Phonons in graphene with point defects

Vadym Adamyan and Vladimir Zavalnyuk

Department of Theoretical Physics, Odessa I I Mechnikov National University, 2 Dvoryanskaya Street, Odessa 65026, Ukraine
E-mail: vadamyan@onu.edu.ua and vzavalnyuk@onu.edu.ua

Received 29 September 2010
Published 6 December 2010
Online at stacks.iop.org/JPhysCM/23/015402

Abstract

The phonon density of states (DOS) of graphene with different types of point defects (carbon isotopes, substitution atoms, vacancies) is considered. Using a solvable model which is based on the harmonic approximation and the assumption that the elastic forces act only between nearest neighboring ions we calculate corrections to the graphene DOS dependent on the type and concentration of defects. In particular the correction due to isotopic dimers is determined. It is shown that a relatively small concentration of defects may lead to significant and specific changes in the DOS, especially at low frequencies, near the Van Hove points and in the vicinity of the K points of the Brillouin zone. In some cases defects generate one or several narrow gaps near the critical points of the phonon DOS as well as resonance states in the Brillouin zone regular points. All types of defects are characterized by the appearance of one or more additional Van Hove peaks near the (Dirac) K points and their singular contribution may be comparable with the effect of electron–phonon interaction. Besides, for low frequencies and near the critical points the relative change in density of states may be many times higher than the concentration of defects.

1. Introduction

Due to the low atomic mass of carbon and high binding energy of the valent sp2 bonds [1], graphene-based nanostructures (single- or several-layered graphene and nanotubes of different kinds) have high rigidity in one direction combined with excellent flexibility in the others [2, 3] leading to their extraordinary sound velocity (about 20 000 km s−1) [4–6] and thermal conductivity [7–10]. Due to these properties carbon compounds can be used not only for plastic and hydrocarbon resin reinforcement, but also as one of the basis materials for nano-mechanics and nano-electronics [11, 12].

It is natural to expect that as well as in bulk crystals even small concentrations of point defects in graphene-based 1D and 2D nanostructures (directly observed in [13, 14]) may lead to specific shifts, broadenings and additional characteristic singularities in the electron and phonon densities of states and thus change their optical absorption, low temperature specific heat and transport properties. Such effects in graphene and carbon nanotubes are significant because of the occurrence of three isotopes in natural carbon (12C, 13C, 14C) with the part of the 13C isotope in the chemically pure carbon exceeding one per cent and also because of the high solubility of substitution defects of trivalent atoms (such as aluminum, boron and nitrogen) and monovalent atom adsorption susceptibility. According to [15], the defect density in a graphene monolayer stabilized on a substrate can reach several per cent and for some applications it can be additionally doped to raise the electrical conductivity. It is shown that unintentional doping of pristine unprocessed graphene under ambient conditions can reach as high as 1% [16], while the highest achieved doping level of N is about 5% [17]. It was also computationally established that the graphene planar structure is kept even for 12% Al and 20% N concentrations [18, 19]. In addition, most of the chemically adsorbed atoms (especially monovalent ones) can be treated as isotopic defects because they are bound to carbon atoms by the π-electron bonds which are not involved in lattice formation (this may need slight correction of σ electrons’ binding energies and angles, but as a first approximation they can be taken as in the ideal graphene). It is worth mentioning that the impact of defects on the electronic properties of graphite, graphene and carbon nanotubes along with a detailed investigation of how electron–phonon interaction affects the phonon dispersion curves especially near the K points of the Brillouin zone has been thoroughly studied in a large number of works [8–10, 20–24], while too little attention has been paid so far to description of the direct influence of defects on the phonon spectra. However the anomalies of the phonon spectra due to the electron–phonon interaction may be visibly distorted by the Van Hove spikes induced by defects.
This paper is devoted to the description of the effect of some point defects (isotopic defects, substitutional atoms, vacant lattice sites) on the phonon spectrum of graphene. As a starting point we consider in section 2 the ideal graphene phonon spectrum in the simple harmonic approximation assuming that elastic forces act only between nearest neighboring hard ions and are described by three harmonic force constants \(J_1, J_2, J_3\) corresponding to three different parts of the interatomic interaction: the central (1) and non-central (2) in-plane forces and the empirical to-the-plane backmoving non-central force (3). The values of these constants are chosen to get the least discrepancy of the eigenfrequencies calculated in the framework of a simple model for the ideal graphene we specify for graphene approaches based on the three-parameter nearest neighbors model. For example, by using of such a model it is impossible to explain the phenomenon of ‘overbending’, which was observed on the simple three-parameter nearest neighbors model. For more complicated cases along with masses of defects the force constants between defect sites and their nearest neighbors should be changed.

In section 3 we discuss the contribution of isotopic defects to the graphene phonon DOS, analyzing separately the cases of single defect, dimer and pair of distant defects. In doing so we specify for graphene approaches based on the method of classic Green functions which were developed more than fifty years ago in [28–31].

In section 4 the same problem is considered for other point defects: substitutional atoms and vacancies. In these more complicated cases along with masses of defects the force constants between defect sites and their nearest neighbors should be changed.

Finally in section 5 we discuss characteristic traces of considered point defects in optical spectra and the heat capacity of graphene.

As illustrations we demonstrate linear in defect concentration contributions to DOS as more important for comparison with real experiments and estimations of defect manifestations in the phonon spectra.

2. Phonons in ideal graphene

The ideal graphene is a 2D crystal with two carbon atoms per elementary cell (further we will call them ‘A’ and ‘B’) (figure 1).

