A theory of flexural modes in graphene

I.O. Raikov\textsuperscript{1}, D.A. Conyuh\textsuperscript{2}, A.N. Ipatov\textsuperscript{3,1}, D.A. Parshin\textsuperscript{3,1}

\textsuperscript{1}St.Petersburg Academic University, 199034 Saint-Petersburg, Russia
\textsuperscript{2}Ioffe Institute, 194021 Saint-Petersburg, Russia
\textsuperscript{3}Peter the Great St.Petersburg Polytechnic University, 195251 Saint-Petersburg, Russia

E-mail: dmitry.a.parshin@gmail.com

Abstract. We present a theory of flexural modes in graphene. The theory is based on the idea of negative springs in the second coordination circle between next nearest neighbours. As a result these negative springs change the dispersion law of vibrational modes in graphene from phonon-like linear dispersion $\omega \propto q$ to a flexural kind dispersion $\omega \propto q^2$, when the elastic modulus of the lattice goes to zero. At this point positive springs of the first shell are completely compensated by the negative springs which are $1/6$ of the positive springs. Phonons cannot propagate through such a soft lattice with zero Young modulus and sound velocities, but flexural modes can.

1. Introduction

One of the most important topics in condensed matter nano-physics today is the study of such an unusual material as crystalline graphene. It is a monoatomic, two-dimensional hexagonal carbon lattice where each atom is connected by $sp^2$ valence forces with its three nearest neighbours. Graphene due to its unique and unusual Briliouine zone construction possesses exceptional mechanic, physical, and optical properties [1, 2], which are now used in many applications. For example, it has a record-breaking thermal conductivity value. It is very important for heat export in nano-devices. As it is well known, the heat transfer in dielectrics and semiconductors is due to the vibration of the crystalline lattice. Usually, these vibrations are phonons which propagate through the crystal with a constant velocity of sound $v$ and have a linear dispersion law $\omega = vq$ and a linear contribution to the density of states $g(\omega) \propto \omega$. The phonon modes in graphene are polarized in the graphene plane. But besides phonon modes graphene probably has another type of vibrational modes — flexural modes with perpendicular polarization to the graphene plane. Flexural modes have a quadratic dispersion law $\omega = \beta q^2$ and at small wave vectors $q$ it results in the density of states $g(\omega) \propto \text{const}$. Due to the symmetry, the flexural modes are not mixed with phonon modes at all [3]. Their contribution to the heat transfer is necessary to take into account. They also interact with electrons and holes in graphene and their contribution is very important for electronic properties.

If the existence of phonon modes is obvious and can be easily explained, the nature of flexural modes in graphene is still under discussion. In many works it is generally accepted that the flexural modes have their quadratic dispersion relation $\omega \propto q^2$ only due to symmetry of the 1-d and 2-d system [4, 3, 5]. However, this approach can not give the microscopic mechanism of occurrence of flexural modes. In this paper, we present a theory of flexural modes in graphene which is based on the idea of negative springs in the system.
2. Dispersion relation of flexural modes in a crystalline graphene lattice

![Graphene lattice diagram](image)

**Figure 1.** Sketch of a hexagonal lattice of graphene. Blue and red colors show the nodes of two different crystal sublattices. The elementary cell with two carbon atoms and translation vectors of the lattice $a_1$ and $a_2$ is shown in gray (left part). First (1–3 atoms) and second (4–9 atoms) coordination circle shown by numeration of atom (right part).

We will consider vibrations of atoms from two different crystal sublattices with the amplitudes of their displacements $V_{n,m}$ and $U_{n,m}$ respectively along the direction of the two translation vectors

$$a_1 = \frac{3}{2}a_e x + \frac{\sqrt{3}}{2}a_e y, \quad a_2 = \frac{3}{2}a_e x - \frac{\sqrt{3}}{2}a_e y,$$

as it shown on Fig. 1. Index $n$ denote the position of the atom along the direction of the vector $a_1$, index $m$ – along the direction of the vector $a_2$. Let $\kappa_1$ and $\kappa_2$ be the force constants of the atom’s interactions with its neighbours from the first and second coordination circles, consisting of three and six atoms respectively. Considering the atom masses equal, we write the motion equations:

