy} \left(e_{xx}^2 + e_{yy}^2\right) + \lambda_{xxyy} e_{xx} e_{xy} + 2\lambda_{xxyy} e_{xy}^2.
\]  

So far as in (9) \(\lambda_{xxxx} = c_{11}, \lambda_{xxyy} = c_{12}, \lambda_{xxyy} = c_{33}\) [25], the expressions for non-zero components of elastic moduli tensor for (X)\(_{44}\) type of 2D supracrystal can be written as

\[
c_{11} = \frac{4(2\alpha + 3\beta)}{(1 + \sqrt{2})^2}, \quad c_{12} = \frac{4(2\alpha - \beta)}{(1 + \sqrt{2})^2}, \quad c_{33} = \frac{2\alpha + \beta}{(1 + \sqrt{2})^2}.
\]  

4. Elastic waves in 2D supracrystals: the velocities of propagation and pure modes

Consider the peculiarities of elastic waves propagation in 2D supracrystals regarding them as an infinite two-dimensional continuum where only in-plane displacements of the particles are possible. Love waves and other types of shell waves are excluded from the consideration here.

In general, along an arbitrary direction \(X'\) (Fig. 2) only one quasi-longitudinal and two quasi-transverse elastic waves can propagate. These waves satisfy to Green-Christoffel equation [26]

\[
\rho_2 v^2 u_\alpha = \lambda_{\alpha\beta\delta} a_\beta a_\delta u_\gamma,
\]  

where \(\rho_2\) is the two-dimensional (in this case) medium density, \(v\) is phase velocity of the wave, \(u_\alpha\) and \(u_\gamma\) are the components of the particles displacement, \(\lambda_{\alpha\beta\delta}\) is the tensor of elastic moduli, \(a_\beta\) and \(a_\delta\) are the elements of the direction cosines matrix-column:

\[
\begin{pmatrix}
a_{11} \\
a_{12}
\end{pmatrix} = \begin{pmatrix}
\cos \varphi \\
\sin \varphi
\end{pmatrix}.
\]  

The velocities of quasi-longitudinal and quasi-transverse elastic waves are the roots of a corresponding characteristic equation

\[
|\lambda_{\alpha\beta\delta} a_\beta a_\delta - \rho_2 v^2| = 0
\]  

and depends on the elastic moduli, density of the crystal and the direction cosines. A similar problem was solved successfully for three-dimensional crystals. Moreover, there are computer programs which allow to construct 3D surfaces of phase velocities for the elastic waves propagating in these crystals [27–29]. They also may be used for 2D lines of phase velocities construction in 2D crystals. Propagation directions for pure longitudinal and pure transverse elastic waves correspond to the extreme values of the phase velocities and are perpendicular to the velocities lines at the extremes points [30].

The analytical methods for propagation directions calculation of pure modes for elastic waves were suggested in [31–36]. Their application to the effective elastic moduli in the case of pure longitudinal and pure transverse waves in 2D crystal yields to the following expressions:

- for the 4mm symmetry class

\[
\begin{align*}
\lambda'_{111} &= (\sin^4 \varphi + \cos^4 \varphi)c_{11} + 2\sin^2 \varphi \cos^2 \varphi (c_{12} + 2c_{33}), \\
\lambda'_{121} &= (\cos^4 \varphi + \sin^4 \varphi)c_{12} + 2\sin^2 \varphi \cos^2 \varphi (c_{11} - c_{12} - c_{33}),
\end{align*}
\]

\[
\varphi = n\frac{\pi}{4}, \quad n = 0, 1, 2, ..., 7.
\]
– for the 6mm symmetry class

\[ \lambda'_{1111} = c_{11}, \quad \lambda'_{2121} = \frac{1}{2}(c_{11} - c_{12}). \]  

(15)

The propagation velocities of pure longitudinal and pure transverse elastic waves accordingly may be defined from the expressions

\[ v_L = \sqrt{\lambda'_{1111}s}, \quad v_T = \sqrt{\lambda'_{2121}s}, \]  

(16)

where \( s = \rho_2^{-1} \) is a specific surface of 2D crystal. Its values for carbon 2D supracrystals, in comparison with graphene, are presented in Table 2. In the equations written there \( N_A \) is the Avogadro number, \( \mu = 0.012 \) kg/mol is molar mass for carbon, \( l \) is bond length.

