Quantized long-wavelength optical phonon modes in graphene nanoribbon in the elastic continuum model

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\textbf{A B S T R A C T}

This paper presents an analytical displacements and dispersion relations for optical phonons of a graphene sheet. These results are used to derive the optical deformation potential interactions for graphene as well as to obtain descriptions of the confined optical phonons for graphene.

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\begin{abstract}

The optical phonons in a graphene nanoribbon are studied using an elastic continuum model with a deformation potential. The analytical solutions for the displacements and dispersion relations are derived. The results are used to derive the optical deformation potential interactions for graphene as well as to obtain descriptions of the confined optical phonons for graphene.

\end{abstract}

\section{Introduction}

Graphene has attracted a great deal of attention since it was first successfully made by Geim [1,2] for its unique electronic, magnetic and thermal properties [3–8]. Carrier-phonon scattering will affect the electrical properties of graphene, such as resistivity and Fermi level shift [9–13]. It is important to study both the acoustic and optical phonons in graphene. Phonon dispersion has been studied by Raman and neutron scattering in graphite [14–16] and
Fig. 1. The clamped graphene nanoribbon lattice structure. The dashed lines illustrate a construction of the unit cell containing two carbon atoms A and B, while two primitive vectors are denoted as a and b. The coordinate system (x, y) is chosen respecting to the deposited electrodes with the x axis perpendicular and y axis parallel to the clamping electrodes. An angle analogous to the chiral angle θ is defined identical to the carbon nanotube with a chiral angle between the vector a and the x axis.

graphene [17–20]. Theoretical works have been undertaken to simulate the dispersion curves [15,21]. Graphene nanoribbon (GNR) can be seen as unwrapped carbon nanotube and is suitable for future device applications [22–25]. Herein we concentrate on the optical phonon modes, since one-center acoustic modes can only cause intraband carrier transitions but not interband carrier transitions [13]. It is important to study confined phonon modes in clamped graphene nanoribbons (GNRs), since boundaries occur in many device applications; for example, metal electrodes may be deposited on electric devices [24,25]. The continuum model is widely used to study phonon modes in semiconductor nanostructure [26] and provide a high accuracy for long wavelength phonons in the carbon based materials, such as C_{60} [27], carbon nanotubes [28–32] and graphene [10].

In this paper, we used the elastic continuum model to study the optical phonon in GNRs subject to a long wavelength limit. First, we employed Goupalov’s generalized equation [30] for LO phonons to derive detailed expressions for the relative displacement. Then, using a frequently assumed form of the boundary condition, it is assumed that the GNR is clamped at the boundaries, we apply quantized phonon modes and have dispersion curves for both armchair-end and zigzag-end GNRs. These results are limited to the few lowest order modes, i.e. lowest quantum numbers, since the elastic continuum model applies most accurately to these lower modes which have long wavelengths. The quantum normalized amplitude is calculated and used to obtain the optical deformation potential.

2. Model: Optical phonon in graphene sheet

As shown in Fig. 1 of the configuration of clamped GNR, x and y axes are in-plane perpendicular and parallel to the “clamping” boundaries or electrodes, respectively; the z axis is out-of-plane and perpendicular to the graphene surface. The width of the GNR is L, the length is infinite, and the thickness is neglected. We can treat the GNR as a 2D elastic sheet in a long wavelength limit and use the elastic continuum model to describe the optical vibration modes. The unit length along the x axis is \( a \cos \theta \), where \( a = \sqrt{3}a_{c-c} = 2.46 \text{ Å} \) is the length of the unit vector and \( \theta \) is the ‘chiral’ angle from the unit vector a with respect to the x axis. In a purely formal analogy with carbon nanotubes, we define two kinds of specific GNRs depending on the carbon atoms arrangement on the free-standing sides, which is identical to the definition of the carbon nanotubes [33]. The armchair-end and zigzag-end GNRs correspond to \( \theta = 30^\circ \) and \( 0^\circ \), respectively. Thus, the unit lengths along the x axis of armchair-end and zigzag-end graphene nanoribbons are \( \sqrt{3}a/2 \) and \( a \).
We use Goupalov’s generalized mechanical equations of a relative displacement of the two sublattices in a graphene sheet for the long-wavelength optical phonon modes [26]. The displacement is written as

$$\mathbf{\ddot{U}} = \hat{\Lambda}^{opt} \mathbf{U}, \quad (1)$$

where $\mathbf{U}$ is the relative displacement of the two sublattices $\mathbf{U} = \mathbf{u}_A - \mathbf{u}_B = (u \ v \ w)$ and the $\hat{\Lambda}^{opt}$ is the operator for optical phonons given as