$$\frac{d^2 U_{n,m}}{dt^2} = \Omega_1^2 \left(U_{n+1,m} + U_{n-1,m} + U_{n,m+1} + U_{n,m-1} - 3U_{n,m}\right) + \Omega_2^2 \left(U_{n+1,m} + U_{n-1,m} + U_{n,m+1} + U_{n,m-1} + 3U_{n,m}\right),$$

$$\frac{d^2 V_{n,m}}{dt^2} = \Omega_1^2 \left(V_{n+1,m} + V_{n-1,m} + V_{n,m+1} + V_{n,m-1} - 3V_{n,m}\right) + \Omega_2^2 \left(V_{n+1,m} + V_{n-1,m} + V_{n,m+1} + V_{n,m-1} + 3V_{n,m}\right),$$

in which $\Omega_1^2 = \omega_1^2/m_1$ and $\Omega_2^2 = \omega_2^2/m_2$. Solution of equations on displacements (2) can be found in the form of plane displacement waves

$$U_{n,m} = U_0 e^{i(\omega t - \mathbf{q}(\mathbf{n}_1 + \mathbf{m}_2))}, \quad V_{n,m} = V_0 e^{i(\omega t - \mathbf{q}(\mathbf{n}_1 + \mathbf{m}_2))},$$

and the system (2) is rewritten as follows:

$$U_{n,m} \left(\omega^2 - 3\Omega_1^2 - 2\Omega_2^2(3 - f(q))\right) + V_{n,m} \Omega_1^2 A(q) = 0,$$

$$V_{n,m} \left(\omega^2 - 3\Omega_1^2 - 2\Omega_2^2(3 - f(q))\right) + U_{n,m} \Omega_2^2 A^*(q) = 0,$$

where the functions $A(q) = (1 + e^{i\mathbf{a}_1 \mathbf{q}} + e^{i\mathbf{a}_2 \mathbf{q}})$ and $f(q) = \cos(\mathbf{a}_1 \mathbf{q}) + \cos(\mathbf{a}_2 \mathbf{q}) + \cos((\mathbf{a}_1 - \mathbf{a}_2) \mathbf{q})$. 

The equations (4) have a nontrivial solution when its determinant is zero. After some simple manipulations, we obtained the dispersion relation of flexural modes in graphene in the model of two coordinate circles:

$$\omega^2(q) = \Omega_1^2 \left( 3 \pm \sqrt{3 + 2f(q)} \right) + 2\Omega_2^2 (3 - f(q)).$$  \hspace{1cm} (5)

The "critical" ratio of the force constants $$\kappa_1$$ and $$\kappa_2$$ can be acquired in the limit of small values of $$aq \ll 1$$ for the acoustic branch near zero frequency. The optical branch frequencies are always nonzero, so they are not affected by this requirement. In the first approximation, the function $$f(q)$$ is equal to

$$f(q) \approx 3 - \frac{9}{4} a^2 q^2 + \frac{27}{64} a^4 q^4,$$  \hspace{1cm} (6)

and the frequency of the acoustic branch near zero is determined by the equation

$$\omega^2(q) \approx \frac{3}{4} \left( \Omega_1^2 + 6\Omega_2^2 \right) a^2 q^2 - \frac{3}{64} \left( \Omega_1^2 + 18\Omega_2^2 \right) a^4 q^4.$$  \hspace{1cm} (7)

With the relationship $$\kappa_2 = -\kappa_1/6$$, $$\kappa_2 < 0$$ between the force constants, the $$q$$-quadratic part of (7) vanishes, yielding the dispersion law of flexural modes:

$$\omega^2_f(q) = \frac{3}{32} \Omega_1^2 a^4 q^4.$$  \hspace{1cm} (8)

This is easy to understand physically. With the critical ratio of force constants $$\kappa_2 = -\kappa_1/6$$ the flexural Young modulus of the graphene sheet is equal to zero. Flexural phonons cannot propagate in such a soft medium, where their Young modulus and speed of sound are zero. They are replaced by flexural waves with a different, more complicated dispersion law. Close to the critical state, this can be phenomenologically written as

$$\omega^2(q) = \alpha q^2 + \beta q^4,$$  \hspace{1cm} (9)

where $$\alpha \propto \kappa_2 + \kappa_1/6$$, and $$\beta \sim 1$$. In the flexural transition point $$\alpha = 0$$. From this, follows that in the case of low frequencies $$\omega < \sqrt{\alpha}$$ these vibrations are phonons with a linear dispersion law. The speed of sound is $$v \propto \sqrt{\alpha}$$ and reaches zero in the critical point. On higher frequencies, they are flexural waves with a quadratic dispersion law. It should be noted that the $$q$$-quadratic part in the dispersion law (7) can only be canceled out by considering even further reaching negative links.