![Figure 1. The graphitic plane structure. A (full circles) and B (hollow circles) represent two sublattices, \(a_1\) and \(a_2\) are two primitive translation vectors, with \(a = b = \sqrt{3}a\) and \(b = 0.142\) nm is the interatomic distance or the length of the carbon–carbon \(\sigma\)-bond.](image)

The equilibrium position of atoms on sublattices of the carbon plane can be described by the vectors

\[
\begin{align*}
R_{n,A}^0 &= n_1 A_1 + n_2 A_2, \\
R_{n,B}^0 &= n_1 B_1 + n_2 B_2 + \frac{1}{\sqrt{3}} (a_1 + a_2)
\end{align*}
\]

with integer \(n_1, n_2, A_1, B_1, n_1 B_1, n_2 B_2\). The instantaneous ion configuration of the graphene plane is characterized by the actual positions of atoms

\[
R_{n,\sigma} = R_{n,\sigma}^0 + u_{n,\sigma}(t), \quad \sigma = (A, B),
\]

with time-dependent displacements

\[
u_{n,\sigma}(t) = u_{n,\sigma,1}(t) a_1 + u_{n,\sigma,2}(t) a_2 + u_{n,\sigma,3}(t) a_3
\]

around \(R_{n,\sigma}^0\), where \(a_1\) is the orthogonal to the lattice plane unit vector. Since the angle between translation vectors \(a_1\) and \(a_2\) is \(\pi/3\), then the scalar product of displacement vectors \(u_{n,\sigma}\) and \(u_{n,\sigma'}\) has the form

\[
(u_{n,\sigma} u_{n,\sigma'}) = u_{n,\sigma,1} u_{n,\sigma',1} + \frac{1}{2} \left( u_{n,\sigma,1} u_{n,\sigma',2} + u_{n,\sigma,2} u_{n,\sigma',1} + u_{n,\sigma,2} u_{n,\sigma',2} + u_{n,\sigma,3} u_{n,\sigma',3} \right)
\]

Therefore the kinetic energy \(K\) of lattice atoms can be written as follows:

\[
K = \frac{1}{2} \sum_n \sum_\sigma \left( m_0 \left( \mu_{n,\sigma,1}^2 + \mu_{n,\sigma,2}^2 + \mu_{n,\sigma,3}^2 \right) \right)
\]

where \(m_0\) is the mass of the carbon atom (isotope \(^{12}\)C).

The total potential energy \(W\) of ideal graphene is modeled as a sum of three components determined by three different force constants:

\[
W = W_c + W_{l,p,n} + W_{o,p,n},
\]
the potential energy due to the central forces, $W_{p,n}$, is the component depending only on magnitudes of in-plane relative displacements of interacting nearest neighbors, $W_{o,p,n}$ is the non-central component conditioned by $\pi$-electron interaction, which depends on the out-of-plane relative displacements of neighboring atoms. For our parametrization the nearest neighbors to a site $nA(nB)$ of the graphene lattice are sites $(n + S)B((n - S)A)$, where $S$ either 0-vector, or $-a_1$, or $-a_2$. Using this notation and setting

$$\Delta u_{nS,BA} = u_{n+S,B} - u_{n,A}, \quad \Delta u_{nS,AB} = u_{n-S,A} - u_{n,B},$$

we get the following expressions for the components of potential energy in (1):

$$W_c = \frac{1}{4d^2} J_1 \sum \sum_n \sum_S [ (\Delta u_{nS,BA} \cdot R_{n+S,B} - R_{n,A})^2 + (\Delta u_{nS,AB} \cdot R_{n+S,B} - R_{n,A})^2],$$

$$W_{i,p,n} = \frac{1}{2} J_2 \sum \sum_n \sum_S [ (\Delta u_{nS,BA} \cdot a_1)^2 + (\Delta u_{nS,AB} \cdot a_1)^2],$$

$$W_{o,p,n} = \frac{1}{2} J_3 \sum \sum_n \sum_S (\Delta u_{nS,BA} \cdot a_3)^2 + (\Delta u_{nS,AB} \cdot a_3)^2],$$

with indeterminate force constants $J_1, J_2, J_3$.

As usual in lattice dynamics, we use further the Bloch theorem, according to which the atom or ion displacements on the set of $n$-sites in a periodic lattice are of the form $e^{i kn}$, where $k = (k_1, k_2)$ is the wave vector. In this way we obtain that the squares of the frequencies $\omega_j(k)$ for the different branches of the ideal graphene phonon spectra coincide with eigenvalues of the dynamical matrix

$$D(k) = M^{-1/2} (J_1 G_c + J_2 G_{i,p,n} + J_3 G_{o,p,n}) M^{-1/2},$$

where $M$ is the mass matrix:

$$M = \begin{pmatrix} M_0 & 0 \\ 0 & M_0 \end{pmatrix}, \quad M_0 = m_0 (M_{i,p} + M_{o,p}),$$

$$M_{i,p} = \begin{pmatrix} 1 + \frac{1}{2} & 0 \\ 0 & 1 \end{pmatrix}, \quad M_{o,p} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

and $G_c, G_{i,p,n}$, and $G_{o,p,n}$ are Hermitian $2 \times 2$-block matrices of the form

$$G = \begin{pmatrix} G^d & G^z \\ G^z & G^d \end{pmatrix}$$

with $3 \times 3$ diagonal and anti-diagonal blocks $G^d$ and $G^a$, respectively:

$$G^d = 2 M_{i,p}, \quad G^a = -\frac{3}{2} M_{i,p},$$

$$G^z = \begin{pmatrix} 1 - e^{i k_1 a} & 0 & 0 \\ 0 & 1 - e^{i k_2 a} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$G_{i,p,n}^d = 3 M_{i,p}, \quad G_{i,p,n}^a = - \left( 1 + e^{i k_1 a} + e^{i k_2 a} \right) M_{i,p},$$

Table 1: Exact expressions for phonon frequencies (in cm$^{-1}$) in the $\Gamma$, $M$ and $K$ points of the Brillouin zone.

| $\Gamma$ | $M$ | $K$ | $\omega_{1}$ | $\omega_{2}$ | $\omega_{3}$ | $\omega_{4}$ | $\omega_{5}$ | $\omega_{6}$ |
|----------|-----|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| $\sqrt{\frac{2J_1}{m}}$ | $\sqrt{\frac{2J_2}{m}}$ | $\sqrt{\frac{2J_2}{m}}$ | $\sqrt{\frac{2J_1 + 2J_2}{m}}$ | $\sqrt{\frac{2J_1 + 4J_2}{m}}$ | $\sqrt{\frac{3J_1 + 2J_2}{m}}$ | $\sqrt{\frac{3J_1 + 4J_2}{m}}$ | $\sqrt{\frac{3J_1 + 4J_2}{m}}$ | $\sqrt{\frac{3J_1 + 4J_2}{m}}$ |

$$G_{o,p,n}^d = 3 M_{o,p}, \quad G_{o,p,n}^a = - \left( 1 + e^{i k_1 a} + e^{i k_2 a} \right) M_{o,p}.$$  

Hence for the ideal graphene plane there are six branches $\omega_j(k)$ ($j = \Gamma, \Lambda, T, Z, A, L, O, ZO$) of phonon spectra: for two of them ($\omega_{ZA}$ and $\omega_{ZO}$) the atom displacements are perpendicular to the lattice plane while for the other four branches the atoms do not come out of the plane.

