

Chapter 2

Phonons in Bulk and Low-Dimensional Systems

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Abstract This review highlights selected advances of the last decade in the theory of acoustic and optical phonons in dimensionally confined structures. The basic concepts of the elastic continuum and dielectric continuum models are reviewed. Following this review, specific examples of phonon confinement in dimensionally confined structures are highlighted. These examples include: phonons in single wall carbon nanotubes (CNTs), phonons in multi wall nanotubes, graphene sheets, graphene nanoribbons, graphene quantum dots, graphite confined along the c -axis, and wurtzite structures including quantum wells and quantum dots. The review also covers a number of mechanisms underlying carrier–phonon scattering processes. Finally, this review summarizes the mode amplitudes for a variety of nanostructures.

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2.1 Introduction

The application of continuum models in describing acoustic and optical phonon phenomena has been surveyed by Strosio and Dutta [1]. Over the last decade there have been additional applications of these continuum models to describe phonon phenomena both in conventional and in novel materials systems. Such applications have been extended to carbon nanotubes (CNTs), graphene, and graphite. In addition, over the last decade there have been many applications to conventional materials including those with cubic and wurtzite structure. This review highlights selected applications of continuum models to describe phonon effects in bulk and low-dimensional structures. In this section, a very brief review of basic material for elastic continuum model and dielectric continuum models will be summarized.

2.1.1 Elastic Continuum Model of Phonons

The elastic continuum model of acoustic phonons provides an adequate description of acoustic phonons for nanostructures having confined dimensions of about two atomic monolayers or greater [1]. The case of a longitudinal acoustic mode propagating in a quasi-one-dimensional structure provides an illuminating application of the elastic continuum model.

Consider an element dx on a quasi-one-dimensional structure located between x and $x + dx$. Let us take a longitudinal displacement as an example. The stress $T(x)$, which is the force per unit area in this structure of area A , is given following from Hooke's law:

$$T = Ye, \quad (2.1)$$

where $e = du/dx$ is the strain, $u(x,t)$ describes the uniform longitudinal displacement of the element dx , and Y is a proportionality constant known as Young's modulus. In such a case, Newton's second law,

$$\rho(x)A dx \frac{\partial^2 u(x,t)}{\partial t^2} = [T(x + dx) - T(x)]A, \quad (2.2)$$

describes the dynamics of the element dx of density $\rho(x)$. Moreover $\rho A dx$ is the mass associated with the element dx and $\partial^2 u / \partial t^2$. Using Hooke's law

$$T(x + dx) - T(x) = \left(\frac{\partial T}{\partial x} \right) dx = \left(Y \frac{\partial e}{\partial x} \right) dx = \left(Y \frac{\partial^2 u}{\partial x^2} \right) dx, \quad (2.3)$$

and from Eq. (2.2) it follows that

$$\frac{\partial^2 u}{\partial x^2} = \left(\frac{\rho(x)}{Y} \right) \frac{\partial^2 u}{\partial t^2}, \quad (2.4)$$

which is recognized as the one-dimensional wave equation, also known as the classical Helmholtz equation.

To generalize these results to three dimensions, we make the replacements $u(x) \rightarrow \mathbf{u}(x,y,z) = (u,v,w)$ and $T = Ye \rightarrow T = c : S$ with $T_i = c_{ij}S_j$. In these three-dimensional expressions, Y is replaced by a 6×6 matrix of elastic constants c_{ij} ; e is replaced by a six-component object S_j ; T is replaced by a six-component object T_i . For the commonly encountered and practical cases of cubic, zincblende, and wurtzite crystals the most general form of the stress-strain relation, $T_{ij} = c_{ijkl}S_{kl}$, where i, j, k, l run over x, y, z , may be represented by $T_i = c_{ij}S_j$. In this last result, i and j run over the integers from one to six. The resulting forms for the stress, T_i , are [2]

$$\begin{aligned} T_1 &= T_{xx}, & T_2 &= T_{yy}, & T_3 &= T_{zz}, \\ T_4 &= T_{yz} = T_{zy}, & T_5 &= T_{xz} = T_{zx}, & T_6 &= T_{xy} = T_{yx}. \end{aligned} \quad (2.5)$$

For the strain, S_j , the forms are

$$\begin{aligned} S_1 &= S_{xx} = \frac{\partial u}{\partial x}, & S_2 &= S_{yy} = \frac{\partial u}{\partial y}, & S_3 &= S_{zz} = \frac{\partial u}{\partial z}, \\ S_4 &= S_{yz} = S_{zy} = \frac{1}{2} \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \\ S_5 &= S_{xz} = S_{zx} = \frac{1}{2} \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right), \\ S_6 &= S_{xy} = S_{yx} = \frac{1}{2} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right). \end{aligned} \quad (2.6)$$

In many cases of practical and widespread interest in electronics and optoelectronics, nanostructures are generally fabricated from zincblende and wurtzite crystals. Taking into account that the elastic energy to be single valued $c_{ij} = c_{ji}$, only 21 distinct elements are necessary to define the 6×6 matrix c_{ij} . For cubic crystals, the matrix, c_{ij} , takes the form [2]

$$\begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \quad (2.7)$$

and for wurtzite crystals, c_{ij} , may be expressed in the form [2]

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & (c_{11} - c_{12})/2 \end{pmatrix}. \quad (2.8)$$

As is well known, cubic crystal, including zincblende crystals, may be described in terms of only three independent elastic constants, c_{11} , c_{12} , and c_{44} . Indeed, these independent constants replace Y ; c_{11} , relates the compressive stress to the strain along the same direction, c_{44} , relates the shear stress and the strain in the same direction, and c_{12} , relates the compressive stress in one direction and the strain in another direction.

Furthermore, for an isotropic cubic medium, $c_{12} = c_{11} - 2c_{44}$. Thus, only two constants are necessary to specify the c_{ij} :

$$\begin{aligned} c_{12} &= c_{13} = c_{21} = c_{23} = c_{31} = c_{32} = \lambda, \\ c_{44} &= c_{55} = c_{66} = \frac{1}{2} (c_{11} - c_{22}) = \mu, \\ c_{11} &= c_{22} = c_{33} = \lambda + 2\mu. \end{aligned} \quad (2.9)$$

In the previous results, the constants λ and μ are recognized as the well-known Lamé's constants. In the isotropic case, the previous results imply that

$$\begin{aligned} T_{xx} &= \lambda (S_{xx} + S_{yy} + S_{zz}) + 2\mu S_{xx} = \lambda \Delta + 2\mu S_{xx}, \\ T_{yy} &= \lambda (S_{xx} + S_{yy} + S_{zz}) + 2\mu S_{yy} = \lambda \Delta + 2\mu S_{yy}, \\ T_{zz} &= \lambda (S_{xx} + S_{yy} + S_{zz}) + 2\mu S_{zz} = \lambda \Delta + 2\mu S_{zz}, \\ T_{yz} &= T_{zy} = \mu S_{yz}, \quad T_{zx} = T_{xz} = \mu S_{zx}, \quad T_{xy} = T_{yx} = \mu S_{xy}, \end{aligned} \quad (2.10)$$

where $\Delta = \partial u / \partial x + \partial v / \partial y + \partial w / \partial z$ is known as the dilatation of the medium. Then, the three-dimensional generalization of Eq. (2.2) is given by

$$\begin{aligned} \rho \frac{\partial^2 u}{\partial t^2} &= \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{yx}}{\partial y} + \frac{\partial T_{zx}}{\partial z} = (\lambda + \mu) \frac{\partial \Delta}{\partial x} + \mu \nabla^2 u, \\ \rho \frac{\partial^2 v}{\partial t^2} &= \frac{\partial T_{xy}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{zy}}{\partial z} = (\lambda + \mu) \frac{\partial \Delta}{\partial y} + \mu \nabla^2 v, \\ \rho \frac{\partial^2 w}{\partial t^2} &= \frac{\partial T_{xz}}{\partial x} + \frac{\partial T_{yz}}{\partial y} + \frac{\partial T_{zz}}{\partial z} = (\lambda + \mu) \frac{\partial \Delta}{\partial z} + \mu \nabla^2 w, \end{aligned} \quad (2.11)$$

where $\nabla^2 = \partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2$ is Laplace operator.

There are two highly useful alternative forms of the three-dimensional force equations that are encountered frequently in the literature. The first of these forms may be obtained by writing the components of $\mathbf{u}(x,y,z) = (u_x, u_y, u_z)$ as u_α . Accordingly, the three force equations take the form

$$\rho \frac{\partial^2 u_\alpha}{\partial t^2} = \frac{\partial T_{\alpha\beta}}{\partial r_\beta}, \quad (2.12)$$

with

$$T_{\alpha\beta} = \lambda S_{\alpha\alpha} \delta_{\alpha\beta} + 2\mu S_{\alpha\beta}, \quad (2.13)$$

where $\alpha, \beta = x, y, z$, and $\delta_{\alpha\beta}$ is the Kronecker delta function. Following the Einstein summation convention, a repeated index in a term implies summation.

In a second highly useful alternative form, the three force equations may be summarized in terms of a single vector equation

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = c_t^2 \nabla^2 \mathbf{u} + (c_l^2 - c_t^2) \text{grad} (\nabla \cdot \mathbf{u}), \quad (2.14)$$

where c_t and c_l are the transverse and longitudinal sound speeds, respectively, and where

$$c_t^2 = \frac{\lambda}{\rho} \quad \text{and} \quad c_l^2 = \frac{\lambda + 2\mu}{\rho}. \quad (2.15)$$

In the classical theory of acoustics, the solutions for the displacement fields may be specified in terms of two potential functions: a vector potential, $\Psi = (\Psi_x, \Psi_y, \Psi_z)$ as Ψ_i ($i = x, y, z$), and a scalar potential ϕ , through

$$\begin{aligned} u &= \frac{\partial \phi}{\partial x} + \frac{\partial \Psi_x}{\partial y} - \frac{\partial \Psi_y}{\partial z}, \\ v &= \frac{\partial \phi}{\partial y} + \frac{\partial \Psi_x}{\partial z} - \frac{\partial \Psi_z}{\partial x}, \\ w &= \frac{\partial \phi}{\partial z} + \frac{\partial \Psi_y}{\partial x} - \frac{\partial \Psi_x}{\partial y}, \end{aligned} \quad (2.16)$$

where Ψ_i and ϕ obey simple wave equations of the form

$$\nabla^2 \Psi_i = \frac{1}{c_t^2} \frac{\partial^2 \Psi_i}{\partial t^2} \quad \text{and} \quad \nabla^2 \phi = \frac{1}{c_l^2} \frac{\partial^2 \phi}{\partial t^2}. \quad (2.17)$$

The vector potential represents the “rotational” fields, and the scalar potential represents the “irrotational” part of the solution. The irrotational part is referred

to in a number of different ways in the literature; specifically, it is referred to as the longitudinal, compressional, or dilatational solutions. Likewise, the rotational solutions are referred to as transverse, shear, equivoluminal, and distortional solutions.

2.1.2 Dielectric Continuum Model of Phonons

The continuum theory of optical phonons in polar materials is described by the dielectric continuum model, which is based on the fact that the associated lattice vibrations produce an electric polarization that is given in terms of the equations of electrostatics for a dielectric medium [3–11].

