The phonon dispersion of graphene

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ABSTRACT
In frame of De Launay model we calculated phonon dispersion of graphene in ΓM direction using radial and tangential force constants for first four neighbor atoms. Calculated phonon dispersion is in satisfactory agreement with experimental phonon spectra of graphite. In long wave approximation we estimated elastic modulus of graphene in comparison with experimental results for graphite and carbon nanotube.

Keywords: *De Launay model, phonon spectra of graphene, crystal structure, dynamical matrix, radial force constant, tangential force constant, elastic constant*

1. INRODUCTION

Several models applied to description of dynamical matrix of graphene [1-3]. The expressions for elements of dynamical matrix in De Launay model were described for carbon nanotubes and used for estimations of elastic constant, Young modulus, and Poisson`s ratio [1] from the Raman frequencies. In frame of Born model Falcovsky suggested elements of dynamical matrix via force constants of graphite on first three neighbor atoms in framework Born-von Karman model [2]. Using dynamical matrix elements Falcovsky calculated phonon dispersion of graphene in high-symmetry directions but did not compare with experimental phonon dispersion of graphite.

Two-dimensional crystal structure of graphene shown in Fig.1. It has two sublattices: red balls belong to one sublattice, and blue balls belong to another sublattice. Absolute values of translation vectors $\vec{a}_1$ and $\vec{a}_2$ are $a = a_0\sqrt{3}$ where $a_0 = 1.42$ Ådistance between nearest atoms is. Apparently, in above mentioned papers [1, 2] authors built the reciprocal lattice of graphene similarly to three-dimensional graphite lattice. In Fig. 2 shown first Brillouin zone of graphene. For graphite the distance between high-symmetry point Γ-M is $2\pi/a\sqrt{3}$. But in our opinion, due to the linear chain of atoms in X direction, in graphene the distance between high-symmetry point Γ-M is π/a (see Fig. 1). According to this assumption, we calculated phonon dispersion of graphene in X direction.

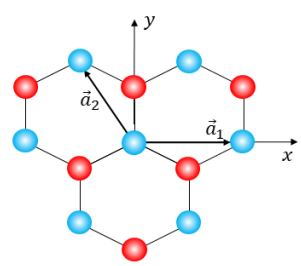

Figure 1 Crystal structure of graphene layer. There are two atoms in unit cell.

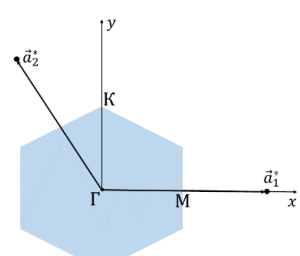

Figure 2 First Brillouin zone of graphene.

2. DYNAMICAL MATRIX OF GRAPHENE

Graphene has two atoms in its unit cell with three degrees of freedom. Therefore, graphene matrix is formed with six rows and six columns.
Dynamical matrix for propagation of waves in X and Y directions has the form:

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$$\begin{bmatrix} D_{xx}^{AA} & D_{xx}^{AB} & 0 & 0 & 0 & 0 \\ D_{xx}^{AB^*} & D_{xx}^{AA} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{yy}^{AA} & D_{yy}^{AB} & 0 & 0 \\ 0 & 0 & D_{yy}^{AB^*} & D_{yy}^{AA} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{zz}^{AA} & D_{zz}^{AB} \\ 0 & 0 & 0 & 0 & D_{zz}^{AB^*} & D_{zz}^{AA} \end{bmatrix}$$

In frame of De Launay model we derived expressions for the elements of dynamical matrix accounting interaction in first four neighbor atoms Equation (1). There are:

$$\begin{aligned} D_{xx}^{AA} &= \tfrac{3}{2}\alpha_1 + \tfrac{3}{2}\beta_1 + 2\alpha_2\{1-\cos(aq_x)\} \\ &\quad +(\alpha_2+3\beta_2)\left\{1-\cos\left(\tfrac{1}{2}aq_x\right)\right\} \\ &\quad +\tfrac{3}{2}\alpha_3 + \tfrac{3}{2}\beta_3 + 3\alpha_4 + 3\beta_4; \\ D_{xx}^{AB} &= -\beta_1 - \left(\frac{3}{2}\alpha_1 + \frac{1}{2}\beta_1\right)\cos\left(\frac{1}{2}aq_x\right) \\ &\quad -\beta_3 - \left(\frac{3}{2}\alpha_3 + \frac{1}{2}\beta_3\right)\cos(aq_x) \\ &\quad -\left(\frac{3}{14}\alpha_4 + \frac{25}{14}\beta_4\right)cos\left(\frac{1}{2}aq_x\right) \\ &\quad -\left(\frac{27}{14}\alpha_4 + \frac{1}{14}\beta_4\right)\cos\left(\frac{3}{2}aq_x\right) \\ &\quad -\left(\tfrac{6}{7}\alpha_4 + \tfrac{8}{7}\beta_4\right)\cos(aq_x)\,; \\ D_{yy}^{AA} &= \tfrac{3}{2}\alpha_1 + \tfrac{3}{2}\beta_1 + 2\beta_2\{1-\cos(aq_x)\} \\ &\quad +(\alpha_2+3\beta_2)\left\{1-\cos\left(\frac{1}{2}aq_x\right)\cos\left(\frac{\sqrt{3}}{2}aq_y\right)\right\} \\ &\quad +\tfrac{3}{2}\alpha_3 + \tfrac{3}{2}\beta_3 + 3\alpha_4 + 3\beta_4; \\ D_{yy}^{AB} &= -\alpha_1 - \left(\tfrac{1}{2}\alpha_1 + \tfrac{3}{2}\beta_1\right)\cos\left(\tfrac{1}{2}aq_x\right) \\ &\quad -\left(\tfrac{1}{2}\alpha_3 + \tfrac{3}{2}\beta_3\right)\cos(aq_x) \\ &\quad -\alpha_3 - \left(\frac{25}{14}\alpha_4 + \frac{3}{14}\beta_4\right)\cos\left(\frac{1}{2}aq_x\right) \\ &\quad -\left(\tfrac{1}{14}\alpha_4 + \tfrac{27}{14}\beta_4\right)\cos\left(\tfrac{3}{2}aq_x\right) \\ &\quad -\left(\tfrac{8}{7}\alpha_4 + \tfrac{6}{7}\beta_4\right)\cos(aq_x); \\ D_{zz}^{AA} &= 3\gamma_1 + 2\gamma_2\{1-\cos(aq_x)\} \\ &\quad +4\gamma_2\left\{1-\cos\left(\tfrac{1}{2}aq_x\right)\right\} + 3\gamma_3 + 6\gamma_4; \\ D_{zz}^{AB} &= -\gamma_1\left\{2\cos\left(\tfrac{1}{2}aq_x\right)+1\right\} - \gamma_3\{2\cos(aq_x)\} \\ &\quad -2\gamma_4\left\{\cos\left(\tfrac{1}{2}aq_x\right) + \cos(aq_x) + \cos\left(\tfrac{3}{2}aq_x\right)\right\} \end{aligned} \tag{1}$$

Where α_i is radial force constant, β_i is tangential force constant (in plane), γ_i is tangential force constant (out plane), i =1, 2, 3, 4.

For calculation of phonon dispersion of graphene we adopted force constants from paper [4], which shown in Table 1. Calculated phonon dispersion for graphene in X direction plotted in Fig. 3 in comparison with experimental data for graphite [5, 6]. We can conclude, that calculated phonon dispersion curves are in satisfactory coincidence with experimental values of phonon frequencies of graphite.

Table 1. Force constants for carbon nanotubes (N/m) [4]

Shell number	Radial α_i	Tangential in plane β_i	Tangential out plane γ_i
1	365.0	245.0	98.2
2	88.0	-23.3	-4.0
3	30.0	-52.5	1.5
4	-19.2	22.9	-5.8

From the expressions for dynamical matrix in longwave approximation ($\boldsymbol{q}\to 0$) we derived formulas Equation (2) for elastic constants of graphene:

$$\begin{aligned} c_{11} &= \frac{a^2\rho}{m}\left(\frac{9}{16}\alpha_1 + \frac{3}{16}\beta_1 + \frac{27}{8}\alpha_2 \right. \\ &\quad \left. +\tfrac{9}{8}\beta_2 + \tfrac{9}{4}\alpha_3 + \tfrac{3}{4}\beta_3 + \tfrac{257}{112}\alpha_4 + \tfrac{219}{112}\beta_4\right); \\ c_{11} - c_{12} &= \tfrac{a^2\rho}{m}\left(\tfrac{3}{8}\alpha_1 + \tfrac{9}{8}\beta_1 + \tfrac{9}{4}\alpha_2 + \tfrac{27}{4}\beta_2 \right. \\ &\quad \left. +\tfrac{3}{2}\alpha_3 + \tfrac{9}{2}\beta_3 + \tfrac{219}{56}\alpha_4 + \tfrac{257}{56}\beta_4\right) \\ c_{44} &= \tfrac{a^2\rho}{m}\left(\tfrac{3}{4}\gamma_1 + \tfrac{9}{2}\gamma_2 + 3\gamma_3 + \tfrac{17}{4}\gamma_4\right). \end{aligned} \tag{2}$$

Where m=12.0107 u is atomic mass of carbon, $\rho = 2.266\ g/cm^3$ is density of graphite.