Setting

$$F_0(k) = 2 \left( \cos (k_1 a - k_2 a) + \cos k_2 a + \cos k_1 a \right),$$

$$F_1(k) = 12 (J_1^2 + 2 J_1 J_2 + 2 J_2^2) + F_0(k) (J_1^2 + 8 J_1 J_2 + 8 J_2^2),$$

$$X_1 = J_1^2 + 16 J_1 J_2 + 16 J_2^2, \quad X_2 = J_1^2 - 8 J_1 J_2 - 8 J_2^2,$$

$$F_2(k) = [18 J_1^2 + 2 X_1 + 4 X_2 \cos (k_1 a - k_2 a) - \cos k_1 a + \cos k_2 a + 4 \cos k_1 a \cos k_2 a]$$

we get the following expressions for the eigenfrequencies $\omega_j(k)$:

$$\omega_{ZA,ZO}(k) = \frac{J_1}{m} \left( 3 \pm \sqrt{3 + F_0(k)} \right)^{1/2},$$

$$\omega_{LA,TA,LO,TO}(k) = \left[ \frac{3 (J_1 + 2 J_2)}{2 m} \pm \frac{\sqrt{2}}{4 m} \sqrt{F_1(k) \pm \sqrt{2} J_1 F_2(k)} \right]^{1/2}.$$

The last expressions take a very simple form at the high-symmetry points $\Gamma (k = (0, 0))$, $A (k = (\frac{1}{2} \pi, \frac{1}{2} \pi))$ and $M (k = (\pi, \pi))$ of the graphene first Brillouin zone (table 1).

In the vicinity of the $\Gamma$ point there are three acoustic branches of the graphene phonon spectra, the eigenfrequencies of which in the limit $k \rightarrow 0$ do not depend on the direction of propagation. They can be distinguished by polarization of oscillations as the longitudinal branch $\omega_{LA} = c_{LA} k + O(k^2)$ with longitudinal sound velocity

$$c_{LA} = \frac{(J_1 + J_2)(J_1 + 4 J_2)}{6 (J_1 + 2 J_2) m_0} \sqrt{\frac{(J_1 + J_2)(J_1 + 4 J_2)}{6 (J_1 + 2 J_2) m_0}},$$

the transverse in-plane branch $\omega_{TA} = c_{TA} k + O(k^2)$ with in-plane transverse sound velocity

$$c_{TA} = \frac{3 J_1 J_2 + 4 J_2}{6 (J_1 + 2 J_2) m_0} \sqrt{\frac{3 J_1 J_2 + 4 J_2}{6 (J_1 + 2 J_2) m_0}}.$$
branches respectively.

Longitudinal, transversal and out-of-plane acoustical (optical) branches respectively.

The transverse out-of-plane branch \( \omega_{ZA} = c_{ZA} k + O(k^2) \) with transverse out-of-plane sound velocity

\[
c_{ZA} = a \sqrt{\frac{J_3}{3m_0}}
\]

(7)

By definition the density of states \( \rho(\omega) \) of any oscillatory system is given by the expressions

\[
\rho(\omega) = 2\omega \Re (\omega^2), \quad \omega > 0,
\]

\[
\Re(\lambda) = \sum_v \delta (\lambda - \omega_v^2) = \frac{1}{\pi} \lim_{\epsilon \to 0} \sum_v \frac{\epsilon}{(\lambda - \omega_v^2)^2 + \epsilon^2}.
\]

(8)

where \( \omega_v \) are eigenfrequencies of the system counted with respect to their multiplicities. In our case the normalized to six (=the number of degrees of freedom per elementary cell) DOS is given by the formula

\[
\Re(\lambda) = \frac{1}{\pi} \lim_{\epsilon \to 0} \left( \frac{a}{2\pi} \right)^2 \times \int_{-\pi/a}^{\pi/a} \int_{-\pi/a}^{\pi/a} \sum_{j=1}^{6} \frac{\epsilon}{(\lambda - \omega_j^2(k_1, k_2))^2 + \epsilon^2} \, dk_1 \, dk_2
\]

\[
= \frac{1}{\pi} \lim_{\epsilon \to 0} \text{Im} \left( \frac{a}{2\pi} \right)^2 \times \int_{-\pi/a}^{\pi/a} \int_{-\pi/a}^{\pi/a} \text{Tr} [\mathbf{D}(k) - (\lambda + i\epsilon)\mathcal{I}]^{-1} \, dk_1 \, dk_2,
\]

\[
\int_0^\infty \Re(\lambda) \, d\lambda = 6,
\]

(9)

where \( \mathcal{I} \) is the 6 \times 6 unity matrix.

In order to obtain the phonon dispersion curves and DOS for ideal graphene on the base of expressions (4) and (12) concrete numerical values of the force constants \( J_1, J_2, J_3 \) are necessary. We derived these constants by the least-squares method using experimental values of graphene phonon frequencies at the \( \Gamma, K \) and \( M \) points measured using the method of inelastic x-ray scattering. From now on we assume that

\[
J_1 = 3.79 \times 10^{-21} \text{ J m}^{-2}, \quad J_2 = 6.89 \times 10^{-21} \text{ J m}^{-2}, \quad J_3 = 2.36 \times 10^{-21} \text{ J m}^{-2}. \quad (10)
\]

With the constants (10) we get the values of phonon frequencies at the \( \Gamma, K \) and \( M \) points of the Brillouin zone (table 2) and the sound velocities (which are in a good agreement with [4–6])

\[
c_{LA} = 18.4 \text{ km s}^{-1}, \quad c_{TA} = 16.5 \text{ km s}^{-1}, \quad c_{ZA} = 9.2 \text{ km s}^{-1}.
\]

For demonstration of how the fitted three-parameter model works we give below the phonon dispersion curves (figure 2) and density of states (figure 3) for ideal graphene.