Assuming the volume of the structure is to be L^3 ($-L/2 \leq x, y, z \leq L/2$) and under periodic boundary conditions, the optical phonon potential, $\Phi(\mathbf{r})$, and the associated polarization field, $\mathbf{P}(\mathbf{r})$, are related by Strocio and Dutta [1]

$$\nabla^2 \Phi(\mathbf{r}) = 4\pi \nabla \cdot \mathbf{P}(\mathbf{r}) . \quad (2.18)$$

In addition, the polarization field, $\mathbf{P}(\mathbf{r})$, and the electric field, $\mathbf{E}(\mathbf{r})$, are related through the dielectric susceptibility, $\chi(\omega)$, with phonon frequency, ω , in medium g ; that is,

$$\mathbf{P}(\mathbf{r}) = \chi(\omega) \mathbf{E}(\mathbf{r}) , \quad (2.19)$$

where as usual,

$$\mathbf{E}(\mathbf{r}) = -\nabla \Phi(\mathbf{r}) , \quad (2.20)$$

and

$$\chi(\omega) = [\varepsilon(\omega) - 1] / 4\pi . \quad (2.21)$$

The dielectric function $\varepsilon(\omega)$ of medium g is given by

$$\varepsilon(\omega) = \varepsilon^\infty \frac{\omega^2 - \omega_{\text{LO}}^2}{\omega^2 - \omega_{\text{TO}}^2} , \quad (2.22)$$

in the case of a binary polar semiconductor, AB , and is expressible as

$$\varepsilon(\omega) = \varepsilon^\infty \frac{\omega^2 - \omega_{\text{LO},a}^2}{\omega^2 - \omega_{\text{TO},a}^2} \frac{\omega^2 - \omega_{\text{LO},b}^2}{\omega^2 - \omega_{\text{TO},b}^2} , \quad (2.23)$$

for the case of a ternary polar material, $A_xB_{1-x}C$, where as usual ε^∞ is the high-frequency dielectric constant. In addition, ω_{LO} and ω_{TO} are the frequency of the longitudinal optical (LO) phonons and transverse optical (TO) phonons, respectively, the subscript a denotes frequency associated with the dipole pairs AC and the subscript b denotes frequency associated with the dipole pairs BC .

The displacement field $\mathbf{u}(\mathbf{r})$ is related to the fields $\mathbf{E}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$ through the so-called driven oscillator equation. In the case of a binary medium g ,

$$\begin{aligned} -\mu\omega^2\mathbf{u}(\mathbf{r}) &= -\mu\omega_0^2\mathbf{u}(\mathbf{r}) + e\mathbf{E}_{\text{local}}(\mathbf{r}), \\ \mathbf{P}(\mathbf{r}) &= ne\mathbf{u}(\mathbf{r}) + n\alpha\mathbf{E}_{\text{local}}(\mathbf{r}), \end{aligned} \quad (2.24)$$

where e is the effective charge, $\mu = mM/(m+M)$ is the reduced mass, $\omega_0^2 = 2\alpha(1/m + 1/M)$ is the resonant frequency squared, and α is the electronic polarizability per unit cell, n is the number of unit cells in region g , and $\mathbf{E}_{\text{local}}(\mathbf{r})$ is the local field given by the Lorentz relation

$$\mathbf{E}_{\text{local}}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \frac{4\pi}{3}\mathbf{P}(\mathbf{r}). \quad (2.25)$$

Using the virtual-crystal approximation, for the dipole pairs AC (BC) in a ternary medium m , it follows that

$$\begin{aligned} -\mu_{m,a(b)}\omega^2\mathbf{u}_{m,a(b)}(\mathbf{r}) &= -\mu_m\omega_{0m,a(b)}^2\mathbf{u}_{m,a(b)}(\mathbf{r}) + e_{m,a(b)}\mathbf{E}_{\text{local}}(\mathbf{r}), \\ \mathbf{P}(\mathbf{r}) &= n_m [xe_{m,a(b)}\mathbf{u}_{m,a}(\mathbf{r}) + (1-x)e_{m,b}\mathbf{u}_{m,b}(\mathbf{r})] + n_m\alpha_m\mathbf{E}_{\text{local}}(\mathbf{r}). \end{aligned} \quad (2.26)$$

From Huang–Born theory [12], an alternative and useful form of these equations for the case of a diatomic polar material may be written as

$$\begin{aligned} \ddot{\mathbf{u}} &= -\omega_{TO}^2\mathbf{u} + \sqrt{\frac{V}{4\pi\mu N}}\sqrt{\varepsilon^0 - \varepsilon^\infty}\omega_{TO}\mathbf{E}, \\ \mathbf{P} &= \sqrt{\frac{\mu N}{4\pi V}}\sqrt{\varepsilon^0 - \varepsilon^\infty}\omega_{TO}\mathbf{u} + \frac{\varepsilon^\infty - 1}{4\pi}\mathbf{E}, \end{aligned} \quad (2.27)$$

where ε^0 is static dielectric constant, V is the volume of the material, and it has been assumed that $\ddot{\mathbf{u}}$ has a general form for the time dependence and may not necessarily be simply sinusoidal in ω .

Equation (2.27) provides the basis for the derivation of the macroscopic equations describing optical phonons in polar uniaxial materials such as the hexagonal wurtzite structures of GaN, AlN, and $\text{Ga}_x\text{Al}_{1-x}\text{N}$ [13]. By introducing one dielectric constant associated with the direction parallel to the c -axis, ε_z , and another dielectric constant associated with the direction perpendicular to the c -axis, ε_\perp , the macroscopic equation for a uniaxial polar crystal may be derived [13]. In describing the phonon mode displacements, it is convenient to separate the displacements

parallel to the c -axis, denoted by \mathbf{u}_z , and those perpendicular to c -axis, denoted by \mathbf{u}_\perp . For medium g , we then have

$$\begin{aligned}\ddot{\mathbf{u}}_\perp &= -\omega_{\text{TO},\perp}^2 \mathbf{u}_\perp + \sqrt{\frac{V}{4\pi\mu N}} \sqrt{\varepsilon_\perp^0 - \varepsilon_\perp^\infty} \omega_{\text{TO},\perp} \mathbf{E}_\perp, \\ \mathbf{P}_\perp &= \sqrt{\frac{\mu N}{4\pi V}} \sqrt{\varepsilon_\perp^0 - \varepsilon_\perp^\infty} \omega_{\text{TO},\perp} \mathbf{u}_\perp + \frac{\varepsilon_\perp^\infty - 1}{4\pi} \mathbf{E}_\perp, \\ \varepsilon_\perp(\omega) &= \varepsilon_\perp^\infty \frac{\omega^2 - \omega_{\text{LO},\perp}^2}{\omega^2 - \omega_{\text{TO},\perp}^2},\end{aligned}\tag{2.28}$$

and

$$\begin{aligned}\ddot{\mathbf{u}}_z &= -\omega_{\text{TO},z}^2 \mathbf{u}_z + \sqrt{\frac{V}{4\pi\mu N}} \sqrt{\varepsilon_z^0 - \varepsilon_z^\infty} \omega_{\text{TO},z} \mathbf{E}_z, \\ \mathbf{P}_z &= \sqrt{\frac{\mu N}{4\pi V}} \sqrt{\varepsilon_z^0 - \varepsilon_z^\infty} \omega_{\text{TO},z} \mathbf{u}_z + \frac{\varepsilon_z^\infty - 1}{4\pi} \mathbf{E}_z, \\ \varepsilon_z(\omega) &= \varepsilon_z^\infty \frac{\omega^2 - \omega_{\text{LO},z}^2}{\omega^2 - \omega_{\text{TO},z}^2}.\end{aligned}\tag{2.29}$$

It has been assumed that $\ddot{\mathbf{u}}_\perp$ and $\ddot{\mathbf{u}}_z$ have a general form of the dependence and may not necessarily be simply sinusoidal in ω . In Loudon's model, above six equations combined with the following three equations of electrostatics for the case where there is no free charge

$$\begin{aligned}\mathbf{E}(\mathbf{r}) &= -\nabla\phi(\mathbf{r}), \\ \mathbf{D}(\mathbf{r}) &= \varepsilon\mathbf{E}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}(\mathbf{r}) \\ &= \varepsilon_\perp(\omega) E_\perp(\mathbf{r}) \boldsymbol{\rho} + \varepsilon_z(\omega) E_z(\mathbf{r}) \mathbf{z} \nabla \cdot \mathbf{D}(\mathbf{r}) = 0,\end{aligned}\tag{2.30}$$

where $\boldsymbol{\rho}$ and \mathbf{z} are the unit vectors in the perpendicular and parallel directions, respectively.

The nine equations outlined previously provide the equations for describing the fields associated with an optical phonon, and therefore, the carrier-optical-phonon scattering in wurtzite crystals. Moreover, these equations provide a description of the case of cubic, including zincblende crystals, in the limit of $\varepsilon_\perp(\omega) = \varepsilon_z(\omega)$ as discussed in Strosio and Dutta [1].

These phonon modes must be normalized such that the energy in each mode is equal to $\hbar\omega$. For the case of the bulk uniaxial material such as hexagonal wurtzite crystals, this normalization condition may be expressed as [14]

$$[\sqrt{n\mu}\mathbf{u}^*(\mathbf{q})] \cdot [\sqrt{n\mu}\mathbf{u}(\mathbf{q})] = \frac{\hbar}{2\omega V},\tag{2.31}$$

here, $\mathbf{u}(\mathbf{q})$ is the Fourier transform of $\mathbf{u}(\mathbf{r})$. For the case of CNTs, this normalization may be expressed as [15,16]

$$\frac{1}{V} \int \mathbf{u}^*(\mathbf{r}) \mathbf{u}(\mathbf{r}) dV = \frac{\hbar}{2M\omega}, \quad (2.32)$$

where M is the mass of the atoms which constitute CNTs. For the case of a two-dimensional graphene sheet, this normalization condition may be expressed as [15]

$$\frac{1}{S} \int (\mathbf{u}^* \cdot \mathbf{u} + \mathbf{v}^* \cdot \mathbf{v}) dx dy = \frac{\hbar}{M\omega}, \quad (2.33)$$

where \mathbf{u} and \mathbf{v} are the two displacements in the plane of the sheet. As the reader can surmise from examples and from the many references in this review dealing with phonon mode normalization, it is generally advisable to formulate a convenient mode normalization for each problem at hand.

The carrier-phonon interaction plays an important role in the properties of nanostructures. At room temperature, in low-defect polar semiconductors such as GaAs, InP, and GaN, carrier scattering is in many cases dominated by the polar-optical-phonon scattering mechanism and the polar-optical-phonon-carrier interaction is referred to as the Fröhlich interaction, which can be written as

$$H_{\text{Fr}} = -i \sqrt{\frac{2\pi e^2 \hbar \omega_{\text{LO}}}{V}} \sqrt{\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}} \sum_q \frac{1}{q} (a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}), \quad (2.34)$$

where $a_{\mathbf{q}}^\dagger$ and $a_{\mathbf{q}}$ are the phonon creation and annihilation operators, respectively. In many cases, the LO-phonon frequency, ω_{LO} , can be taken as the zone-center value to an excellent approximation. The deformation-potential interaction is one of the most important interactions in modern semiconductor devices and it has its origin in the displacements caused by phonons. The interaction between acoustic phonon and the carrier is known as the acoustic deformation-potential, $H_{\text{aco-def}}$, and is given by [16]

$$H_{\text{aco-def}} = D_{\text{ac}} \nabla \cdot \mathbf{u}, \quad (2.35)$$

where D_{ac} is the acoustic deformation-potential constant whose value may be estimated in a nearly free electron model [17]. For defect-free nanotubes, the carrier interactions are determined by the optical deformation-potential interaction. The optical deformation potential Hamiltonian is given by [18]

$$H_{\text{opt-def}} = \mathbf{D}_{\text{op}} \cdot \mathbf{u}, \quad (2.36)$$

where \mathbf{D}_{op} is the optical deformation potential constant. Since the axial phonons along the length of the CNT are of primary importance for transport along the

nanotube axis, the deformation potential mediating transport in the axial direction can be written as

$$H_{\text{opt-def}} = |D_{\text{op}}| u_z. \quad (2.37)$$

In general, the application of an external strain to a piezoelectric crystal will produce a macroscopic polarization as a result of the displacements of ions. Thus an acoustic phonon mode will drive a macroscopic polarization in a piezoelectric crystal. The piezoelectric interaction may be modeled in terms of the interaction of carriers with the macroscopic electric potential produced by the piezoelectric field. In Cartesian coordinates, the polarization created by the piezoelectric interaction in cubic crystals, including zincblende crystals, may be written as

$$\mathbf{p}^{\text{piezo}} = \left\{ e_{x4} \frac{\partial w / \partial y + \partial v / \partial z}{2}, e_{x4} \frac{\partial u / \partial z + \partial w / \partial x}{2}, e_{x4} \frac{\partial u / \partial y + \partial v / \partial x}{2} \right\}, \quad (2.38)$$

here e_{x4} is the piezoelectric coupling constant and has been described previously, the factors multiplying e_{x4} are the components of the strain tensor that contribute to the piezoelectric polarization in a zincblende crystal. This polarization may be expressed in a more general tensor form as

$$\mathbf{p}^{\text{piezo}} = e_{\lambda,\mu\nu} S_{\mu\nu}, \quad (2.39)$$

where $S_{\mu\nu}$ is the strain tensor discussed previously and $e_{\lambda,\mu\nu}$ is known as the piezoelectric tensor. The components of this strain tensor have been summarized by Auld [2] for a variety of crystals. For a phonon of wave vector q_μ , the corresponding piezoelectric potential may be expressed as [1, 19]

$$V^{\text{piezo}}(q) = 4\pi \frac{q_\lambda e_{\lambda,\mu\nu} q_\mu}{q_\lambda e_{\lambda\mu}^0 q_\mu} u_\nu, \quad (2.40)$$

where $e_{\lambda\mu}^0$ satisfies $D_\lambda = 4\pi e_{\lambda,\mu\nu} S_{\mu\nu} + e_{\lambda\mu}^0 E_\mu$.