$$-\hat{\Lambda}^{opt}_{20G} = \omega^2_{T0} + \frac{\beta_T^2 - \beta_2^2}{2} J_2^2 \nabla^2 + \frac{\beta_T^2 + \beta_2^2}{2} (\nabla^2 J_2^2 + \nabla^2 J_2^2) + \frac{\lambda^2}{2} (\nabla^2 J_2^2 + \nabla^2 J_2^2) \nabla^2$$

$$-\lambda^2 J_2^2 \nabla^2 - \beta_2^2 (J_2^2 - 1) \nabla^2 + (\omega^2_{T0} - \omega^2_{20}) (J_2^2 - 1) \quad (2)$$

where $J_\pm = \mp 1/\sqrt{2} (J_x \pm i J_y)$. $J_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}$, $J_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}$, $J_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ are the matrices of projections of the spin operator $J = 1$ in the Cartesian basis, $\nabla_\pm = \nabla_x \pm i \nabla_y, \nabla^2_\pm = \nabla^2_x + \nabla^2_y, \nabla_x, \nabla_y, \nabla_z$ are the projections of the gradient operator $\nabla$.

The parameters $(\omega_{T0}, \beta_T, \beta_2, \lambda)$ are approximated by fitting the dispersion curves of LO and TO phonons in 2D graphite in the $\Gamma$–M direction in [14], while the $\omega_{20}$ and $\beta_2$ are by ZO results in [15]. For the in-plane LO and TO modes and the out-of-plane ZO mode, the phonon dispersions are fitted by

$$\omega^2(k) = \begin{cases} \omega^2_{T0} - \beta_2^2 k^2, & \text{TO}, \\ \omega^2_{T0} - \lambda k^4 + \beta_2^2 k^2, & \text{LO}, \\ \omega^2_{ZO} - \beta_2^2 k^2, & \text{TO}. \end{cases} \quad (3)$$

For non-polar graphene, $\omega_{T0} = \omega_{LO} = 1581 \text{ cm}^{-1}, \omega_{ZO} = 893 \text{ cm}^{-1}$ are the frequencies of TO, LO and ZO at the center, $\Gamma$ point, of reciprocal lattices of the graphene; $\beta_L = 7.8 \times 10^5 \text{ cm/s}, \beta_T = 9.6 \times 10^5 \text{ cm/s}, \beta_2 = 7.9 \times 10^5 \text{ cm/s}, \lambda = 9.3 \times 10^{-3} \text{ cm/s}$.

Applying the operator on the relative displacement, we can have explicit expressions as follows

$$-\ddot{u} = \begin{bmatrix} \omega^2_{T0} - \beta_2^2 \nabla^2 + \beta_T^2 \nabla^2 - \lambda^2 \nabla^2 (\nabla^2 + \nabla^2) \\ \beta_2^2 \nabla^2 + \beta_T^2 \nabla^2 - \lambda^2 \nabla^2 (\nabla^2 + \nabla^2) \end{bmatrix} u$$

$$-\ddot{v} = \begin{bmatrix} \omega^2_{T0} - \beta_2^2 \nabla^2 + \beta_T^2 \nabla^2 - \lambda^2 \nabla^2 (\nabla^2 + \nabla^2) \\ \beta_2^2 \nabla^2 + \beta_T^2 \nabla^2 - \lambda^2 \nabla^2 (\nabla^2 + \nabla^2) \end{bmatrix} v$$

$$-\ddot{w} = \begin{bmatrix} \omega^2_{ZO} - \beta_2^2 \nabla^2 (\nabla^2 + \nabla^2) \\ \omega^2_{ZO} + \beta_2^2 \nabla^2 (\nabla^2 + \nabla^2) \end{bmatrix} w. \quad (4)$$

So, the in-plane vibrations, $u$ and $v$, and out-of-plane vibration, $w$, are decoupled, while the in-plane vibrations, $u$ and $v$, are coupled each other. Thus, the solution in the form of the in-plane travelling wave can be taken as

$$\mathbf{U}(x, y, t) = \mathbf{A} \exp \left[ i \left( q_x x + q_y y - \omega t \right) \right]. \quad (5)$$