### 3. Isotopic defects

The kinetic energy \( K \) and potential energy \( W \) of the non-ideal graphene can be written as the following quadratic forms:

\[
K = \frac{1}{2} \sum_{\rho, \sigma} m(\rho) \hat{u}_{\rho\sigma}^2
\]

\[
W (\{u_{\sigma}(l)\}) = \frac{1}{2} \sum_{\rho, \sigma} \sum_{\alpha, \beta = A} \sum_{l' \neq l} 3 \epsilon_{\sigma j} \hat{u}_{\rho \alpha}(l') \hat{u}_{\beta j}(l),
\]
where \( \mathcal{I}_\sigma \) enumerate the graphene lattice sites. From now on we will denote by \( \mathcal{M} \) and \( \mathcal{C} \) the matrices of the quadratic forms \( 2 \mathcal{K} \) and \( 2 \mathcal{W} \), respectively. We will call \( \mathfrak{M} \) the mass matrix and \( \mathfrak{C} \) the force constant matrix. For the case of the ideal graphene \( \mathfrak{M} \) is the block diagonal matrix \( \mathfrak{M}_0 \) with equal diagonal blocks

\[
\mathfrak{M}^0_{\kappa, \kappa} = \mathfrak{M}_0
\]

and \( \mathfrak{C} \) is the matrix of the doubled sum of the quadratic forms (2). For graphene with substitutional defects the mass matrix is block diagonal and all its diagonal blocks have form (11) but with masses of substitutional ions instead of \( m_0 \) for some \( \kappa \).

Let \( \mathcal{M} \) be the mass matrix of a non-ideal graphene plane with some host \( ^{12}\text{C} \) atoms replaced by other stable carbon isotopes. Note that the block diagonal matrices \( \mathcal{M}_0 \) and \( \mathcal{M} \) commute. Let \( \rho_0(\omega) \) and \( \rho_\mathcal{M}(\omega) \) denote the DOS of carbon planes with mass matrices \( \mathcal{M}_0 \) and \( \mathcal{M} \), respectively. As \( \omega_0^2 \) in (8) are eigenvalues of the matrix

\[
\mathcal{D} = \mathcal{M}^{-\frac{1}{2}} \mathcal{C} \mathcal{M}^{-\frac{1}{2}}
\]

or the linear pencil \( \mathcal{C} - z \mathcal{M} \), i.e. \( \omega_0^2 \) are those values of \( z \) for which \( \mathcal{C} - z \mathcal{M} \) is non-invertible, then

\[
\mathcal{R}(\omega^2) = \frac{1}{\pi} \lim_{\epsilon \downarrow 0} \text{Im Tr}[(\mathcal{D} - (\omega^2 + i \epsilon)\mathcal{I})^{-1}]
\]

\[
= \frac{1}{\pi} \lim_{\epsilon \downarrow 0} \text{Im Tr}[\mathcal{C} - (\omega^2 + i \epsilon) \mathcal{M}]^{-1} \mathcal{M}
\]

(12)

where \( \mathcal{I} \) is the unity matrix.

Note that for any positive definite matrices \( \mathcal{C} \) and \( \mathcal{M} \) of any finite order and non-real \( \epsilon \) we can write

\[
\text{Tr}((\mathcal{C} - z \mathcal{M})^{-1} \mathcal{M}) = -\frac{d}{dz} \text{Tr} \ln(\mathcal{C} - z \mathcal{M})
\]

\[
= \frac{d}{dz} \ln \det(\mathcal{C} - z \mathcal{M}).
\]

Therefore from (8) and (13) we get

\[
\rho_{\mathcal{M}}(\omega) = \rho_0(\omega) - \frac{2 \omega}{\pi} \lim_{\epsilon \downarrow 0} \text{Im} \ln[\mathcal{C} - z \mathcal{M}]^{-1}
\]

\[
\times \left[ \frac{d}{dz} \ln \det(\mathcal{C} - z \mathcal{M}) \right]_{|z=\omega^2+i\epsilon}
\]

or

\[
\rho_{\mathcal{M}}(\omega) = \rho_0(\omega) - \frac{2 \omega}{\pi} \lim_{\epsilon \downarrow 0} \text{Im} \ln[\mathcal{C} - z \mathcal{M}]^{-1}
\]

\[
\times \left[ \frac{d}{dz} \ln \det(\mathcal{C} - z \mathcal{M}) \right]_{|z=\omega^2+i\epsilon}
\]

(14)

From now on we will assume, for simplicity, that only one species of isotopes with mass \( m \) can replace the host atoms of the ideal graphene lattice and assign to each site \( I_\sigma \) of non-ideal graphene the occupation number

\[
n_{I_\sigma} = \begin{cases} 0 & \text{if the host carbon atom sits at } I_\sigma; \\ 1 & \text{if the carbon isotope is there}. \end{cases}
\]

We can express diagonal blocks of \( \mathfrak{M} \) in terms of \( n_{I_\sigma} \) as follows:

\[
M_{\kappa,\kappa} = M_{0} + m - m_{0} n_{I_\sigma} 
\]

(17)

By (17) \( (\mathfrak{M}_0^{-1} - 3) \) is a block diagonal matrix with \( 3 \times 3 \) diagonal blocks of the form

\[
A_{\kappa,\kappa} = \mu \cdot n_{I_\sigma} I, \quad \mu = \frac{m - m_{0}}{m_{0}}
\]

(18)

where \( I \) is the \( 3 \times 3 \) unity matrix.