2.2 Phonons in CNTs

CNTs discovered by Iijima [20] are single graphene sheets rolled up into cylinders of nanometer diameters along a chiral vector of the tube surface, which exhibit novel electronic and optical properties. CNTs have been studied extensively for possible uses as nanodevices such as field-effect transistors [21], flat-panel display [22], MIS capacitor [23], and infrared detectors [24].

In this section, the elastic continuum model is applied to determine the phonon modes, both optical and acoustic, in the finite length CNTs. The dispersion relations and deformation potential of the CNTs are obtained. Phonon bottleneck effects in short CNTs and thermal conductivity of CNTs are investigated in detail.

2.2.1 Phonon Modes in Single Wall Nanotubes

Herein we consider a short single wall nanotubes clamped in the ends of the tube. The approach taken here is to treat the CNT as a thin cylindrical membrane with elastic properties specified in terms of Poisson's ratio, ν , density, ρ , and Young's modulus, Y . The case has treated by Donnell [25] for an arbitrary cylindrical elastic sheet. The Donnell's equations of equilibrium for a thin wall cylindrical membrane are given by [16, 26, 27]

$$\begin{aligned} \frac{\partial^2 u_z}{\partial z^2} + \frac{1-\nu}{2a^2} \frac{\partial^2 u_z}{\partial \theta^2} + \frac{1+\nu}{2a} \frac{\partial^2 u_\theta}{\partial z \partial \theta} + \frac{\nu}{a} \frac{\partial u_r}{\partial z} - \frac{1-\nu^2}{Y} \rho \frac{\partial^2 u_z}{\partial t^2} &= 0, \\ \frac{1+\nu}{2a} \frac{\partial^2 u_z}{\partial z \partial \theta} + \frac{1-\nu}{2} \frac{\partial^2 u_\theta}{\partial z^2} + \frac{1}{a^2} \frac{\partial^2 u_\theta}{\partial \theta^2} + \frac{1}{a^2} \frac{\partial u_r}{\partial \theta} - \frac{1-\nu^2}{Y} \rho \frac{\partial^2 u_\theta}{\partial t^2} &= 0, \\ \frac{\nu}{a} \frac{\partial u_z}{\partial z} + \frac{1}{a^2} \frac{\partial^2 u_\theta}{\partial \theta^2} + \frac{u_r}{a^2} + \frac{d^2}{12} \nabla^4 u_r + \frac{1-\nu^2}{Y} \rho \frac{\partial^2 u_r}{\partial t^2} &= 0, \end{aligned} \quad (2.41)$$

where u_z is the displacement in the axial direction, u_θ the displacement in the circumferential direction, u_r the displacement in the radial direction, a the radius and d the thickness of the nanotubes, respectively.

The solution is divided into two parts—odd and even. For the odd part, the phonon displacements can be assumed as

$$\begin{aligned} u_z &= A \left[-\sin \frac{\lambda}{a} \left(\frac{l}{2} - z \right) + k \sin h \frac{\lambda}{a} \left(\frac{l}{2} - z \right) \right] \cos(n\theta) \cos(\omega t), \\ u_\theta &= B \left[\cos \frac{\lambda}{a} \left(\frac{l}{2} - z \right) + k \cosh \frac{\lambda}{a} \left(\frac{l}{2} - z \right) \right] \sin(n\theta) \cos(\omega t), \\ u_r &= C \left[\cos \frac{\lambda}{a} \left(\frac{l}{2} - z \right) + k \cosh \frac{\lambda}{a} \left(\frac{l}{2} - z \right) \right] \cos(n\theta) \cos(\omega t), \end{aligned} \quad (2.42)$$

where A , B , and C are arbitrary constants, λ is a variable and will be determined later, and l is the length of the tube segment.

For the case of CNT with the so-called clamped ends, the boundary conditions are taken as

$$u_z = u_\theta = u_r = \partial u_r / \partial z = 0 \quad \text{at } z = 0 \quad \text{and} \quad z = l. \quad (2.43)$$

Applying the above condition to Eq. (2.42) leads to the following results:

$$k = \sin\left(\frac{\lambda l}{2a}\right) / \sinh\left(\frac{\lambda l}{2a}\right) \quad \text{and} \quad \tan\left(\frac{\lambda l}{2a}\right) + \tanh\left(\frac{\lambda l}{2a}\right) = 0, \quad (2.44)$$

together with the roots of the above transcendental equation, $\lambda l/a = 1.5\pi, 3.5\pi, 5.5\pi, \dots$ corresponding to 1, 3, 5, ... axial half waves.

Substituting the displacement of Eq. (2.42) into the Donnell's equation, and solving for A/C and B/C yields

$$\frac{A}{C} = \frac{v\lambda \left(n^2 + \frac{1-v}{2}\lambda^2 \frac{\theta_2}{\theta_1} - \Delta\right) + \frac{1+v}{2}\lambda n^2}{\left(\lambda^2 \frac{\theta_1}{\theta_2} + \frac{1-v^2}{2}n^2 - \Delta\right) \left(n^2 + \frac{1-v}{2}\lambda^2 \frac{\theta_2}{\theta_1} - \Delta\right) - \left(\frac{1+v}{2}\right)^2 \lambda^2 n^2 \frac{\theta_2}{\theta_1}}, \quad (2.45)$$

$$\frac{B}{C} = \frac{v\lambda^2 n \frac{1+v}{2} \frac{\theta_2}{\theta_1} - n \left(\lambda^2 \frac{\theta_1}{\theta_2} + \frac{1-v^2}{2}n^2 - \Delta\right)}{\left(\lambda^2 \frac{\theta_1}{\theta_2} + \frac{1-v^2}{2}n^2 - \Delta\right) \left(n^2 + \frac{1-v}{2}\lambda^2 \frac{\theta_2}{\theta_1} - \Delta\right) - \left(\frac{1+v}{2}\right)^2 \lambda^2 n^2 \frac{\theta_2}{\theta_1}}, \quad (2.46)$$

where $\Delta = \rho a^2(1-v^2)\omega^2/Y$, $\theta_1 = 1 + k^2$, and $\theta_2 = 1 - k^2 + (2a/\lambda l)\sin(\lambda l/a)$.

The phonon displacement modes can be quantized by using Eq. (2.32)

$$\frac{1}{V} \int (u_z u_z^* + u_\theta u_\theta^* + u_r u_r^*) dV = \frac{\hbar}{2M\omega}. \quad (2.47)$$

Imposing this normalization condition leads to the results

$$C = \frac{\pi l d}{2\pi M\omega} \left\{ \left(\frac{A}{C}\right)^2 I_+ + \left[\left(\frac{B}{C}\right)^2 + 1 \right] I_- \right\}^{-1}, \quad (2.48)$$

with

$$\begin{aligned} I_\pm = & \mp \frac{\pi}{4\lambda} e^{-\lambda l/a} \left[4 \cos\left(\frac{\lambda l}{2a}\right) \sin\left(\frac{\lambda l}{2a}\right) a e^{\lambda l/a} + 4ka \cos\left(\frac{\lambda l}{2a}\right) e^{\lambda l/2a} \right. \\ & \pm 4ka \sin\left(\frac{\lambda l}{2a}\right) e^{\lambda l/2a} \pm 4ka \sin\left(\frac{\lambda l}{2a}\right) e^{3\lambda l/2a} \mp 4ka \cos\left(\frac{\lambda l}{2a}\right) e^{3\lambda l/2a} \\ & \left. \pm k^2 a \mp k^2 a e^{2\lambda l/a} \mp 2\lambda l e^{\lambda l/a} + 2k^2 \lambda l e^{\lambda l/a} \right] \end{aligned} \quad (2.49)$$

Carrying out similar analyses for the even modes, the even phonon mode displacements in the three directions are found easily by a similar analysis, and it is written as

$$\begin{aligned} u_z &= A \left[-\cos\left(\frac{\lambda}{a}\left(\frac{l}{2} - z\right)\right) + k \cosh\left(\frac{\lambda}{a}\left(\frac{l}{2} - z\right)\right) \right] \cos(n\theta) \cos(\omega t), \\ u_\theta &= B \left[\sin\left(\frac{\lambda}{a}\left(\frac{l}{2} - z\right)\right) + k \sinh\left(\frac{\lambda}{a}\left(\frac{l}{2} - z\right)\right) \right] \sin(n\theta) \cos(\omega t), \\ u_r &= C \left[\sin\left(\frac{\lambda}{a}\left(\frac{l}{2} - z\right)\right) + k \sinh\left(\frac{\lambda}{a}\left(\frac{l}{2} - z\right)\right) \right] \cos(n\theta) \cos(\omega t), \end{aligned} \quad (2.50)$$

where

$$k = \cos\left(\frac{\lambda l}{2a}\right) / \cosh\left(\frac{\lambda l}{2a}\right) \quad \text{and} \quad \tan\left(\frac{\lambda l}{2a}\right) - \tanh\left(\frac{\lambda l}{2a}\right) = 0, \quad (2.51)$$

together with the roots, of the above transcendental equation, $\lambda l/a = 2.5\pi, 4.5\pi, 6.5\pi, \dots$ corresponds to 2, 4, 6, \dots axial half waves, and A, B, C also satisfy Eqs. (2.45)–(2.47) with

$$\begin{aligned} I_{\pm} = & \mp \frac{\pi}{4\lambda} e^{-\lambda l/a} \left[4 \cos\left(\frac{\lambda l}{2a}\right) \sin\left(\frac{\lambda l}{2a}\right) a e^{\lambda l/a} \mp 4ka \cos\left(\frac{\lambda l}{2a}\right) e^{\lambda l/2a} \right. \\ & \mp 4ka \sin\left(\frac{\lambda l}{2a}\right) e^{\lambda l/2a} - 4ka \cos\left(\frac{\lambda l}{2a}\right) e^{3\lambda l/2a} \mp 4ka \sin\left(\frac{\lambda l}{2a}\right) e^{3\lambda l/2a} \\ & \left. \mp k^2 a \pm k^2 a e^{2\lambda l/a} \pm 2\mu l e^{\lambda l/a} + 2k^2 \lambda l e^{\lambda l/a} \right]. \end{aligned} \quad (2.52)$$

The dispersion relations for a number of different CNTs have been obtained by Raichura et al. [16, 18, 26]. The relations reveal that wave number versus the wave vector is composed of a series of points rather than a continuous function, as is to be expected since a CNT of finite length is basically a quantum dot with confinement in all three dimensions having no free, continuous wave vector. From these dispersion relations, it is found that the frequency of the well-known breathing mode for the (10, 10) nanotube is found to be about 30 THz which agrees well with that given by Suzurra and Ando [17].