Then, the displacement equations can be written as

$$\omega^2 u = \begin{bmatrix} \omega^2_{T0} + \beta_2^2 q_x^2 - \beta_T^2 q_y^2 - \lambda^2 q_x^2 (q_x^2 + q_y^2) \\ \beta_2^2 \omega^2_{T0} + \beta_2^2 \omega^2_{ZO} - \beta_2^2 q_x^2 - \lambda^2 q_x^2 (q_x^2 + q_y^2) \end{bmatrix} u$$

$$\omega^2 v = \begin{bmatrix} \omega^2_{T0} + \beta_2^2 q_y^2 - \beta_T^2 q_x^2 - \lambda^2 q_y^2 (q_x^2 + q_y^2) \\ \beta_2^2 \omega^2_{T0} + \beta_2^2 \omega^2_{ZO} - \beta_2^2 q_y^2 - \lambda^2 q_y^2 (q_x^2 + q_y^2) \end{bmatrix} v$$

$$\omega^2 w = \begin{bmatrix} \omega^2_{ZO} - \beta_2^2 (q_x^2 + q_y^2) \\ \omega^2_{ZO} + \beta_2^2 (q_x^2 + q_y^2) \end{bmatrix} w. \quad (6)$$

Then we reproduce dispersion relationships of Goupalov in the form,

$$\omega^2(q) = \begin{bmatrix} \omega^2_{T0} - \beta_2^2 (q_x^2 + q_y^2) \\ \omega^2_{T0} - \lambda^2 (q_x^2 + q_y^2)^2 + \beta_T^2 (q_x^2 + q_y^2) \\ \omega^2_{ZO} - \beta_2^2 (q_x^2 + q_y^2) \end{bmatrix} \quad (7)$$
Fig. 2. (a) Armchair-end graphene nanoribbon, \( \theta = 30^\circ \), the width is \( N \frac{\sqrt{3}}{2} a \) when \( N \) is even, and \( (N + \frac{1}{2}) \frac{\sqrt{3}}{2} a \) when \( N \) is odd; (b) Zigzag-end graphene nanoribbon, \( \theta = 0^\circ \).

for long wavelength phonons propagating in the GNR. This implies that the phonon propagation in GNR in this continuum model has the same dispersion curves in the arbitrary propagation direction.

### 3. Confined optical phonons in clamped graphene nanoribbons and the normalization of the displacements

Assuming vanishing displacements at boundaries, in an approximation commonly known as “clamped” boundary conditions or mechanical boundary conditions and referring to Fig. 1, we have,

\[
\mathbf{u} = 0 \quad \text{at} \quad x = 0 \text{ and } L.
\]

These boundary conditions imply,

\[
q_x = q_n = \frac{2\pi n}{L} \quad \text{and let} \quad q_y = q; \quad \text{we have the displacement as}
\]

\[
\mathbf{U}(x, y, t) = A \exp \left[ i (q_n x + q y - \omega t) \right]. \tag{8}
\]

Since along the \( x \) axis, the displacement \( u \) is confined between the two electrodes, \( u \) is represented as a standing wave equation:

\[
u = u_0 \sin (q_n x). \tag{9}\]

The dispersion relations with confined wavevectors are,

\[
\omega_n^2 = \begin{cases} 
\omega_{10}^2 - \beta_T^2 (q_n^2 + q^2) \\
\omega_{20}^2 - \lambda^2 (q_n^2 + q^2)^2 + \beta_T^2 (q_n^2 + q^2) \\
\omega_{30}^2 - \beta_T^2 (q_n^2 + q^2) 
\end{cases} \tag{10}
\]

We consider armchair-end and zigzag-end GNRs with \( N \) periods. For armchair-end GNR, the widths is \( N \frac{\sqrt{3}}{2} a \) when \( N \) is even, and \( (N + \frac{1}{2}) \frac{\sqrt{3}}{2} a \) when \( N \) is odd. For the zigzag-end GNR, the width is \( Na \) for all \( N \). We will have dispersion curves for optical phonon modes for four kinds of GNRs: armchair-end of 5 periods and 10 periods with the width of 1.14 nm and 2.13 nm, respectively; and a zigzag-end of 5 units and 10 units with the width of 1.23 nm and 2.46 nm, respectively. Since our model applies to the long wavelength limit, we focus on the few lowest vibration modes with a quantized number up to half \( N \), since in real confined vibration modes of nanostructures only the several lowest modes appear \([28,31]\), while for higher modes the elastic continuum model does not work since the graphene can not be treated as continuum media. For a 5-period GNR, we have \( n \) from 0 to 3; for a 10-period GNR, we have \( n \) from 0 to 5 (Fig. 2).
Fig. 3. Dispersion curves of optical vibrational modes in armchair-end graphene nanoribbon that are (a) 1.14 nm wide and (b) 2.13 nm wide. The quantized number \( n \) of the wave vector \( q_x = q_y = \frac{n \pi}{L} \) are from 0 to (a) 3 and (b) 5. The inserted images are LO dispersion curves near the zone-center: the \( x \) axis is the wave vector from 0 to 0.3 \( qa/\pi \), the \( y \) axis is the mode frequency.