In view of the obvious property of occupation numbers \( n_{I_\sigma}^2 = n_{I_\sigma} \), we can represent \( \rho_{\mathcal{M}}(\omega) \) formally as follows:

\[
\rho_{\mathcal{M}}(\omega) = \rho_0(\omega) + \frac{1}{2!} \sum_{\kappa} \mathcal{E}_I(\omega; I_\sigma) n_{I_\sigma}
\]

\[
+ \frac{1}{2^2} \sum_{\kappa \neq \kappa'} \mathcal{E}_I(\omega; I_\sigma, I_\sigma') n_{I_\sigma} n_{I_\sigma'}
\]

\[
+ \frac{1}{3!} \sum_{\kappa \neq \kappa' \neq \kappa''} \mathcal{E}_I(\omega; I_\sigma, I_\sigma', I_\sigma'') n_{I_\sigma} n_{I_\sigma'} n_{I_\sigma''} + \cdots
\]

(19)

In fact, the decomposition (19) is an identity, which holds for any number of isotopes (or other point defects) and their distribution over the graphene lattice sites. Particularly, if there is only one isotopic defect located at the lattice site \( I_0 \), that is if \( n_{I_0} = \delta_{kr, I_0} \), then according to (19)

\[
\mathcal{E}_I(\omega; I_0) = \rho(\omega; I_0) - \rho_0(\omega)
\]

(20)

where \( \rho(\omega; I_0) \), is the DOS of a graphene lattice with a single defect at the site \( I_0 \). In much the same way we find that

\[
\mathcal{E}_I(\omega; I_\sigma) = \rho(\omega; I_\sigma) - \rho_0(\omega)
\]

(21)

where \( \rho(\omega; I_\sigma) \), is the DOS of a graphene lattice with only two isotopic defects at the sites \( I_{0} \) and \( I_{0} \) and \( \sigma \) so on.

Let \( \Gamma(z) \) denote the \( 3 \times 3 \) diagonal block of \( (\mathcal{D} - z \mathcal{I})^{-1} \) with some index \( I_\sigma \). By the translational and point symmetry of the graphene plane \( \Gamma(z) \) does not depend on \( I_\sigma \). It follows from (15) and (17) that the coefficients \( \mathcal{E}_I(\omega; I_0) \) in (19) actually do not depend on \( I \) and \( \sigma \),

\[
\mathcal{E}_I(\omega; I_0) = \mathcal{E}_I(\omega; I_0)
\]

\[
= -\frac{2 \omega}{\pi} \lim_{\epsilon \downarrow 0} \text{Im} \ln \left[ \text{det}[\mathcal{D} - z \mathcal{I}] \right]_{|z=\omega^2+i\epsilon}
\]

Note that for \( 3 \times 3 \) blocks \( \mathcal{D}_{\kappa,\sigma'} \) of \( \mathcal{D} = (\mathcal{M}_0^{-\frac{1}{2}} \mathcal{C} \mathcal{M}_0^{-\frac{1}{2}}) \) we have

\[
\mathcal{D}_{\kappa,\sigma'} = \mathcal{D}_{\kappa,\sigma'}\mathcal{D}_{\kappa,\sigma'}^*, \quad \mathcal{D}_{\kappa,\sigma'}\mathcal{D}_{\kappa,\sigma'} = \mathcal{D}_{\kappa,\sigma'}, \quad \sigma \neq \tau
\]

Making use of the explicit expression for the dynamical matrix \( \mathcal{D}(\mathbf{k}) = \left( \mathcal{D}_{\sigma\tau}(\mathbf{k}) \right)_{\sigma, \tau = 1}^{3} \) of the ideal graphene plane

\[
\mathcal{D}_{\sigma\tau}(\mathbf{k}) = \int \frac{d^2 \mathbf{t}}{2\pi} d_{\kappa,\sigma} e^{-i\mathbf{k}\cdot\mathbf{t}},
\]

(22)
where $k$ is the wavevector from the Brillouin zone, we obtain that
\[ \Gamma(z) = \frac{1}{N} \sum_k \left( [D(k) - zI]^{-1} \right)_{\sigma\sigma}. \tag{23} \]
where $N$ is the number of unit cells in the periodicity area. Hence
\[ \Xi_1(\omega) = \frac{2\omega}{\pi} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det \left[ I - \mu z \frac{1}{N} \right] \times \sum_k \left( [D(k) - zI]^{-1} \right)_{\sigma\sigma} \bigg|_{z = \omega^2 + i\epsilon}. \tag{24} \]

Proceeding in the same fashion and setting
\[ \Gamma_{\sigma\tau}(z; I) = \frac{1}{N} \sum_k e^{ikz} \left( [D(k) - zI]^{-1} \right)_{\sigma\tau} \tag{25} \]
we find that
\[ \Xi(z; I, \sigma, \Gamma_\tau) = \Xi(z; I - I, \sigma, 0\tau) \]
\[ = -2\Xi(\omega) - \frac{2\omega}{\pi} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det \left( I - z\mu \Gamma(z) \right) \times \left( -z\mu \Gamma_{\sigma\tau}(z; I - I) \right) \bigg|_{z = \omega^2 + i\epsilon}. \tag{26} \]

We now pay attention to the fact that for the graphene plane of finite size $p_0(\omega), p_0(\omega)$ in (19) have order $N$ while the coefficients $\Xi_1(\omega), \Xi_2(\omega; I, \sigma, 0\tau), \ldots$ are finite quantities. Let us consider the equilibrium distribution of defects (isotopes) with concentrations $c$ and the pair distribution function of defects
\[ g_{\sigma\tau}(I) = \lim_{N \to \infty} N \langle n_{\sigma\tau} n_{\sigma\tau} \rangle, \]
where angle brackets denote thermal (other) average. Then for the phonon spectral densities per unit cell of the graphene plane
\[ \Delta_\rho(\omega) = \frac{1}{N} \lim_{N \to \infty} \left( \rho(\omega) \right), \quad \rho = \mathfrak{R}, 0, \]
by (19), (24), (26) we have
\[ \Delta_\rho(\omega) = \Delta_0(\omega) + c \Xi_1(\omega) \]
\[ + \frac{1}{2\pi} \sum_{I, \sigma, \tau} \Xi(z; I, \sigma, 0\tau) g_{\sigma\tau}(I) + \cdots. \tag{27} \]
If for some reason there is a visible concentration $p$ of isotopic dimers on the graphene plane, that is cells occupied by pairs of isotopes, then their contribution to $\Delta_\rho(\omega)$ is (figure 5)
\[ \Delta_\rho(\omega) = \cdots + p \cdot \Xi_{\text{dim}}(\omega) \cdots, \]
\[ \Xi_{\text{dim}}(\omega) = -\frac{2\omega}{\pi} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det \left( I - z\mu \Gamma(z) \right) \times \ln \det \left( I - z\mu \Gamma_{\sigma\tau}(z; 0) \right) -z\mu \Gamma_{\sigma\tau}(z; 0) I - z\mu \Gamma(z) \bigg|_{z = \omega^2 + i\epsilon}. \tag{28} \]