From the analytic solutions given by Eqs. (2.42)–(2.51), the mode amplitudes are determined in terms of simple trigonometric and hyperbolic functions; due to the clamped boundary conditions many of the modes resemble half-wavelength confined modes and the corresponding deformation potentials have a similar character as expected from Eq. (2.35).

2.2.2 Optical Phonon Modes in Multi Wall Nanotubes

As discussed in the last section, the acoustic modes in a CNT may be determined in terms of the elastic continuum model. In this section, optical phonon modes of multi wall CNTs are derived using the method of Constantinou and Ridley [28, 29] whereby differences of acoustic mode displacements are used to construct optical mode displacements, as first applied to CNTs by Strosio et al. [30].

Consider a nanotube of outer radius, b , inner radius, a , and length, l , where the length is taken to be relatively large compared to any of the relevant physical scales in the system. As motivated by Born and Huang [12], herein we use the modified ionic displacement, w , rather than the actual ionic displacement, u . As discussed by Born and Huang [12], two displacements are related by

$$w = \sqrt{\mu/V} u, \quad (2.53)$$

where μ is the reduced mass, V is the volume of the unit cell. Moreover, the displacement, w , satisfies the classical Helmholtz equation,

$$(\nabla^2 + k_i^2) w^{(i)} = 0, \quad (2.54)$$

where

$$k_i^2 = (\omega_i^2 - \omega^2) \beta_i^{-2}. \quad (2.55)$$

In this last expression, ω_i is the zone-center LO-phonon frequency for material region i , and β_i is the acoustic phonon velocity.

The solutions for the three components of the optical mode displacements may be determined by Eq. (2.53) and can be written as [18]

$$\begin{aligned} w_z &= C_{mn} e^{im\theta} [N'_m(q_{mn}a) J_m(q_{mn}r) - J'_m(q_{mn}a) N_m(q_{mn}r)] \sin(q_z z), \\ w_\theta &= -\frac{C_{mn} i m e^{im\theta}}{r q_z} [N'_m(q_{mn}a) J_m(q_{mn}r) - J'_m(q_{mn}a) N_m(q_{mn}r)] \cos(q_z z), \\ w_r &= -\frac{C_{mn} q_{mn} e^{im\theta}}{q_z} [N'_m(q_{mn}a) J'_m(q_{mn}r) - J'_m(q_{mn}a) N'_m(q_{mn}r)] \cos(q_z z). \end{aligned} \quad (2.56)$$

Furthermore, as a result of the conditions

$$\left[\frac{1}{r} \frac{\partial}{\partial r} (r w_r) + \frac{1}{r} \frac{\partial}{\partial \theta} (w_\theta) + \frac{\partial}{\partial z} (w_z) \right]_{a,b} = 0, \quad (2.57)$$

it follows that we have the “double infinite” set of eigenvalues

$$q = q_{mn}, \quad m = 0, 1, 2, \dots \quad n = 0, 1, 2, \dots, \quad (2.58)$$

obtained from the positive roots of

$$N'_m(q_{mn}a) J'_m(q_{mn}b) - J'_m(q_{mn}a) N'_m(q_{mn}b) = 0. \quad (2.59)$$

Using the clamped boundary conditions

$$w_z = w_r = dw_r/dz = 0 \quad \text{at } z = 0, l \quad \text{and} \quad z = a, b, \quad (2.60)$$

it is found that $q_z = k\pi/l$ with k being an integer.

Thus, the frequencies are

$$\omega_{mn}^2 = \omega_{LO}^2 - \beta^2 (q_{mn}^2 + q_z^2), \quad (2.61)$$

where the frequency ω_{LO} is the zone-center LO-phonon frequency of the material composing the nanotube.

As discussed previously, the phonon displacement modes can be quantized by using Eq. (2.32)

$$\frac{1}{V} \int (w_z w_z^* + w_\theta w_\theta^* + w_r w_r^*) dV = \frac{\hbar}{\mu \omega_{mn}}, \quad (2.62)$$

Applying this normalization condition, we find

$$C_{mn} = \frac{\sqrt{a^2 - b^2} \sqrt{l}}{\sqrt{2}} \sqrt{\frac{\hbar}{\mu \omega_{mn}}} \sqrt{\frac{1}{I_r^{(m)}}}, \quad (2.63)$$

with

$$I_r^{(m)} = \frac{l}{2} \left[I_{r1}^{(m)} + (q_{mn}/q_z)^2 I_{r2}^{(m)} + (m/q_z)^2 I_{r3}^{(m)} \right] + \frac{\sin(2q_z l)}{4q_z} \left[-I_{r1}^{(m)} + (q_{mn}/q_z)^2 I_{r2}^{(m)} + (m/q_z)^2 I_{r3}^{(m)} \right], \quad (2.64)$$

and

$$\begin{aligned} I_{r1}^{(m)} &= N_m'^2 (q_{mn} a) I_1^{(m)} + J_m'^2 (q_{mn} a) I_2^{(m)} - 2N_m' (q_{mn} a) J_m' (q_{mn} a) I_3^{(m)}, \\ I_{r2}^{(m)} &= N_m'^2 (q_{mn} a) I_4^{(m)} + J_m'^2 (q_{mn} a) I_5^{(m)} - 2N_m' (q_{mn} a) J_m' (q_{mn} a) I_6^{(m)}, \\ I_{r3}^{(m)} &= N_m'^2 (q_{mn} a) I_7^{(m)} + J_m'^2 (q_{mn} a) I_8^{(m)} - 2N_m' (q_{mn} a) J_m' (q_{mn} a) I_9^{(m)}, \end{aligned} \quad (2.65)$$

where

$$\begin{aligned} I_1^{(m)} &= \frac{b^2}{2} [J_m^2 (q_{mn} b) - J_{m-1} (q_{mn} b) J_{m+1} (q_{mn} b)] \\ &\quad - \frac{a^2}{2} [J_m^2 (q_{mn} a) - J_{m-1} (q_{mn} a) J_{m+1} (q_{mn} a)], \\ I_2^{(m)} &= \frac{b^2}{2} [N_m^2 (q_{mn} b) - N_{m-1} (q_{mn} b) N_{m+1} (q_{mn} b)] \\ &\quad - \frac{a^2}{2} [N_m^2 (q_{mn} a) - N_{m-1} (q_{mn} a) N_{m+1} (q_{mn} a)], \\ I_3^{(m)} &= \frac{b^2}{4} [2J_m (q_{mn} b) N_m (q_{mn} b) - J_{m+1} (q_{mn} b) N_{m-1} (q_{mn} b) \\ &\quad - J_{m-1} (q_{mn} b) N_{m+1} (q_{mn} b)] - \frac{a^2}{4} [2J_m (q_{mn} a) N_m (q_{mn} a) \\ &\quad - J_{m+1} (q_{mn} a) N_{m-1} (q_{mn} a) - J_{m-1} (q_{mn} a) N_{m+1} (q_{mn} a)], \end{aligned}$$

$$\begin{aligned}
I_4^{(m)} = & \frac{b^2}{2} [J_{m+1}^2(q_{mn}b) - J_m(q_{mn}b) N_{m+1}(q_{mn}b)] \\
& - \frac{a^2}{2} [J_{m+1}^2(q_{mn}a) - J_m(q_{mn}a) N_{m+1}(q_{mn}a)] \\
& + \frac{m}{2q_{mn}^2} \left[-J_0^2(q_{mn}b) - J_m^2(q_{mn}b) - 2 \sum_{k=1}^{m-1} J_k^2(q_{mn}b) \right. \\
& \quad \left. + J_0^2(q_{mn}a) - J_m^2(q_{mn}a) + 2 \sum_{k=1}^{m-1} J_k^2(q_{mn}a) \right] \\
& - \frac{2m}{q_{mn}^2} \left[-J_0^2(q_{mn}b) - \sum_{k=1}^m J_k^2(q_{mn}b) + J_0^2(q_{mn}a) + \sum_{k=1}^m J_k^2(q_{mn}a) \right], \\
\\
I_5^{(m)} = & \frac{b^2}{2} [N_{m+1}^2(q_{mn}b) - N_m(q_{mn}b) N_{m+2}(q_{mn}b)] \\
& - \frac{a^2}{2} [N_{m+1}^2(q_{mn}a) - N_m(q_{mn}a) N_{m+2}(q_{mn}a)] \\
& \quad + \frac{m}{2q_{mn}^2} [-N_0^2(q_{mn}b) - N_m^2(q_{mn}b) \\
& - 2 \sum_{k=1}^{m-1} N_k^2(q_{mn}b) + N_0^2(q_{mn}a) - N_m^2(q_{mn}a) - 2 \sum_{k=1}^{m-1} N_k^2(q_{mn}a)] \quad (2.66) \\
& - \frac{2m}{q_{mn}} \int_a^b N_{m+1}(q_{mn}r) N_m(q_{mn}r) dr,
\end{aligned}$$

$$\begin{aligned}
I_6^{(m)} = & \frac{b^2}{4} [2J_{m+1}(q_{mn}b) N_{m+1}(q_{mn}b) - J_{m+1}(q_{mn}b) N_{m-1}(q_{mn}b) \\
& - J_{m-1}(q_{mn}b) N_{m+1}(q_{mn}b) - \frac{a^2}{4} [2J_{m+1}(q_{mn}a) N_{m+1}(q_{mn}a) \\
& - J_{m+1}(q_{mn}a) N_{m-1}(q_{mn}a) - J_{m-1}(q_{mn}a) N_{m+1}(q_{mn}a)] \\
& - \frac{m}{2q_{mn}^2} [J_0(q_{mn}b) N_0(q_{mn}b) + J_m(q_{mn}b) N_m(q_{mn}b) \\
& + 2 \sum_{k=1}^{m-1} J_k(q_{mn}b) J_k(q_{mn}b)] + \frac{m}{2q_{mn}^2} [J_0(q_{mn}a) N_0(q_{mn}a) \\
& + J_m(q_{mn}a) N_m(q_{mn}a) + 2 \sum_{k=1}^{m-1} J_k(q_{mn}a) J_k(q_{mn}a)] \\
& - \frac{m}{q_{mn}} \int_a^b N_{m+1}(q_{mn}r) J_m(q_{mn}r) dr - \frac{m}{q_{mn}} \int_a^b J_{m+1}(q_{mn}r) N_m(q_{mn}r) dr,
\end{aligned}$$

$$I_7^{(m)} = -\frac{1}{2m} \left[J_0^2(q_{mn}b) + J_m^2(q_{mn}b) + 2 \sum_{k=1}^{m-1} J_k^2(q_{mn}a) \right. \\ \left. - J_0^2(q_{mn}a) - J_m^2(q_{mn}a) - 2 \sum_{k=1}^{m-1} J_k^2(q_{mn}a) \right],$$

$$I_8^{(m)} = -\frac{1}{2m} \left[N_0^2(q_{mn}b) + N_m^2(q_{mn}b) + 2 \sum_{k=1}^{m-1} N_k^2(q_{mn}a) \right. \\ \left. - N_0^2(q_{mn}a) - N_m^2(q_{mn}a) - 2 \sum_{k=1}^{m-1} N_k^2(q_{mn}a) \right],$$

$$I_9^{(m)} = -\frac{1}{2m} \left[J_0(q_{mn}b) N_0(q_{mn}b) + J_m(q_{mn}b) N_m(q_{mn}b) \right. \\ \left. + 2 \sum_{k=1}^{m-1} J_k(q_{mn}b) J_k(q_{mn}b) \right] + \frac{1}{2m} \left[J_0(q_{mn}a) N_0(q_{mn}a) \right. \\ \left. + J_m(q_{mn}a) N_m(q_{mn}a) + 2 \sum_{k=1}^{m-1} J_k(q_{mn}a) J_k(q_{mn}a) \right].$$