We calculated by these expression elastic constants of graphene via the radial and tangential force constants which suggested in [4] (see Table 1). The results of calculations are given in Table 2. For comparison, the experimental data for graphite and carbon nanotube are given in Table 2.

Table 2. Elastic constants for graphite, carbon nanotube and graphene (10^9 N/m^2)

	C_{11}	C_{12}	C_{44}
Experiment for graphite [7]	106	18	0.035
Carbon nanotube [1]	84.45	-18.89	-
Graphene [2]	86	18	0.57
Graphene [this work]	123.9	70.9	10.8

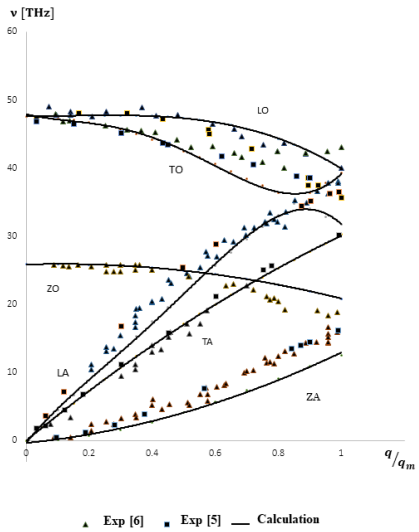

Figure 3. Calculated phonon dispersion for graphene in X direction. For comparison, experimental data for graphite is shown.

Calculated value of C_{11} agrees satisfactorily with experimental data for graphite [7]. Calculated C_{12} has same order of magnitude with the corresponding experimental value for graphite. Authors of [1] satisfactorily calculated only C_{11} although they used same set of force constants. The elastic constant C_{11} of graphene calculated by Falcovsky [2] agree in order of magnitude with the experimental values for graphite. Also C_{12} coincides with corresponding experimental values for graphite. We can explain this coincidence by fact that he used in calculations force constants for graphite.

CONCLUSIONS

We have suggested expressions for elements of dynamical matrix for calculations of the phonon dispersion in X direction. The phonon dispersion curves calculated in assumption that for graphene the distance between high-symmetry point Γ-M is π/a agree satisfactorily with experimental phonon dispersion for graphite. Calculated value of elastic constant C_{11} for graphene agrees satisfactorily with experimental data for graphite.

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REFERENCES

[1] A. Charlier, Mc. E. Rae, M. F. Charlier, A. Spire, S. Forster, Lattice dynamics study of zigzag and armchair carbon nanotubes, Phys. Rev. B, 57 (1998), pp. 6689-6696. https://doi.org/10.1103/PhysRevB.57.6689

[2] L. A. Falcovsky, Symmetry constraints on phonon dispersion in graphene, Physics Letters A. 372 (2008), pp. 5189-5192. https://doi.org/10.1016/j.physleta.2008.05.085

[3] D. Gray, A. McCaughan, B. Mookerji, Physics for Solid State Applications, 2009.

[4] R. A. Jishi, L. Venkatarm, M. S. Dresselhause, G. Dresselhause, Chemical Physics Letter, 209 (1993), pp. 77-82. https://doi.org/10.1016/0009-2614(93)87205-H

[5] J. Maultzsch et al, Phonon dispersion of graphite by inelastic X-ray scattering, Phys.Rev. B, 76 (2007), 035439. https://doi.org/10.1103/PhysRevB.76.035439

[6] S. Siebentritt, R. Pues, K. H. Rieder, Surface phonon dispersion in graphite and a lanthanum graphite intercalation compound, Phys.Rev. B, 55 (1997), pp. 7927-7937. https://doi.org/10.1103/PhysRevB.55.7927

[7] O. L. Blakslee, D. G. Proctor et al, Elastic constant of compression-annealed pyrolytic graphite, Journal of Applied Physics, 41 (1970), pp. 3373-3382. https://doi.org/10.1063/1.1659428