If only one coordination circle (nearest neighbours) is taken into account (which is equivalent to the requirement $$\kappa_2 = 0$$), the equation (5) reduces to

$$\omega^2_1(q) = \Omega_1^2 \left( 3 \pm \sqrt{3 + 2f(q)} \right).$$  \hspace{1cm} (10)

As it can be shown, the dispersion law of the flexural modes $$\omega_f(q)$$ corresponds to $$\omega^2_1(q)$$ in the case of "critical" relationship between force constants $$\kappa_2 = -\kappa_1/6$$:

$$\omega^2_f(q) = \Omega_1^2 \left( 2 \pm \sqrt{3 + 2f(q)} + \frac{f(q)}{3} \right) = \frac{1}{6\Omega_1^2} \omega^4_1(q).$$  \hspace{1cm} (11)

As a result, taking into account the interactions with the atoms from the second coordination circle drastically changes the dispersion law of the flexural modes in graphene and, in the case of the "critical" relationship between the force constants, results in a shift from a linear dispersion law (resulting from the interactions with the atoms in the first coordination circle) to a quadratic
one. In Fig. (2) one can see that our result (11) and the dispersion of flexural modes in graphene from [3] has a good agreement. We cannot answer the question of what is the true dispersion law for flexural modes in graphene. It is determined by the ratio between the force constants $\kappa_1$ and $\kappa_2$, which needs to be determined either from experiment or from a deeper theoretical understanding.

Using Eqs. (10)–(11) for the dispersion law of flexural modes of the graphene sheet, one can obtain their vibrational density of states (VDOS) in an analytical form [6]:

$$
g(\omega) = \begin{cases} \frac{\sqrt{3} - \omega^2}{\pi^2} K \left( \frac{1}{4} \sqrt{\frac{\omega(4-\omega)^3}{\omega - \omega^3}} \right), & 0 \leq \omega \leq 2, \\ \frac{2(3-\omega)}{\pi^2 \sqrt{\omega(4-\omega)}} K \left( \frac{3-\omega}{\omega(4-\omega)^3} \right), & 2 \leq \omega \leq 3, \end{cases} \quad (12)
$$

where the function $K(p) = \int_0^1 [(1-x^2)(1-p^2x^2)]^{-1/2}dx$ is an elliptical integral of the first kind. At the same time, the function $g(\omega)$ is symmetric with regards to the point $\omega = 3$. On Fig. 3 the analytical result (12) is represented by the green color line.

Another approach for obtaining the VDOS is to calculate all eigenvalues of the dynamical matrix $\hat{M}$, which corresponds to the force constant matrix [7] and describes the atomic vibrations. The motion equation in the harmonic approximation in the scalar model can be written in the following form:

$$
\omega_i^2 u_i = \sum_j M_{ij} u_j, \quad (13)
$$

where $u_i$ is the scalar displacement of the number $i$ atom. From this representation follows that the eigenvalues $\lambda_i$ of the dynamical matrix correspond to squares of the system’s vibrational eigenfrequencies $\omega_i^2$.

For crystalline graphene the scalar dynamical matrix $\hat{C}_f$ describing the flexural vibrations can be constructed as the square of the dynamical matrix $\hat{C}_p$, describing the interactions only between nearest neighbours. If the atoms $i$ and $j$ are nearest neighbours, the corresponding matrix element $C_{pij}$ is equal to $-1$, which corresponds to unit elastic links (scalar springs) between nearest neighbour atoms. If atoms $i$ and $j$ aren’t nearest neighbours, the matrix element $C_{pij}$ is zero. The diagonal elements of $\hat{C}_p$ are equal to minus the sum of non-diagonal elements in the same column. This fullfills the equation $\sum_j C_{pij} = 0$, which corresponds to the important requirement of the system being translationally invariant. Constructing the dynamical matrix $\hat{C}_p$.