4. Substitutional atoms

Let us consider now a non-ideal graphene plane with low concentration $c_X$ of impurity atoms $X$ replacing carbon atoms at some lattice sites. Applying the same arguments as above we can again assert that in this case the phonon spectral density per unit cell $\Delta_X(\omega)$ can be written as follows:
\[ \Delta_X(\omega) = \Delta_0(\omega) + c_X \Theta_1(\omega) \]
\[ + \frac{1}{2\pi} \sum_{I, \sigma, \tau} \Theta_2(\omega; I, \sigma, 0\tau) g_{\sigma\tau}(I) + \mathcal{O}(c_X^2). \tag{29} \]
Here
\[ \Theta_1(\omega) = p_X(\omega) - \rho_0(\omega), \]
$\rho_X(\omega)$ being the DOS of a graphene lattice with a single defect at some site $\mathfrak{R}_0$; \[ \Theta_2(\omega; I, \sigma, 0\tau') = \rho_X(\omega; I, \sigma, 0\sigma') - 2\Theta_1(\omega) + \rho_0(\omega), \]
$\rho_X(\omega; I, \sigma, 0\sigma')$ being the DOS of a graphene lattice with only two impurity atoms $X$ at some sites $I, \sigma, \sigma'$ such that $I = I'$. Denote by $M_X$ the mass matrix and by $C_X$ the force constants matrix of the graphene lattice with a small number of impurity atoms $X$ replacing carbon at some sites and put
\[ \delta M_X = M_X - M_0, \quad \delta C_X = C_X - C. \]

As a starting point for calculation of $\Theta_1(\omega), \Theta_2(\omega; I, \sigma, 0\sigma'), \ldots$ we make use of the relation
\[ \rho_X(\omega) - \rho_0(\omega) = -\frac{2\omega}{\pi} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det \left( I + \delta C_X - \delta M_X^{-1} \right) \bigg|_{z = \omega^2 + i\epsilon}. \tag{32} \]

Note that as well as for the graphene lattice with only isotopic defects the matrix
\[ T_X(z) := M^{-\frac{1}{2}} \left( \delta C_X - z \delta M_X \right) M^{-\frac{1}{2}} \]
can be represented in the block form, elements of which are $3 \times 3$ matrices being enumerated by pairs of the multi-indices $I, \Gamma'$ that enumerate the graphene lattice sites. Actually, only those blocks of $T_X(z)$ are non-zero, for which each of the indices $I, \Gamma'$ belongs to the subset of indices $\mathfrak{D}$ of those enumerating either sites occupied by $X$-atoms or their nearest neighbors. Therefore if there are $N_X$ impurities in the periodicity area, then the rank of $T_X(z)$ does not exceed $12N_Y$. For these reasons the determinant in (32) can be replaced by the minor determinant obtained from $\det(T + \cdots)$ by deleting all rows and columns with ‘numbers’ other then those from $\mathfrak{D}$. By this argument setting
\[ \mathcal{Q}(z) = [\Gamma_{\sigma\tau}(z; I - I)]_{\mathfrak{R}, \mathfrak{R} \in \mathfrak{D}}, \]
\[ T_X(z) = [T_X(z)]_{\mathfrak{R}, \mathfrak{R} \in \mathfrak{D}} \]
we can write
\[ \rho_X(\omega) - \rho_0(\omega) = -\frac{2\omega}{\pi} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det \left( T_X(z) \bigg| [T_X(z)^{-1} + \mathcal{Q}(z)]^{-1} \right) \bigg|_{z = \omega^2 + i\epsilon}. \tag{33} \]
Let us assume for certainty that the single defect is located at the site \(0A\) and therefore its ‘normal’ nearest neighbors are located at the sites \(1B, 1_1B, 1_1B,\) where \(1_1 = 0, \ 1_2 = −a_1, \ 1_3 = −a_2\), respectively. In this case the subset introduced above

\[
\mathcal{D} = \{0A, \ 1_1B, 1_1B, 1_1B, 1_1B\}.
\]

We may count further for brevity \(0\) instead of \(0A\) and \(s\) instead of \(1, 2, 3\).

With this enumeration the \(12 \times 12\) matrices \(T_\chi(z)\) and \(T_\chi(z)^{-1}\) can now be represented as \(4 \times 4\) block matrices

\[
T_\chi(z) = \begin{pmatrix}
-\delta G + \sum_{i=1}^{3} \delta G_i & -\delta G_1 & \delta G_2 & -\delta G_3 \\
-\delta G_1 & \delta G_1 & 0 & 0 \\
-\delta G_2 & 0 & \delta G_2 & 0 \\
-\delta G_3 & 0 & 0 & \delta G_3
\end{pmatrix},
\]

\[
T_\chi(z)^{-1} = -\frac{1}{z \mu}
\begin{pmatrix}
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1
\end{pmatrix}
\left(\begin{array}{cccc}
0 & 0 & 0 & 0 \\
0 & \delta G_1^{-1} & 0 & 0 \\
0 & 0 & \delta G_2^{-1} & 0 \\
0 & 0 & 0 & \delta G_3^{-1}
\end{array}\right)
\]

where

\[
\delta M = \mu I
\]

and

\[
\delta G_1 = \frac{1}{2m_0} \begin{pmatrix}
1 & 1 & 1 & 0 \\
1 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}, \quad \delta G_2 = \frac{1}{4m_0} \begin{pmatrix}
2 + \sqrt{3} & 1 & 0 & 0 \\
-1 & 2 - \sqrt{3} & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}, \quad \delta G_3 = \frac{1}{4m_0} \begin{pmatrix}
2 - \sqrt{3} & 1 & 0 & 0 \\
-1 & 2 + \sqrt{3} & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]

By (34) and (35) we have

\[
\det T_\chi(z) = -\left(\text{det} \sum_{s=1}^{3} \delta G_s\right) \mu^3 z^3.
\]

Substitution of the above given expressions (34)–(36) and

\[
\Theta_1(\omega) = \frac{2\omega}{\pi \epsilon \omega} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det (3 + T_0(\omega)) |_{\Im \omega^2 + \pi i},
\]

(38)

into (33) gives the sought expression for the ‘coefficient’ \(\Theta_1(\omega)\) in (29).