For the lowest azimuthal mode, $m = 0$, and

$$C_{0n} = \frac{\sqrt{a^2 - b^2} \sqrt{l}}{\sqrt{2}} \sqrt{\frac{\hbar}{\mu \omega_{0n}}} \sqrt{\frac{1}{I_r^{(0)}}}, \quad (2.67)$$

where

$$I_r^{(0)} = \frac{l}{2} \left[I_{r1}^{(0)} + \left(\frac{q_{0n}}{q_z} \right)^2 I_{r2}^{(0)} \right] + \frac{\sin(2q_z l)}{4q_z} \left[-I_{r1}^{(0)} + \left(\frac{q_{0n}}{q_z} \right)^2 I_{r2}^{(0)} \right], \quad (2.68)$$

and

$$I_{r1}^{(0)} = N_0'^2(q_{0n}a) I_1^{(m)} + J_0'^2(q_{0n}a) I_2^{(0)} - 2N_0'(q_{0n}a) J_0'(q_{0n}a) I_3^{(0)}, \\ I_{r2}^{(0)} = N_0'^2(q_{0n}a) I_4^{(0)} + J_0'^2(q_{0n}a) I_5^{(0)} - 2N_0'(q_{0n}a) J_0'(q_{0n}a) I_6^{(0)}, \quad (2.69)$$

with

$$I_1^{(0)} = \frac{b^2}{2} [J_0^2(q_{0n}b) + J_1^2(q_{0n}b)] - \frac{a^2}{2} [J_0^2(q_{0n}a) + J_1^2(q_{0n}a)],$$

Table 2.1 The roots, q_{mn} , for $m = 0, 1, 2$ and $n = 0, 1, 2$ for radii ratios $b/a = 1.5, 2.0$ and 2.5

		$n = 0$	$n = 1$	$n = 2$
$b/a = 1.5$	$m = 0$	0.39953479	6.32429094	2.58589799
	$m = 1$	0.80513571	6.37648698	12.61258158
	$m = 2$	1.60796911	6.53788074	12.69223312
$b/a = 2.0$	$m = 0$	0.3239608	3.19842986	6.31220220
	$m = 1$	0.67724429	3.28240592	6.35291530
	$m = 2$	1.34058549	3.53129775	6.47312708
$b/a = 2.5$	$m = 0$	0.27107423	2.15646816	4.22295780
	$m = 1$	0.58499003	2.26364240	4.27287650
	$m = 2$	1.13689860	2.56697694	4.42339550

$$\begin{aligned}
I_2^{(0)} &= \frac{b^2}{2} [N_0^2(q_{0n}b) + N_1^2(q_{0n}b)] - \frac{a^2}{2} [N_0^2(q_{0n}a) + N_1^2(q_{0n}a)], \\
I_3^{(0)} &= \frac{b^2}{2} [J_0(q_{0n}b) N_0(q_{0n}b) + J_1(q_{0n}b) N_1(q_{0n}b)] \\
&\quad - \frac{a^2}{2} [J_0(q_{0n}a) N_0(q_{0n}a) + J_1(q_{0n}a) N_1(q_{0n}a)], \\
I_4^{(0)} &= \frac{b^2}{2} [J_1^2(q_{0n}b) - J_0(q_{0n}b) J_2(q_{0n}b)] \\
&\quad - \frac{a^2}{2} [J_1^2(q_{0n}a) - J_0(q_{0n}a) J_2(q_{0n}a)], \\
I_5^{(0)} &= \frac{b^2}{2} [N_1^2(q_{0n}b) - N_0(q_{0n}b) N_2(q_{0n}b)] \\
&\quad - \frac{a^2}{2} [N_1^2(q_{0n}a) - N_0(q_{0n}a) N_2(q_{0n}a)], \\
I_6^{(0)} &= \frac{b^2}{4} [2J_1(q_{0n}b) N_1(q_{0n}b) - J_2(q_{0n}b) N_0(q_{0n}b) - J_0(q_{0n}b) N_2(q_{0n}b)] \\
&\quad - \frac{a^2}{4} [2J_1(q_{0n}a) N_1(q_{0n}a) - J_2(q_{0n}a) N_0(q_{0n}a) - J_0(q_{0n}a) N_2(q_{0n}a)],
\end{aligned} \tag{2.70}$$

The dispersion relation is found from Eq. (2.61) by substituting the values of q_{mn} for values of $m = 0, 1, 2, \dots$ and $n = 0, 1, 2, \dots$. Table 2.1 summarizes selected values of q_{mn} for the lowest modes in n and m .

2.2.3 Phonon Bottlenecks in Short CNTs

The quantization of the phonons in CNTs of finite length results in a phonon bottlenecks of importance in the use of finite length CNTs used as infrared detectors [24] and as transistors [31]. As described previously, short CNTs have discrete

dispersion relations analogous to those of quantum dots. Moreover, the electronic bands in these CNTs are also discrete due to the dimensional confinement in three dimensions. The discreteness of both the phonon and carrier dispersion relations implies that it is difficult to satisfy both momentum and energy conservation in phonon emission and absorption processes. To analyze the severity of this expected phonon bottleneck, Raichura et al. [16, 27] have calculated the discrete phonon dispersion curves for a number of different CNTs and they have quantized the tight-binding electron energy dispersion curves of Pennington and Goldsman [32] along the CNT axis to take into account dimensional confinement for short CNTs. In particular, Raichura et al. [16, 27] have noted that the wavevector for quantized electronic states in the axial direction since the nanotube is short and is given by $k_z = n' \pi / l$ where n' labels the multiples of half-wavelength standing carrier modes in the axial direction [33]. For the given case of a (10, 0) nanotube, the circumferential unit cell width is $T_c = \pi(2a)/10 = 0.251$ nm and the unit cell in the axial direction is given by $T = 0.43$ nm. In particular for a (10, 0) nanotube that is ten unit cells in circumference and nine unit cells in length, the allowed values of k_z are $k_z = n' \pi / 9 T$ and the maximum value of k_z is π / T corresponding to $n' = 9$.

In this previous work, Raichura et al. [16, 27] examined different possible electronic transitions for intravalley intrasubband ($1 \leftrightarrow 1$, $2 \leftrightarrow 2$ and $3 \leftrightarrow 3$) and intravalley intersubband ($1 \leftrightarrow 2$, $2 \leftrightarrow 3$ and $1 \leftrightarrow 3$) transitions. In order to avoid a phonon bottleneck and for an electron to make any one of the possible transitions, there should be a phonon available that allows momentum conservation and whose energy is equal to the difference in the energy of the two transition bands. As described by Pennington and Goldsman [32], the subbranch quantum number for the phonons is $n = 0$ for intrasubband transition, $n = 1$ for intersubband ($1 \leftrightarrow 2$, $1 \leftrightarrow 3$) and $n = 2$ for $2 \leftrightarrow 3$ intersubband transition. The phonon energies for $n = 0, 1, 2$ are shown for the breathing modes, torsional modes, and the axial modes have been calculated by Raichura et al. [16, 27] in order to assess the degree of the phonon bottleneck; these authors considered a (10, 0) nanotube of length 4 nm. Raichura et al. [16, 27] found that for the intravalley intrasubband transition, there are no phonons available to assist the electron transition. Furthermore they found that for the intravalley intersubband $1 \leftrightarrow 2$ case, allowing for a 10 % broadening of the transition energies, there is only one allowed transition involving an axial phonon with energy of 55 meV. Finally they found that for the $1 \leftrightarrow 3$ intravalley intersubband case, there is a phonon (torsional)-assisted transition allowed at 39 meV. For the $2 \leftrightarrow 3$ intravalley intersubband case, there are only two allowed transitions. One of those involves an axial phonon at 87 meV and the other, a torsional mode phonon at 65 meV.

From these results for short CNTs, it is evident that the electron scattering due to phonons is very limited due to the confinement-related phase space restriction of phonon energies. This is, of course, different from the case of infinite length nanotubes, where most of the transitions are allowed due to the continuous nature of the phonon energies. These phonon bottleneck effects are expected to lead to reduced scattering and the suppression of phonon-assisted transitions in infrared devices using nanotubes as well as the consequent enhancement of quasi ballistic transport in nanotube-based transistors.

2.2.4 Thermal Conductivity

The thermal conductivities of both CNTs and other graphene-based structures have considerable practical interests. In this section, the thermal conductivity of a CNT with metallic and contacts is considered using the Klemens model. In a subsequent section, these Klemens model results will be combined with continuum model results that predict dimensional confinement effects in few-larger graphite structures. Herein, we discuss the case of CNT in contact with metallic regions at each end [34]. By using the Klemens's model for thermal transport in graphite [35], Sun et al. [34] investigated the thermal transport properties of CNTs at high temperatures based on a Debye-type continuum model that assumes equipartition. From the graphite dispersion relations [36], it is observed that above 4 THz, lattice waves propagate in the basal plane and a two-dimensional (2D) phonon gas model is appropriate. As discussed by Klemens [35], the phonon spectral specific heat in two dimensions is

$$C_2(f) = \frac{4k_B f}{a^3 f_d^2}, \quad (2.71)$$

where a^3 is the volume of one molecular group of the solid, k_B is Boltzmann's constant, f is the phonon frequency, and $f_d = 4.6 \times 10^{13}$ Hz is the Debye frequency.

In CNTs, there are three dominant phonon scattering mechanisms: intrinsic, point-defect, and grain boundary scattering. As discussed by Klemens, the expression for the two-dimensional intrinsic mean free path is

$$l_i(f, T) = \frac{M v^3 f_d}{4\pi \gamma^2 k_B T f^2} \quad (2.72)$$

where v is the phonon velocity and γ is the Grüneisen parameter. In this discussion, $\gamma^2 = 4$ is adopted, based on Klemens' treatment [35]. Accordingly, to the thermal conductivity in the basal plane of graphite is thus given by

$$\lambda_i(T) = \frac{1}{2} \int_{f_c}^{f_d} C_2(f) v l_i(f, T) df, \quad (2.73)$$

where $f_c = 4$ THz, the low-frequency limit below which lattice waves propagate along the c -axis in three dimensions. As discussed by Klemens, the expression for the 2D thermal conductivity is given by

$$\lambda_i(T) = \frac{M v^4}{2\pi a^3 \gamma^2 T f_d} (\ln f_d - \ln f)_c. \quad (2.74)$$

Hence, as the temperature increases the intrinsic thermal conductivity decreases. This result also predicts thermal conductivities in the range of approximately

2,000 W/mK at 300 K and 1,000 W/mK at 600 K. In making these estimates, the group velocity is taken as $v = 1.86 \times 10^4$ m/s, which is obtained by averaging the longitudinal (2.36×10^4 m/s) and fast transverse (1.59×10^4 m/s) velocities from the phonon dispersion relation for the basal plane as calculated by Klemens (1994)

$$\frac{2}{\langle v \rangle^2} = \frac{1}{\langle v_{LA} \rangle^2} + \frac{1}{\langle v_{TA} \rangle^2}. \quad (2.75)$$

As discussed by Sun et al. [34], for the case of frequency below 4 THz, significant interplanar vibrations make a three-dimensional model necessary, which takes into account the LA and TA branches with velocities of 1,960 and 700 m/s, respectively, as calculated from the phonon dispersion relation. Accordingly, when this approach is applied to CNTs, it is necessary to make certain modifications. In the limit of a long CNT, the wave vectors along the tube axis are continuous and the dispersion relation is the same as that of graphene. However, as expected, in the perpendicular or the circumferential direction, the wave vectors are discrete. Moreover, at low temperatures it is important to consider the effects of the discreteness on the specific heat and the three-phonon interactions. However, at high temperatures where equipartition is assumed, these effects are unimportant. Thus, it is not essential to consider the effects of graphene sheet orientation with respect to the tube axis in a Debye continuum model. Indeed, the effects of graphene sheet orientation on the acoustic modes at high temperatures are small. For such a scenario, the lower cutoff frequency for CNTs is determined by the breathing modes that can decay anharmonically into two acoustic modes. As argued clearly by Klemens, the equivalent cutoff frequency is about $f_c = 3$ THz, below which the two-dimensional mean free path is greatly reduced.