**Figure 2.** Comparison of the dispersion law of phonon modes in graphene from [3] with the result (11) for ZO and ZA phonons. The colors indicate the acoustic and optical branches.
Figure 3. The VDOS $g(\omega)$ for flexural modes of crystalline graphene in a scalar model. The blue color line shows the result of numerical calculation to the eigenvalues of the dynamic matrix $\hat{C}_f$ for a system of $N = 1000^2$ atoms. The green color line marks the exact analytical solution (12). Special points of van Hove singularities is marked.

this way results in it being stable. The square of the matrix $\hat{C}_p$ describes interactions with atoms from first and second coordinate circles, and the extra force constants $\omega_2$ end up negative and equal to $1/6$. From this representation follows that the eigenvalues of the matrix $\hat{C}_f$ correspond to squares of the matrix $\hat{C}_p$’s eigenvalues, which is consistent with (11).

On Fig. 3 shown the VDOS $g(\omega)$ obtained by numerical diagonalization of the scalar dynamical matrix $\hat{C}_f = \hat{C}_p^2$ using the KP-method [8]. Two high-frequency peaks are van Hove singularities for optical and acoustic phonons.

3. Flexural modes in amorphous graphene case
In amorphous graphene, due to the local disorder, the dynamical matrix $\hat{M}$ has a random nature and can be presented in the next form:

$$\hat{M} = \hat{A}\hat{A}^T + \mu\hat{C}_f.$$  \hspace{1cm} (14)

Here the matrix $\hat{A}$ is a random matrix constructed in a way analogous to the matrix $\hat{C}_p$ with random nonzero elements $A_{ij}$, which have a Gaussian distribution. The system parameter $\mu$ describing the rigidity of a single spring is responsible for the level of order in the system, and lays in the interval $0 \leq \mu < \infty$. The case $\mu \gg 1$ corresponds to a system with comparatively small force constant fluctuations, i.e. low disorder. In this case the second term in (14) is much higher than the first, and the system’s Young modulus $E$ depends on $\mu$ as $E \propto \mu$. However, of greatest interest is the opposite case $\mu \ll 1$, which corresponds to an amorphous body with high fluctuations, i.e. high disorder. In that case the system’s Young modulus $E$ depends on $\mu$ as $E \propto \sqrt{\mu}$ [9, 10, 11].

As it can be seen on Fig. 4, with rather weak disorder, two high-frequency peaks are observed in the $\mu \gg 1$ system, which are due to van Hove singularities for optical and acoustic phonons. Then a small plateau is clearly observed, associated with the dispersion law of flexural modes $\omega \propto q^2$. However, as the disorder $\mu \ll 1$ increases, the peaks of the Van Hove singularities disappear, and phonons with Debye contribution $g(\omega) \propto \omega$ occupy the dominant part of the low-frequency spectrum in amorphous graphene. This, in turn, means that it is difficult or even impossible to observe flexural modes at low frequencies in amorphous graphene.
Figure 4. The VDOS $g(\omega)$ of the flexural modes in amorphous graphene system with the dynamical matrix $\hat{M} = \hat{A}\hat{A}^T + \mu \hat{C}_f$ for different parameters $\mu$. Lines show the Debye phonons $VDOS\ g(\omega) \propto \omega$.

4. Conclusion

Summarizing, we have made a theory of flexural modes in graphene which is based on the idea of negative springs. In the scalar model, we considered the motion equation and found the dispersion relation $\omega(q)$ in the frames of one and two coordination circles. At the critical ratio between force constants of the atom’s interactions $\kappa_1/\kappa_2 = -6$ the dispersion law of vibrational modes in graphene changes from phonon-like linear dispersion $\omega = vq$ to a flexural kind dispersion $\omega = \beta q^2$, when the elastic modulus of the lattice goes to zero. Moreover, it can be shown that the dispersion law of the flexural modes $\omega_f(q)$ corresponds to the square of the dispersion law in one coordination circle case $\omega_1^2(q)$. The resulting vibrational density of states $g(\omega)$ contains all special points such as Van Hove singularities. In the amorphous graphene case, we numerically calculated the eigenfrequencies corresponding to eigenvalues of the dynamical matrix, which is based on the random matrix approach. With increasing disorder in the system, Van Hove singularity peaks vanish, and low-frequency phonons with the Debye state density $g(\omega) \propto \omega$ blur flexural modes.

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