| Symbol of structure | Formula | Specific surface, \( s \times 10^6 \text{ m}^2/\text{kg} \) |
|---------------------|---------|----------------------------------|
| (C)\(_6\) graphene   | \( s = \frac{3\sqrt{3} N_A l^2}{2 \mu} \) | 2.63 |
| (C)\(_{64}\)         | \( s = \frac{1}{2} (1 + \sqrt{3})^2 \frac{N_A l^2}{\mu} \) | 2.99 |
| (C)\(_{63(6)}\)     | \( s = \frac{4\sqrt{3}}{3} \frac{N_A l^2}{\mu} \) | 4.01 |
| (C)\(_{63(12)}\)    | \( s = \frac{\sqrt{3}}{6} (2 + \sqrt{3})^2 \frac{N_A l^2}{\mu} \) | 5.79 |
| (C)\(_{664}\)        | \( s = \frac{\sqrt{3}}{12} (3 + \sqrt{3})^2 \frac{N_A l^2}{\mu} \) | 3.94 |
| (C)\(_{634}\)        | \( s = \frac{\sqrt{3}}{6} (1 + \sqrt{3})^2 \frac{N_A l^2}{\mu} \) | 5.09 |

Table 2. Specific surface for carbon 2D structures

The phase velocities for elastic waves in 2D supracrystal of type (C)\(_{64}\) and graphene constructed with the computer program used are shown in Fig. 3. Our program is based on the solution of Green-Christoffel equation. In this figure you can see that in (C)\(_{64}\) structure belonging to 4mm symmetry class there are four directions (over each 45°) in which pure modes of elastic waves can propagate. Graphene as well as others 2D supracrystals belonging to 6mm symmetry class is acoustically isotropic two-dimensional medium.
Fig. 3. The phase velocities lines for longitudinal (a) and transverse (b) elastic waves in 2D supracrystals (C\textsubscript{44}) and graphene (b).

The results of calculations by formulas (14)–(16) for longitudinal and transverse velocities (\(v\textsubscript{L}\) and \(v\textsubscript{T}\), accordingly) in carbon 2D structures are represented in Table 3. The lower and upper values of the velocities range correspond to pure longitudinal and pure transverse waves propagating at the angles \(\phi_1 = 0\) and \(\phi_2 = 45^\circ\) to the \(x_1\) axis.

Table 3. Characteristics of the elastic waves in carbon 2D structures

| Parameter   | (C\textsubscript{b}) graphene | (C\textsubscript{44}) | (C\textsubscript{63}(6)) | (C\textsubscript{63}(12)) | (C\textsubscript{664}) | (C\textsubscript{634}) |
|-------------|-------------------------------|----------------------|---------------------------|---------------------------|----------------------|----------------------|
| \(c_{11}\), N/m | 533                          | 328                  | 9.84                      | 75.7                      | 361                  | 10.5                 |
| \(c_{12}\), N/m | 331                          | 215                  | 6.15                      | 47.1                      | 226                  | 6.52                 |
| \(c_{33}\), N/m |                               | 68                   |                           |                           |                      |                      |
| \(v\textsubscript{L}\), km/s | 37.4                          | 31.3–31.9            | 6.30                      | 20.9                      | 37.7                | 7.30                 |
| \(v\textsubscript{T}\), km/s | 29.5                          | 13.0–14.3            | 5.00                      | 16.5                      | 29.8                | 5.80                 |

5. Conclusions

The calculated Young modulus \(E\) for graphene in this paper is 267 N/m. In [37, 38] and [39] was obtained 235 N/m and 312 N/m, respectively. Thus, the method of the nanostructures study is successful and its application to supracrystals is justified.

The force constants which would describe the interaction of carbon atoms in 2D supracrystals depend on their structure and may differ each other by a factor of tens. We see that \(sp^3\) nanoallotropes unlike \(sp^2\) nanoallotropes have the least values of the force constants so far so all four their valence electrons are bonded in the plane of 2D supracrystals by strong \(\sigma\)-bonds. Accordingly, the covalent energy in \(sp^3\) nanoallotropes is higher (less by modulus) then in \(sp^2\) nanoallotropes although their...
metallic energy is the same of order, and formulas (4), (5) give that the constants \( \alpha \) and \( \beta \) are less, than in \( sp^2 \) allotropes.

As it follows from Fig. 3 and Table 3, the velocities of elastic waves propagation in graphene are nearly twice higher their values for the bulk elastic waves in a diamond [40]. The velocities of elastic waves in 2D supracrystals of \((C)_{44}\) and \((C)_{664}\) types are close to them. But due to small value of \( c_{33} \) compared with \( c_{11} \) and \( c_{12} \) the velocity of pure transverse wave in \((C)_{44}\) structure are essentially less than in graphene and \((C)_{664}\) structure. The velocities of elastic waves in \((C)_{63(12)}\) structure are characterized by some less values. As for 2D carbon \( sp^3 \) nanoallotropes, the velocities of elastic waves propagation in these structures are less than in \( sp^2 \) nanoallotropes in several times due their much worse elastic characteristics.

The calculated values of force constants, elastic moduli and propagation velocities for elastic waves in carbon 2D supracrystals should be considered as estimations. For more accurate values the experimental data on lattice parameters, bond lengths and elastic moduli of corresponding structures are required. Nevertheless, these results do seem quite useful. We believe that the possibility to change within wide limits the structural, electric and mechanical characteristics of 2D nanoscale materials consist of the same basic chemical element can stimulate the work on their synthesis.

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