Fig. 4. Dispersion curves of optical vibrational modes in zigzag-end graphene nanoribbon that are (a) 1.23 nm wide and (b) 2.46 nm wide. The quantized number \( n \) of the wave vector \( q_x = q_y = \frac{n \pi}{L} \) are from 0 to (a) 3 and (b) 5. The inserted images are LO dispersion curves near the zone-center: the \( x \) axis is the wave vector from 0 to 0.3 \( qa/\pi \), the \( y \) axis is the mode frequency.

The dispersion curves of LO, TO and ZO vibration modes for the armchair-end GNRs of 5 units and 10 units are shown in Fig. 3(a) and (b), respectively. For both armchair–end GNRs, the larger the quantized number \( n \), the smaller the vibration frequencies of the phonon modes for TO and ZO modes during the whole wave vector domain. In a 5-period armchair-end GNR at the zone-center, for LO modes with quantized number \( n \) 2, there exists a maximum frequency 1590.7 cm\(^{-1}\) as in the inserted picture in Fig. 3(a). For the lowest two quantized modes, when \( n \) equals 0 and 1, the LO mode frequencies increase near the zone-center and then decrease along increasing wave vectors. For the \( n \) larger than 3, the LO mode directly decreases with the wave vector from the zone-center. While in the 10-period armchair-end GNR, similarly at the zone-center, a maximum LO frequency 1590.9 cm\(^{-1}\) appears when \( n \) equals 4. When \( n \) is larger than 4, the LO frequencies decrease directly; when \( n \) is smaller than 4, the LO frequencies increase first and then decrease. Thus for both the armchair-end GNRs, there exist a critical quantized number of \( n \), which makes the zone-center LO vibration modes of a maximum frequency. When the quantized number is smaller than \( n \), the maximum vibration frequency does not appear at the zone center. Thus, the critical quantized number performs as a mark to describe two sorts of LO modes having a discretely increasing type.

Fig. 4 shows the dispersion curves of LO, TO and ZO vibration modes for 5- and 10-period zigzag-end GNR in (a) and (b), respectively. We have the quantized number \( n \) from 0 to 3 for the 5-period zigzag-end GNR and 0 to 5 for the 10-period. The dispersion curves present the same properties as the armchair-end GNR with a critical quantized number existing for LO modes, 1590.1 cm\(^{-1}\) and
1590.9 cm\(^{-1}\) when \(n\) equals 2 for 5- and 5 for the 10-period zigzag GNRs, respectively. The 10-period zigzag-end GNR has a larger maximum frequency at the zone-center than the 5-period zigzag-end GNR, since it has higher density quantized wave vectors. Phonon dispersion curves with the quantum number \(n\) for the 5-period and 2\(n\) for the 10-period zigzag-end GNRs are the same, since they have the same quantized wavevectors by \(q=\frac{\pi n}{L}=\frac{\pi n}{N_0}\). Thus, the zigzag-end GNR with the multiplied width has some certain vibration modes with the same multiplying number. If the graphene nanoribbon is of a large width, the quantized dispersion curves will become phonon dispersion bands for quasi-continuous quantized numbers.

Neglecting the thickness of the graphene nanoribbon, we have the normalization in the 2D model. Recall the displacement equations for \(u\) and \(v\) in Eq. (6). In order to solve \(u\) and \(v\), we will replace \(\omega_n^2\) using the dispersion curves for LO and TO modes in Eq. (10):

Putting \(\omega_n^2 = \omega_{TO}^2 - \beta_x^2 (q_n^2 + q^2)\) of the TO mode in the first displacement equation of Eq. (6), it is found that the relationship between \(u\) and \(v\) is

\[
\frac{v}{u} = -\frac{q_n}{q}. \tag{11}
\]

Considering the boundary conditions along the \(x\) axis, the detailed displacements equations for \(u\) and \(v\) are

\[
\begin{cases}
  u = u_0 \sin (q_n x) \\
  v = -\frac{q_n}{q} u_0 \sin (q_n x)
\end{cases} \tag{12}
\]

The mode amplitudes are given by the condition that the energy in each mode is \(\frac{\hbar}{M \omega_n}\), which results in

\[
\frac{1}{S} \int_s (u \cdot u^* + v \cdot v^*) \, dx \, dy = \frac{\hbar}{M \omega_n}. \tag{13}
\]