As discussed by Klemens, in the 2D case, point defects scatter as the third power of frequency. For substitutional atoms which differ only in their masses from the carbon atoms by ΔM , the point defect mean free path is given as

$$\frac{1}{l_p(f)} = A f^3 = c \left(\frac{\Delta M}{M} \right)^2 4\pi^2 \frac{f^3}{v f_d^2}, \quad (2.76)$$

where A depends on properties and the number of defects relative to the number of carbon atoms, c , of the point defects. As is well known, point defects reduce the thermal conductivity relative to the intrinsic thermal conductivity. Indeed, it has been established that CNTs have low densities of point defects ($1/10^{12}$ atoms, [37]). Because the point defect concentration is very low along the length of the tubes, the point defect scattering events occur primarily as end effects for CNTs of submicron lengths and, accordingly, the point defect concentration is a function of the tube length.

To estimate the point defect density, consider unrolling the CNT. Perpendicular to the tube axis, a row is defined such that it has $2N$ atoms, where N is the number of circumferential atoms in the original CNT, assumed to be ten for specificity. Since

for a tube of one row, its length is $0.5d$, where d is the length of the side of the hexagon equal to 0.142 nm and for n rows, the tube length is

$$l_n = 0.5d + (n - 1) \times 1.5d, \quad (2.77)$$

the number of rows is thus

$$n = (1 + l_n/d) / 1.5. \quad (2.78)$$

The total number of atoms in the CNT is $2Nn$. With one defect at each end of the tube the average effective point defect concentration for a CNT with defects at each end is

$$c = \frac{2}{2Nn} = \frac{1.5}{10(1 + l_n/d)}. \quad (2.79)$$

Accordingly the CNT thermal conductivity with point defect end effects is thus given by

$$\begin{aligned} \lambda_p(T) &= \frac{1}{2} \int_{f_c}^{f_d} C_2(f) v l_t(f, T) df \\ &= \frac{2.34 \times 10^5}{T} \{ \ln(f_d/f_c) - \ln[(f_d + f_0)/(f_c + f_0)] \}, \end{aligned} \quad (2.80)$$

where the total mean free path is given in terms of the intrinsic and point-defect-related mean free path by

$$\frac{1}{l_t} = \frac{1}{l_i} + \frac{1}{l_p}, \quad (2.81)$$

with l_p being point defect mean free path, and

$$f_0 = 2.556 \times 10^{-6} f_d T (1 + l_n/d) / 1.35. \quad (2.82)$$

Based on this analysis, the thermal conductivity with end effects as a function of tube length may be estimated. First of all, as the tube length increases, the thermal conductivity increases and the end effects become less important as the intrinsic mean free path becomes dominant. For tube lengths of a few hundred nanometers, the thermal conductivity has values of approximately 2,000 W/mK at 300 K, 1,000 W/mK at 500 K, and 800 W/mK at 800 K; more detailed results are given by Sun et al. [34]. Sun et al. also consider the effects produced by grain boundary scattering at the ends of the CNT, the reader is referred to Sun et al. [34] for additional details.

2.3 Phonons in Graphene

The physical properties of graphene have been investigated extensively since it was first successfully made by Novoselov et al. [38]. A typical structure suitable for potential device applications is a graphene nanoribbon (GNR), which can be visualized as an unwrapped CNT. Rana et al. [39] have examined generation and recombination events intravalley and intervalley phonon scattering in graphene. Herein we review the work of Qian et al. [15] on phonon confinement effects in graphene.

This section highlights the results of Qian et al. [15] on the use of the elastic continuum model to derive analytical displacements and dispersion relations of optical phonons for a graphene sheet. In addition, these results provide expressions for the confined optical phonons for graphene are obtained as well as the optical deformation potential interactions for graphene.

2.3.1 Optical Phonons in Graphene Sheets

Consider a GNR with x and y axes in the plane of the graphene such that they are perpendicular and parallel to the “clamping” boundaries, 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. Using the elastic continuum model for the phonon, the GNR is treated as a 2D elastic sheet in the long wavelength limit. The unit length along the x -axis is $a \cos \theta$, where $a = \sqrt{3}a_{c-c} = 2.46 \text{ \AA}$ is the length of the unit vector in terms of the distance between adjacent carbon atoms, a_{c-c} , and θ is the chiral angle from the unit vector a with respect to the x -axis. In a convenient formal analogy with CNTs, two kinds of specific GNRs are defined: armchair-end and zigzag-end GNRs, depending on the carbon atom arrangement on the free-standing sides, which is identical to the definition of the CNTs [40]. The armchair-end and zigzag-end GNRs correspond to $\theta = 30^\circ$ and 0° , respectively. Therefore, the unit lengths along the x -axis of armchair-end and zigzag-end GNRs are $\sqrt{3}a/2$ and a [15].

Goupalov (2005) has derived generalized mechanical equations describing the relative displacement of the two sublattices in graphene sheet for the long wavelength optical phonon modes. Moreover, Babiker [41] has formulated a method of treating optical modes based on the difference between the displacements of these sublattices. The equation describing this relative displacement is written as

$$\ddot{\mathbf{u}} = \hat{\Lambda}^{\text{opt}} \mathbf{u}, \quad (2.83)$$

where $\hat{\Lambda}^{\text{opt}}$ is the operator for optical phonons given as

$$\begin{aligned} -\hat{\Lambda}_{2\text{DG}}^{\text{opt}} = & \omega_{\text{TO}}^2 + \frac{\beta_T^2 - \beta_L^2}{2} J_z^2 \nabla_{\perp}^2 + \frac{\beta_T^2 + \beta_L^2}{2} (\nabla_{-}^2 J_{+}^2 + \nabla_{+}^2 J_{-}^2) \\ & + \frac{\lambda^2}{2} (\nabla_{-}^2 J_{+}^2 + \nabla_{+}^2 J_{-}^2) \nabla_{\perp}^2 - \frac{\lambda^2}{2} J_z^2 \nabla_{\perp}^4 - \beta_z^2 (J_z^2 - 1) \nabla_{\perp}^2 \\ & + (\omega_{\text{TO}}^2 - \omega_{\text{ZO}}^2) (J_z^2 - 1) \end{aligned} \quad (2.84)$$

where $J_{\pm} = \mp 1/\sqrt{2} (J_x \pm iJ_y)$, $J_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}$, $J_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}$, $J_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ are the matrices of projections of the spin operator $J = 1$ in the Cartesian

basis. The parameters ω_{TO} , β_T , β_L , λ are approximated by fitting the dispersion curves of TO and LO phonons in 2D graphite in the Γ - M direction from Maultzsch et al. [42], while the ω_{ZO} and β_z are by ZO results from Wirtz and Rubio [43]. For the in-plane TO and LO modes and the out-of-plane ZO mode, the phonon dispersions are fitted by

$$\omega^2(k) = \begin{cases} \omega_{\text{TO}}^2 - \beta_T^2 k^2 & \text{TO} \\ \omega_{\text{LO}}^2 - \lambda^2 k^4 + \beta_L^2 k^2 & \text{LO} \\ \omega_{\text{ZO}}^2 - \beta_z^2 k^2 & \text{ZO}, \end{cases} \quad (2.85)$$

For non-polar graphene, $\omega_{\text{TO}} = \omega_{\text{LO}} = 1,581 \text{ cm}^{-1}$, $\omega_{\text{ZO}} = 893 \text{ cm}^{-1}$ are the frequencies of TO, LO, and ZO modes at the center, Γ point, of reciprocal lattices of the graphene; $\beta_T = 9.6 \times 10^5 \text{ cm/s}$, $\beta_L = 7.8 \times 10^5 \text{ cm/s}$, $\beta_z = 7.9 \times 10^5 \text{ cm/s}$, and $\lambda = 9.3 \times 10^5 \text{ cm}^2/\text{s}$.

Explicit expressions are obtained for the two in-plane and single out-of-plane displacements upon applying the above operator to the relative displacements:

$$\begin{cases} -\ddot{u} = \left[\omega_{\text{TO}}^2 - \beta_L^2 \nabla_x^2 + \beta_T^2 \nabla_y^2 - \lambda^2 \nabla_x^2 (\nabla_x^2 + \nabla_y^2) \right] u \\ \quad + \left[-(\beta_L^2 + \beta_T^2) \nabla_x \nabla_y - \lambda^2 \nabla_x \nabla_y (\nabla_x^2 + \nabla_y^2) \right] v \\ -\ddot{v} = \left[\omega_{\text{TO}}^2 - \beta_L^2 \nabla_y^2 + \beta_T^2 \nabla_x^2 - \lambda^2 \nabla_y^2 (\nabla_x^2 + \nabla_y^2) \right] v \\ \quad + \left[-(\beta_L^2 + \beta_T^2) \nabla_x \nabla_y - \lambda^2 \nabla_x \nabla_y (\nabla_x^2 + \nabla_y^2) \right] u \\ -\ddot{w} = \left[\omega_{\text{ZO}}^2 + \beta_z^2 (\nabla_x^2 + \nabla_y^2) \right] w. \end{cases} \quad (2.86)$$

Thus, it is seen that 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. Considering solutions in the form of traveling waves,

$$\mathbf{u}(x, y, t) = \mathbf{A} \exp[i(q_x x + q_y y - \omega t)], \quad (2.87)$$

it follows that the displacement equations can be written as

$$\begin{cases} \omega^2 u = \left[\omega_{\text{TO}}^2 + \beta_L^2 q_x^2 - \beta_T^2 q_y^2 - \lambda^2 q_x^2 (q_x^2 + q_y^2) \right] u \\ \quad + \left[(\beta_L^2 + \beta_T^2) q_x q_y - \lambda^2 q_x q_y (q_x^2 + q_y^2) \right] v \\ \omega^2 v = \left[(\beta_L^2 + \beta_T^2) q_x q_y - \lambda^2 q_x q_y (q_x^2 + q_y^2) \right] u \\ \quad + \left[\omega_{\text{TO}}^2 + \beta_L^2 q_y^2 - \beta_T^2 q_x^2 - \lambda^2 q_y^2 (q_x^2 + q_y^2) \right] v \\ \omega^2 w = \left[\omega_{\text{ZO}}^2 - \beta_Z^2 (q_x^2 + q_y^2) \right] w. \end{cases} \quad (2.88)$$

The dispersion relationships for these modes are found to be those of Goupalov and they have the form

$$\omega^2(q) = \begin{cases} \omega_{\text{TO}}^2 - \beta_T^2 (q_x^2 + q_y^2) \\ \omega_{\text{TO}}^2 - \lambda^2 (q_x^2 + q_y^2)^2 + \beta_L^2 (q_x^2 + q_y^2) \\ \omega_{\text{ZO}}^2 - \beta_Z^2 (q_x^2 + q_y^2). \end{cases} \quad (2.89)$$

Accordingly, for phonon propagation in these graphene sheets, the continuum model has the same dispersion curves for arbitrary propagation directions.

2.3.2 Confined Optical Phonons in Clamped GNRs

In this treatment, the displacements at boundaries are taken to be zero, in an approximation commonly described as “clamped” boundary conditions; that is,

$$u = 0 \quad \text{at } x = 0 \text{ and } L. \quad (2.90)$$

These boundary conditions result in confined modes and they imply that $q_x = q_n = n\pi/L$, and let $q_y = q$. Accordingly the displacements are given by

$$\mathbf{u}(x, y, t) = \mathbf{A} \exp[i(q_n x + q y - \omega t)]. \quad (2.91)$$

The displacement along the x -axis, u , is confined between the two boundaries, u is given by the standing wave equation

$$u = u_0 \sin(q_n x). \quad (2.92)$$

The dispersion relations with confined wavevectors follow immediately from the above dispersion relations with $q_x = q_n$:

$$\omega_n^2 = \begin{cases} \omega_{\text{TO}}^2 - \beta_T^2 (q_n^2 + q^2) \\ \omega_{\text{TO}}^2 - \lambda^2 (q_n^2 + q^2)^2 + \beta_L^2 (q_n^2 + q^2) \\ \omega_{\text{ZO}}^2 - \beta_Z^2 (q_n^2 + q^2) \end{cases} \quad (2.93)$$

As illustrative examples armchair-end and zigzag-end GNRs with N periods are analyzed herein. For the armchair-end GNR, the widths are $N \sqrt{3}a/2$ when N is even, and $(N + 1/3) \sqrt{3}a/2$ when N is odd. In the case of the zigzag-end GNR, the width is Na for all N . As expected from the continuum model these are dispersion curves for optical phonon modes with quantized number n from 0 to N for q_x , since the smallest quantized wave vector should be larger than the unit length along the x -axis.