In the partial case of an ‘isobaric’ defect \(\mu = 0\) we have

\[
\Theta_1(\omega) = -\frac{2\omega}{\pi \epsilon \omega} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det P(z) |_{\Im \omega^2 + \pi i},
\]

(39)

Not much remains to add to prove that for the vacancies at the graphene lattice sites the corresponding coefficient \(\Theta_1(\omega)\) is given by the expression

\[
\Theta_1(\omega) = -\frac{2\omega}{\pi \epsilon \omega} \lim_{\epsilon \to 0} \frac{d}{dz} \ln \det P(z) |_{\Im \omega^2 + \pi i},
\]

(35)

\[
P(z) = \begin{pmatrix}
\Gamma_{BB}(z; 0) - \delta G_1^0 & \Gamma_{BB}(z; a_1) \\
\Gamma_{BB}(z; -a_1) & \Gamma_{BB}(z; 0) - \delta G_1^0
\end{pmatrix},
\]

(40)

where \(\delta G_1^0, \delta G_2^0, \delta G_3^0\) are the particular cases of expressions (36) with \(\Delta J_1, \Delta J_2, \Delta J_3\) replaced by \(-J_1, -J_2, -J_3\), respectively.

5. Discussion

The proposed model for the description of phonon spectra in graphene, where the only nearest neighbor interaction is accounted for, gives rather simple explicit expressions for the phonon dispersion curves and reflects quite satisfactorily their main features for graphene and graphite in the whole frequency range. Certainly, containing only three force constants, such a model cannot reproduce all the specific features of graphite phonon spectra. For example, it cannot in principle reproduce the low-frequency bending mode with \(\omega \sim k^2\) and the overbending of in-plane optical modes near the \(\Gamma\) point so the latter is assumed to be caused by the electron–phonon interaction [20, 23, 24].

Nevertheless, the three force constants of the model being chosen as fitting parameters to obtain a good coincidence with known values (inelastic x-ray scattering on graphite [4]) of optical modes at the symmetrical points of the first Brillouin zone \(\Gamma_{5,6}, K_6, K_{4,5}, K_3, M_6, M_5\) (for in-plane modes) and \(\Gamma_4,\)
M₁ (for out-of-plane modes) gives satisfactory (and sometimes rather good) quantitative agreement with experimental data for graphite throughout the whole frequency range. In particular, the value of in-plane transverse sound velocity agrees closely with the experimental value and results of the more sophisticated theoretical models [4–6]. We took a slightly overstated in-plane Γ point frequency ω\_Γ₅₄ = 1620 cm\(^{-1}\) (instead of a value in between 1580 and 1595 cm\(^{-1}\) according to known experiments) for better fitting of experimental data in a larger part of the Brillouin zone and for a formal account of the in-plane optical modes overbending near the Γ point. Since the experimental data for the K and M points of the graphene phonon spectrum are rather poor and the selection rules are strictly obeyed due to the high crystalline quality of graphene, we take the graphite phonon spectrum as a target of the fitting procedure, more so that the phonon dispersion curves for graphite and graphene are similar in a large part of the Brillouin zone [25].

Another visible discrepancy between our theory and experimental data (in addition to those mentioned above) is the sufficiently lower in frequency in-plane longitudinal acoustic (LA) branch (figure 2) in the Γ–M direction and as a result its incorrect trend between the M and K points. The analytically obtained frequencies ω\_K₄ and ω\_M₄ are connected in the model by the relation ω\_K₄ = √2ω\_M₄, which is different from the x-ray experimental result ω\_K₄ ≈ ω\_M₄ [4]. However, this relation is in a better agreement with Raman experiments which give ω\_K₄ ≈ 1.6ω\_M₄ [32]. Also for the ω\_Γ₅₄ and ω\_K₄, we get ω\_Γ₅₄ = ω\_K₄, while x-ray and Raman experiments give 1.32 and 1.25, respectively, (instead of 1.41 (or 1.38 with account of our ω\_Γ₅₄ overestimation)). The next interesting observation is that the ω\_M₄, ω\_K₄, ω\_Γ₅₄, ω\_Γ₅₄, ω\_Γ₅₄ ratios to ω\_M₄ which are drastically different from the x-ray experiment results are in a good agreement with Raman experiments despite the essential difference in absolute values of some of those frequencies [32]. It is worth mentioning that similar relations and ratios were obtained within a more detailed model with up-to-third nearest neighbor interactions accounted for [26].

Note that since the most substantial spectrum changes due to defects were expected near the Van Hove singularities, all of which are reproduced at the proper places by our simple model, it is evident that further improvements and refinements were not dictated by the objectives and needs of this work.

The study of the influence of point defects on the graphene phonon spectra on the basis of our simplified model for the ideal graphene lattice oscillations showed, as might be expected, that the isotopic defects slightly downshift Van Hove singularities in the phonon DOS for heavier than carbon atom defects and upshift them for light defects. For the defects with a mass of 11 u.amu (like \(^{11}\)B) the additional Van Hove peak appears on the upper edge of the ideal graphene phonon spectra. For lighter defects this peak splits out and corresponds to the localized oscillation mode with frequency above ω\_Γ₅₄. Such peaks may be related to the so-called D′ (ω = 1620 cm\(^{-1}\)) and 2D′ (ω = 3250 cm\(^{-1}\)) bands of the graphite Raman spectra [33, 34] and were directly observed for 2.66% boron doped graphene [35].