The quantized displacement amplitudes, \(u_0\) and \(v_0\) are

\[
u_0 = \left( \frac{2 \hbar}{M \omega_n} \frac{q^2}{q_n^2 + q^2} \right)^{\frac{1}{2}} \quad \text{and} \quad v_0 = -\left( \frac{2 \hbar}{M \omega_n} \frac{q_n^2}{q_n^2 + q^2} \right)^{\frac{1}{2}}. \tag{14}\]

Putting \(\omega^2 = \omega_{LO}^2 - \lambda^2 (q_n^2 + q^2)^2 + \beta_x^2 (q_n^2 + q^2)\) of the LO mode in the first displacement equation of Eq. (6), the relationship between \(u\) and \(v\) is

\[
\frac{v}{u} = -\frac{q}{q_n}. \tag{15}\]

Similarly, the quantized displacement amplitudes, \(u_0\) and \(v_0\) are

\[
u_0 = \left( \frac{2 \hbar}{M \omega_n} \frac{q_n^2}{q_n^2 + q^2} \right)^{\frac{1}{2}} \quad \text{and} \quad v_0 = -\left( \frac{2 \hbar}{M \omega_n} \frac{q^2}{q_n^2 + q^2} \right)^{\frac{1}{2}}. \tag{16}\]

### 4. Deformation potential

The optical deformation potential Hamiltonian describing carrier optical-phonon scattering can be determined from those normalized continuum modes, which is given in [26,34]

\[
H_{\text{opt-def}} = D \cdot U \tag{17}
\]

where \(D\) is the optical-phonon deformation potential constant which is equal to 8.89 eV [35] for graphene. Then replacing \(U\) by \(u\) and \(v\) expression in Section 3, it is found that

\[
H_{\text{opt-def}} = |D| (u + v). \tag{18}\]
The deformation potential Hamiltonian for the TO phonon is given by

\[ H_{\text{opt-def}} = |D| \left( \frac{2\hbar}{M\omega_n} \right)^{\frac{1}{2}} \frac{q - q_n}{\sqrt{q_n^2 + q^2}} \sin(q_n x) \]  

(19)

and, the deformation potential Hamiltonian for the LO phonon is given by

\[ H_{\text{opt-def}} = |D| \left( \frac{2\hbar}{M\omega_n} \right)^{\frac{1}{2}} \frac{q_n - q}{\sqrt{q_n^2 + q^2}} \sin(q_n x). \]  

(20)

Physically, the carrier-phonon interaction described by this optical deformation potential Hamiltonian represents the interaction of a charge carrier in a medium where the energy band structure is modulated alternately to higher and lower energies, or is caused to oscillate in the harmonic approximation, as a result of the phonon-induced modulation of the interatomic separation. Since the kinetic energies of carriers are defined relative to the energies of the energy band structure, the modulation of the energy band structure leads to a modulation of the carrier kinetic energy as described by the above equation. For a more complete discussion of the optical deformation potential, and the related acoustic deformation potential, see Ref. [34].

5. Discussion and conclusion

Exact solutions of Eq. (4) in specific cases involve the use of both of the cardinal boundary conditions of classical acoustics—both continuity of displacement and continuity of the normal component of the stress tensor. In the case where the displacement is approximately zero at the boundary in question, the continuity of the analyzed displacement is referred to as the clamped boundary condition. To render the current problem tractable, we have used clamped boundary conditions – zero displacement at the boundary – as has been done successfully in the past by Ridley [36] and in a number of other works [34] involving acoustic modes in nanostructures. Indeed, solutions for acoustic modes – upon which our solutions are based – are in most cases performed by selecting either clamped or free-standing boundary conditions (zero normal component of the stress tensor), as illustrated by numerous examples in the classic book by Auld [37] on acoustics, due to the complexity of these modes. In addition, our simplified model gives modes of the same form as the modes analyzed in Atalaya’s paper [38] for the longest wavelength modes. Since the continuum model used in this work holds strictly for the long-wavelength modes, and, therefore, we have restricted our presentation of graphene modes to the few lowest (longest-wavelength) modes.

In this paper, approximated optical vibrational modes of graphene nanoribbons are determined analytically using an elastic continuum model. For definiteness, we have assumed the commonly invoked “clamped” boundary condition. The dispersion relationships are given for structures that we describe as armchair-end and zigzag-end graphene nanoribbons. A critical quantized number exists in both armchair- and zigzag-end graphene nanoribbons. The quantized normalization amplitudes for the optical modes are solved analytically. Finally, the deformation potential Hamiltonian is calculated using the deformation normalization amplitude. The approximate analytical optical phonon modes and the associated optical deformational potential Hamiltonian presented in this paper are accurate in the long wavelength limit and the lowest few quantized optical modes.

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References