Qian et al. [15] have considered the dispersion curves of LO, TO, and ZO vibration modes for armchair-end GNR of ten periods. It is found that the larger the quantized number n , the smaller the vibration frequencies of the phonon modes for TO and ZO modes over the whole wave vector domain. At the zone-center, when n equals four, there exists a maximum frequency $1,590.9 \text{ cm}^{-1}$. When n is smaller than four, the LO frequencies increase first and then decrease, while, for n is larger than four, the LO frequencies decrease directly.

Qian et al. [15] have also considered the dispersion curves for LO, TO, and ZO vibration modes for ten units zigzag-end GNR. The dispersion curves manifest the same properties as for the armchair case; there is a critical quantized number existing for LO modes, $1,590.9 \text{ cm}^{-1}$ when n equals five.

By substituting the dispersion relation $\omega_n^2 = \omega_{\text{TO}}^2 - \beta_T^2 (q_n^2 + q^2)$ of the TO mode in the first displacement equation of Eq. (2.88), it follows that there is a relationship between u and v :

$$v/u = -q_n/q. \quad (2.94)$$

Taking the clamping boundaries along the x -axis, the displacements equations for u and v are

$$\begin{cases} u = u_0 \sin(q_n x) \\ v = -(q/q_n) u_0 \sin(q_n x) \end{cases} \quad (2.95)$$

As discussed previously in this review, the mode amplitudes are given by the condition that the energy in each mode is $\hbar\omega_n$; that is,

$$\frac{1}{S} \int_s (u \cdot u^* + v \cdot v^*) dx dy = \frac{\hbar}{M\omega_n}. \quad (2.96)$$

Using this normalization condition, the quantized displacement amplitudes are

$$u_0 = \left(\frac{2\hbar}{M\omega_n} \frac{q^2}{q_n^2 + q^2} \right)^{1/2} \quad \text{and} \quad v_0 = - \left(\frac{2\hbar}{M\omega_n} \frac{q_n^2}{q_n^2 + q^2} \right)^{1/2}. \quad (2.97)$$

In a similar manner for the LO modes, by substituting $\omega^2 = \omega_{\text{TO}}^2 - \lambda^2(q_n^2 + q^2)^2 + \beta_L^2(q_n^2 + q^2)$ of the LO mode in the first displacement equation of Eq. (2.88), it follows that the relationship between u and v is

$$v/u = -q/q_n, \quad (2.98)$$

and the quantized displacement amplitudes are

$$u_0 = \left(\frac{2\hbar}{M\omega_n} \frac{q_n^2}{q_n^2 + q^2} \right)^{1/2} \quad \text{and} \quad v_0 = - \left(\frac{2\hbar}{M\omega_n} \frac{q^2}{q_n^2 + q^2} \right)^{1/2}. \quad (2.99)$$

2.3.3 Deformation Potential in GNRs

As discussed previously in this review, the optical deformation potential Hamiltonian describing carrier optical-phonon scattering can be determined from those normalized continuum modes. Replacing \mathbf{u} by u and v and substituting into Eq. (2.36), one can obtain

$$H_{\text{opt-def}} = |D_{\text{op}}| (u + v), \quad (2.100)$$

where D_{op} is the optical-phonon deformation potential constant as equal to 8.89 eV for graphene [44]. Accordingly the deformation potential Hamiltonian for the TO phonon is given by

$$H_{\text{opt-def}} = |D_{\text{op}}| \left(\frac{2\hbar}{M\omega_n} \right)^{\frac{1}{2}} \frac{q - q_n}{\sqrt{q_n^2 + q^2}} \sin(q_n x), \quad (2.101)$$

while the deformation potential Hamiltonian for the LO phonon is given by

$$H_{\text{opt-def}} = |D_{\text{op}}| \left(\frac{2\hbar}{M\omega_n} \right)^{\frac{1}{2}} \frac{q_n - q}{\sqrt{q_n^2 + q^2}} \sin(q_n x). \quad (2.102)$$

As is well known, the carrier-phonon interaction described by this optical deformation potential Hamiltonian is caused by the interaction of a charge carrier in a medium where the energy band structure is modulated alternately to higher and lower energies. For a more in-depth treatment of the optical deformation potential, and the related acoustic deformation potential, see Stroscio and Dutta [1].

2.4 Phonons in Graphite

In this section, we discuss the c -axis thermal conductivity of thin graphite layers with emphasis on the fact that taking into account phonon confinement [45] results in substantial changes in the c -axis thermal conductivity. As described by Klemens [35], the phonon specific heat in one dimension is

$$C_1(f) = \frac{k_B N}{2\pi f_d} = \frac{k_B}{2\pi f_d} G_1^2 G_3, \quad (2.103)$$

in which $G_3 = 1/a_3$ is the number of layers in a crystal of unit thickness and unit width, each layer having $G_1^2 = 1/a_2^2$ atoms per unit area, and the number of phonon states $N = G_1^2 G_3$. In this formulation, the one-dimensional (1D) specific heat is not a function of the phonon frequency. It is constant for the c -axis transport. Therefore, 1D intrinsic thermal conductivity is given by

$$\lambda_i = \int_{f_{\text{lower}}}^{f_{\text{upper}}} C_1 v l_i \, df, \quad (2.104)$$

where f_{lower} and f_{upper} are determined by the c -axis phonon dispersion relation. In this discussion, the expression used for the mean free path is that derived by Klemens (1994) for the anharmonic relaxation process. In the work of Sun et al. [45], it has been evaluated for the velocity along the c -axis. As commented by Sun et al., the Grüneisen constant for the 1D mean free path is, to the best of our knowledge, not known with precision and, accordingly, the same Grüneisen constant as for the basal plane is assumed. There is, however, some evidence that the c -axis and basal plane Grüneisen constants are within a factor of 2 of each other as indicated by Sun et al. [45]. For film thickness decreases below 10 nm, phonon quantization is expected to occur resulting in discrete dispersion relations. Here we take $f_{\text{upper}} = 2.75$ THz and $f_{\text{lower}} = f_{\text{upper}}/L$, where L is the number of atoms in the one-dimensional chain of carbon atoms. The frequency range over which the thermal conductivity is integrated is about 20 times smaller than that used for the 2D case. Thus, the expression for 1D thermal conductivity is

$$\lambda_i(T, L) = \frac{\rho v^4}{8\pi^2 \gamma^2 T} \left(\frac{1}{f_{\text{upper}}/L} - \frac{1}{f_{\text{upper}}} \right). \quad (2.105)$$

For this situation, instead of a logarithmic function, as for the 2D case, an inverse relation is obtained for c -axis thermal conductivity and frequency. Equation (2.105) predicts a pronounced dependence on the thickness of the graphite layer as a consequence of phonon confinement.

Using this formulation, Sun et al. [45] have calculated the ratio of the 2D thermal conductivity to the 1D thermal conductivity. These authors found that the intrinsic thermal conductivity is about four orders of magnitude smaller in one

dimension than in two dimensions. This finding is consistent with the following scaling argument. Indeed, since the velocity in one dimension is about 20 times smaller than that in two dimensions and since the mean free path varies with the third power of the velocity, it is not unreasonable that the thermal conductivity is four orders of magnitude smaller in 1D than in 2D.

Based on this formulation Sun et al. [45] perform a numerical analysis of the 2D thermal conductivity to 1D thermal conductivity in *c*-axis graphite; over a wide range of temperatures (300–1,000 K), they find that ratio is approximately 1.4×10^5 , 6×10^4 , and 3×10^4 for graphite with a thickness of three, six, and ten atoms, respectively.

These results reveal a dramatic effect caused by phonon dimensional confinement that enters through the lower limit of the thermal conductivity integral.

2.5 Phonons in Wurtzite Structures

As has been discussed by Strocio and Dutta [1], the treatment of the phonons in wurtzite structures is more complicated than for the zincblendes, but it is still possible to obtain a description based on the continuum approach. As is well known, there are four atoms per unit cell for wurtzites and they have lower symmetry than zincblende crystals. Furthermore there are nine optical and three acoustic modes associated with wurtzite crystals. Due to the uniaxial character of wurtzite crystals and the associated optical anisotropy, the long wavelength lattice vibrations may be classified in terms of orientation with respect to the *c*-axis, the phonon wave vector \mathbf{q} , the electric field \mathbf{E} , and the polarization \mathbf{P} [13] Loudon's treatment divides the lattice vibrations into two groups of phonons: ordinary and extraordinary. In the case of the dispersionless ordinary phonons, \mathbf{E} and \mathbf{P} are both perpendicular to \mathbf{q} and the *c*-axis. In the case of the extraordinary phonons, the phonon frequencies are dependent upon the angle between the phonon wave vector and the *c*-axis.

This section reviews the basic properties of phonon modes in bulk wurtzite structures, wurtzite quantum wells (QWs), and wurtzite quantum dots (QDs), respectively. Moreover, phonon frequencies and electron–phonon interaction Hamiltonian of both bulk wurtzite structures and wurtzite QWs are presented. In addition, the formal analytical solutions for interface modes in wurtzite QDs are obtained.

2.5.1 Phonons in Bulk Wurtzite Structures

Within the context of Loudon's model [1], after some algebraic manipulation, the phonon frequency for ordinary phonons has a trivial solution $\omega = \omega_{\perp}$ and $\mathbf{E}(\mathbf{r}) = 0$. The phonon frequencies for extraordinary phonons satisfy [14, 46]

$$\varepsilon_{\perp}(\omega) \sin^2(\theta) + \varepsilon_z(\omega) \cos^2(\theta) = 0, \quad (2.106)$$

such that the direction-related dielectric constants $\varepsilon_{\perp}(\omega)$ and $\varepsilon_z(\omega)$, are given by

$$\varepsilon_{\perp}(\omega) = \varepsilon_{\perp}^{\infty} \frac{\omega^2 - \omega_{\text{LO},\perp}^2}{\omega^2 - \omega_{\perp}^2}, \quad (2.107)$$

$$\varepsilon_z(\omega) = \varepsilon_z^{\infty} \frac{\omega^2 - \omega_{\text{LO},z}^2}{\omega^2 - \omega_z^2}, \quad (2.108)$$

when $|\omega_{\text{LO},\perp} - \omega_{\text{LO},z}|, |\omega_{\perp} - \omega_z| \ll |\omega_{\text{LO},\perp} - \omega_{\perp}|, |\omega_{\text{LO},z} - \omega_z|$, which is the case for the wurtzite-based GaN, ZnO, CdS, and CdSe materials, the solutions become

$$\omega_{\text{LO}}^2 = \omega_{\text{LO},z}^2 \cos^2(\theta) + \omega_{\text{LO},\perp}^2 \sin^2(\theta), \quad (2.109)$$

$$\omega_{\text{TO},z}^2 = \omega_z^2 \sin^2(\theta) + \omega_{\perp}^2 \cos^2(\theta). \quad (2.110)$$

These are predominantly longitudinal and transverse modes, respectively. Herein, the phonon frequencies of GaN will be based on the experimental results in Hellwege et al. [47].

From these results Chen et al. [14, 46] showed that the LO-like mode frequency is nearly constant as a function of θ , indicating that the mode is weakly dependent upon the direction. In contrast, the TO-like mode exhibits weak anisotropy.