Substitutional defects, for which the force constants for defect-carbon bonds are weaker than that for carbon–carbon bonds, may drastically change the phonon DOS in the low-frequency region (from 60 to 200 cm\(^{-1}\)) depending on the defect atom mass and weakened force constants. Note that a trace of an oscillation mode with a frequency of about 100–120 cm\(^{-1}\) near the Γ point was observed in graphite [4, 25, 36]. It turns out in some cases that a defect concentration even of several per cent may result in 100% low-frequency DOS increase in intervals wider than 100 cm\(^{-1}\). Obviously, the changes of the phonon low-frequency DOS stipulated by defects should be manifested in the low temperature specific heat of non-ideal graphene. The isotopic defects with greater than \(^{12}\)C mass lead to increase of the specific heat in proportion to the defect concentration (and temperature). Light defects slightly decrease the DOS and low temperature specific heat, but the difference from ideal graphene is sufficiently less than in the case of heavy defects. For substitutional defects the difference in density of states in the low-frequency region between graphene with defects and ideal graphene is much higher then in the case of isotopic defects and leads to significant changes in the specific heat (of the order of 10%). The specific heat of 3% Al doped graphene, \(ΔJ_1/J_1 = −0.25\), differs by more than 10% from that of ideal graphene.

Apart from slight shifts of the Van Hove points, significant changes in the DOSs are observed for any type of point defect near the ω\_K₄ and ω\_K₅₄ points where the oscillation modes are double-degenerated. For heavier isotopic defects the DOSs have more sharp peaks at the mentioned points. For substitutional atoms the changes near the ω\_K₄ and ω\_K₅₄ points are similar to those for purely isotopic defects (figure 6). For example, the deviation from the ideal DOS can reach as high as 30% for 2% Al doped graphene (figure 4). In comparison with isotopic defects the same concentrations of vacant lattice sites lead to a greater DOS rise for frequencies from ω\_K₄ to ω\_M₄ and to sufficient DOS decrease in the intervals (ω\_M₄, ω\_Γ₅₄) and (ω\_M₄, ω\_Γ₅₄). That lowering may be of the order of several per cent for the wide frequency range (figure 7). Both types of
The influence of 20% nitrogen doping (in the case of dimers) on the ideal graphene phonon density of states. The dashed, solid and dotted lines represent the DOSs of the ideal graphene, defect graphene (20% of N atoms) and defect contribution respectively. Two gaps in the density of states near $\omega_{K_{4,5}}$ and $\omega_{M_6}$ are labeled by the arrows.

The influence of 2% aluminum defect concentration (isobaric case, $J_i = 0.5 J_0$) on the ideal graphene phonon density of states. The dashed, solid and dotted lines represent the DOSs of the ideal graphene, defect graphene (2% of Al atoms) and defect contribution respectively. Defect also lead to the high additional peaks in the $\omega_{K_{1,2}}$ (see also [37]) and $\omega_{K_{4,5}}$ (figures 4 and 6). The singularities near the $\omega_{K_{1,2}}$ and $\omega_{K_{4,5}}$ may indicate the splitting of corresponding modes in the vicinity of the K point and in the case of high defect concentration the appearance of gaps in the density of states near $\omega_{K_{1,2}}$ and $\omega_{M_6}$ is evident (figure 5).

The vacant lattice sites except for the singularity at the $\omega_{K_{1,2}}$, point cause an additional resonant states peak with frequency between $\omega_{K_{1,2}}$ and $\omega_{M_6}$ (figure 7).

In the ideal graphene the momentum conservation allows only one single phonon Raman process which corresponds to the emission of the optical phonon with zero wavevector and frequency near 1580 cm$^{-1}$ ($\omega_{\Gamma_{2,1}}$) [38]. For non-ideal graphene there is also the so-called double-resonant presumably defect-induced peak (the D band) at 1350 cm$^{-1}$ corresponding to emission of an optical phonon with wavevector near the K points of the Brillouin zone [38–40]. Within the commonly accepted interpretation, impurities only assist the photons scattering on single intervalley phonons. On the other hand, our analysis shows that all the considered types of point defect cause additional Van Hove singularities of the DOS in the neighborhoods of the K and M points of optical branches, and that local oscillation modes may induce additional peaks of the Raman spectra.

Acknowledgment

This work was supported by the Ministry of Education and Science of Ukraine, Grant #0109U000929.

References

[1] Coulson C A 1952 Valence (Oxford: Clarendon Press)
[2] Dmeczyk B G, Wang Y M, Cumings J, Hetman M, Han W, Zettl A and Ritchie R O 2002 Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes Mater. Sci. Eng. 334 173–8
[3] Salvatet J P, Briggs G A D, Bonard J M, Bacsa R R, Kulik A J, Stockli T, Burnham N A and Forro L 1999 Elastic and shear moduli of single-walled carbon nanotube ropes Phys. Rev. Lett. 82 944–7
[4] Mohr M, Maultzsch J, Dobard I, Reich S, MiloIevi I, Damjanovi I, Bosak A, Krisch M and Thomsen C 2007 Phonon dispersion of graphite by inelastic x-ray scattering Phys. Rev. B 76 035439
[5] Oshima C, Aizawa T, Souda R, Ishizawa Y and Sumiyoshi Y 1988 Surface phonon dispersion curves of graphite (0 0 0 1) over the entire energy region Solid State Commun. 65 1601–4
[6] Siebenritt S, Pues R, Rieder K-H and Shikin A M 1997 Surface phonon dispersion in graphite and in a lanthanum graphite intercalation compound Phys. Rev. B 55 7927–34
[7] Hone J, Whitney M, Piskoti C and Zettl A 1999 Thermal conductivity of single-walled carbon nanotubes Phys. Rev. B 59 2514–6
[8] Saito R, Dresselhaus G and Dresselhaus M S 1998 Physical Properties of Carbon Nanotubes (London: Imperial College Press)
[9] Loiseau A, Launois P, Petit P, Roche S and Salvatet J P (ed) 2006 Understanding Carbon Nanotubes. From Basics to Applications (Lecture Notes in Physics vol 677) (Berlin: Springer)