As has been discussed previously in this review, the phonon modes must be normalized so that the energy in each mode is $\hbar\omega$. As indicated by Eq. (2.31), the normalized electron–optical–phonon Hamiltonian for the bulk uniaxial material is given as

$$\begin{aligned} H = \sum_{\mathbf{q}} \left[\frac{4\pi e^2 \hbar V^{-1}}{\frac{\partial}{\partial \omega} [\varepsilon_{\perp}(\omega) \sin^2(\theta) + \varepsilon_z(\omega) \cos^2(\theta)]} \right]^{1/2} & \frac{1}{q} \left(a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + a_{\mathbf{q}}^{\dagger} e^{-i\mathbf{q}\cdot\mathbf{r}} \right) \\ & = \sum_{\mathbf{q}} \sqrt{\frac{2\pi e^2 \hbar}{V\omega}} \frac{1}{q} \left(a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + a_{\mathbf{q}}^{\dagger} e^{-i\mathbf{q}\cdot\mathbf{r}} \right) \\ & \times \frac{(\omega_{\perp}^2 - \omega^2)(\omega_z^2 - \omega^2)}{\left[(\varepsilon_{\perp}^0 - \varepsilon_{\perp}^{\infty}) \omega_{\perp}^2 (\omega_z^2 - \omega^2)^2 \sin^2(\theta) + (\varepsilon_z^0 - \varepsilon_z^{\infty}) \omega_z^2 (\omega_{\perp}^2 - \omega^2)^2 \cos^2(\theta) \right]^{1/2}}. \end{aligned} \quad (2.111)$$

Moreover, using the Fermi golden rule, the transition probability from electron state \mathbf{k} to \mathbf{k}' per unit time, $W(\mathbf{k}, \mathbf{k}')$, is given by

$$W(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} |M_{\mathbf{q}}|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}} \pm \hbar\omega_{\mathbf{q}}), \quad (2.112)$$

where $E_{\mathbf{k}}$ is the initial electron energy and $E_{\mathbf{k}'}$ is the final electron energy. $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ is a transferred momentum and $\hbar\omega_{\mathbf{q}}$ is transition energy, with the upper sign “+” (the lower sign “−”) corresponding to phonon emission (absorption). As usual the transition matrix element, $M_{\mathbf{q}}$, may be written as

$$|M_{\mathbf{q}}|^2 = \langle \mathbf{k}' | H | \mathbf{k} \rangle, \quad (2.113)$$

such that the electron states are plane-wave states normalized in volume V ,

$$\begin{aligned} |\mathbf{k}\rangle &= e^{i\mathbf{k}\cdot\mathbf{r}} / \sqrt{V} \\ \langle \mathbf{k}' | &= e^{-i\mathbf{k}'\cdot\mathbf{r}} / \sqrt{V}. \end{aligned} \quad (2.114)$$

As described in Chen et al. [14, 46],

$$|M_{\mathbf{q}}|^2 = \frac{2\pi e^2 \hbar}{V\omega} \frac{1}{q^2} \left(n_{\text{ph}} + \frac{1}{2} \pm \frac{1}{2} \right) \frac{(\omega_{\perp}^2 - \omega^2)^2 (\omega_z^2 - \omega^2)^2}{(\varepsilon_{\perp}^0 - \varepsilon_{\perp}^{\infty}) \omega_{\perp}^2 (\omega_z^2 - \omega^2)^2 \sin^2 \theta + (\varepsilon_z^0 - \varepsilon_z^{\infty}) \omega_z^2 (\omega_{\perp}^2 - \omega^2)^2 \cos^2 \theta}, \quad (2.115)$$

where $n_{\text{ph}} = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the phonon occupation number. Based on this equation, both the LO- and TO-like modes exhibit anisotropy. Moreover, the anisotropy for the TO-like mode is very pronounced, but smaller than those for the LO-like mode.

Following the standard procedures of Chen et al. [14, 46], the scattering rate, $W(\mathbf{k})$, may be written as

$$\begin{aligned} W(\mathbf{k}) &= \sum_{\mathbf{k}'} W(\mathbf{k}, \mathbf{k}') \\ &= \frac{e^2 \sqrt{m}}{4\sqrt{2}\pi^2 \hbar} \int_0^{2\pi} \int_0^{\pi} d\theta \, d\varphi \frac{1}{\omega} \left(n_{\text{ph}} + \frac{1}{2} \pm \frac{1}{2} \right) \sin \theta \frac{\sigma}{\sqrt{E_{\mathbf{k}} \cos^2(\mathbf{k} \cdot \mathbf{q}) \mp \hbar'}} \\ &\quad \frac{(\omega_{\perp}^2 - \omega^2)^2 (\omega_z^2 - \omega^2)^2}{(\varepsilon_{\perp}^0 - \varepsilon_{\perp}^{\infty}) \omega_{\perp}^2 (\omega_z^2 - \omega^2)^2 \sin^2 \theta + (\varepsilon_z^0 - \varepsilon_z^{\infty}) \omega_z^2 (\omega_{\perp}^2 - \omega^2)^2 \cos^2 \theta}, \end{aligned} \quad (2.116)$$

with $\cos(\mathbf{k} \cdot \mathbf{q}) = \sin \theta \sin \theta_k \cos \varphi + \cos \theta \cos \theta_k$, such that θ_k represents the angle between the initial electron wave vector k and the c -axis. In the case of phonon emission, σ is a step function given by

$$\sigma = \begin{cases} 0 & \text{for } \cos(\mathbf{k} \cdot \mathbf{q}) < \sqrt{\hbar\omega/E_{\mathbf{k}}} \\ 2 & \text{otherwise,} \end{cases} \quad (2.117)$$

and for the case of phonon absorption, $\sigma \equiv 1$.

The total scattering rates for LO-like and TO-like phonons for bulk GaN were evaluated numerically in by Chen et al. [14, 46]. The scattering rates as a function of the incident angle of the electron with respect to the c -axis, θ_k , with an initial electron energy of 0.3 eV for GaN, vary little with θ_k for LO-like phonon emission, LO-like phonon absorption, and TO-like phonon absorption, which the TO-like phonon emission rate exhibits variations of a factor of 2 or 3 over the full range of θ_k .

These authors found that the emission of LO-like phonons have the highest scattering rate being of the order of 10^{13} – 10^{14} s⁻¹, while the absorption of TO-like phonons has the lowest scattering rate being of the order of 10^{10} – 10^{11} s⁻¹. LO-like mode absorption rates were found to be in the range of 10^{12} – 10^{13} s⁻¹ and TO-like mode emission rates were found to be smaller by about one order of magnitude.

2.5.2 Phonons in Wurtzite Quantum Wells

As an illustrative example of phonons in wurtzite QWs, this section will review the results of Chen et al. [46] for the GaN/ZnO material system. Following these authors, we consider a double-heterointerface system where material region one occupies $|z| < \pm d/2$, and material region two occupies both $z < -d/2$ and $z > d/2$, where d is the thickness. As has been discussed previously [1], in such a double-heterointerface system, there are four distinct classes of optical-phonon modes; these are the interface (IF), confined, half-space, and propagating modes.

As a result of translational symmetry perpendicular to the z -axis, the Fröhlich potential may be written as

$$\Phi(r) = \sum_{\mathbf{q}} \Phi(\mathbf{q}, z) \exp(i\mathbf{q} \cdot \boldsymbol{\rho}), \quad (2.118)$$

where $\mathbf{q} = (q_x, q_y)$, $\boldsymbol{\rho} = (x, y)$, and $\Phi(\mathbf{q}, z)$ is the electron–optical–phonon interaction potential. As is standard for the dielectric continuum model, the boundary conditions at the interfaces require that the tangential components of \mathbf{E} , E_t , and D_z be continuous at $z = \pm d/2$. Moreover, the normalization condition is given by

$$\int \sqrt{n\mu} \mathbf{u}^*(\mathbf{q}, z) \cdot \sqrt{n\mu} \mathbf{u}(\mathbf{q}, z) dz = \frac{\hbar}{2\omega L^2}. \quad (2.119)$$

In addition, the electron–optical–phonon Hamiltonian may be written

$$H = \sum_q -e\Phi(\mathbf{q}, z) (a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}). \quad (2.120)$$

As for zincblende heterostructures, in these wurtzite structures, there are also symmetric and antisymmetric IF modes. The solutions can be found for the dispersion relation of the symmetric case [11]

$$\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}} \tanh(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qd/2) - \sqrt{\varepsilon_{2\perp}\varepsilon_{2z}} = 0 \quad \text{with } \varepsilon_{1z}\varepsilon_{2z} < 0, \quad (2.121)$$

and of the antisymmetric case

$$\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}} \coth(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qd/2) - \sqrt{\varepsilon_{2\perp}\varepsilon_{2z}} = 0 \quad \text{with } \varepsilon_{1z}\varepsilon_{2z} < 0. \quad (2.122)$$

In the case of the symmetric mode, the interaction Hamiltonian is given as

$$H_{\text{IF}}^S = \sum_q \sqrt{\frac{4\pi e^2 \hbar L^{-2}}{\frac{\partial}{\partial \omega} (\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}} \tanh(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qd/2) - \sqrt{\varepsilon_{2\perp}\varepsilon_{2z}})} \frac{1}{\sqrt{2q}}} \\ \times (a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}) \times \begin{cases} \cosh(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qz) / \cosh(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qd) & |z| < d/2 \\ \exp[-\sqrt{\varepsilon_{2\perp}\varepsilon_{2z}}q(|z| - d/2)] & |z| > d/2. \end{cases} \quad (2.123)$$

where the frequency ω is determined from the dispersion relationship. In the case of the antisymmetric mode, the interaction Hamiltonian is given by

$$H_{\text{IF}}^A = \sum_q \sqrt{\frac{4\pi e^2 \hbar L^{-2}}{\frac{\partial}{\partial \omega} (\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}} \coth(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qd/2) - \sqrt{\varepsilon_{2\perp}\varepsilon_{2z}})} \frac{1}{\sqrt{2q}}} \\ \times (a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}) \times \begin{cases} \sinh(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qz) / \sinh(\sqrt{\varepsilon_{1\perp}\varepsilon_{1z}}qd) & |z| < d/2 \\ \text{sgn}(z) \exp[-\sqrt{\varepsilon_{2\perp}\varepsilon_{2z}}q(|z| - d/2)] & |z| > d/2 \end{cases} \quad (2.124)$$

Based on these results, the zone-center frequencies of the high-frequency symmetric mode, low-frequency symmetric mode, high-frequency antisymmetric mode, and low frequency antisymmetric mode are 705, 422, 690, and 446 cm^{-1} , respectively. In GaN/ZnO/GaN structures, Chen et al. [46] found that the zone-center frequencies of the high frequency symmetric mode, low frequency symmetric mode, high frequency antisymmetric mode, and low frequency antisymmetric mode are 692, 440, 703, and 430 cm^{-1} , respectively.

As a result of the direction-dependent dielectric constant, the confined phonon modes for wurtzite structures are more difficult to calculate than for zincblende structures. As discussed by Komirenko et al. [48], for symmetric modes (even modes), the dispersion relation becomes

$$Q_m^S = \frac{2 \left\{ m\pi + \xi \arctan \left[\frac{\sqrt{|\varepsilon_{2z}(\omega) \varepsilon_{2\perp}(\omega)|} / \sqrt{|\varepsilon_{1z}(\omega) \varepsilon_{1\perp}(\omega)|}}{\sqrt{|\varepsilon_{1\perp}(\omega) / \varepsilon_{1z}(\omega)|}} \right] \right\}}{\sqrt{|\varepsilon_{1\perp}(\omega) / \varepsilon_{1z}(\omega)|}}, \quad (2.125)$$

while for antisymmetric modes (odd modes)

$$Q_m^A = \frac{2 \left\{ m\pi - \xi \arctan \left[\frac{\sqrt{|\varepsilon_{1z}(\omega) \varepsilon_{1\perp}(\omega)|} / \sqrt{|\varepsilon_{2z}(\omega) \varepsilon_{2\perp}(\omega)|}}{\sqrt{|\varepsilon_{1\perp}(\omega) / \varepsilon_{1z}(\omega)|}} \right] \right\}}{\sqrt{|\varepsilon_{1\perp}(\omega) / \varepsilon_{1z}(\omega)|}}. \quad (2.126)$$

where $\xi = \text{sgn}[\varepsilon_{1z}(\omega)\varepsilon_{2z}(\omega)]$. Accordingly, for the symmetric mode, the interaction Hamiltonian is given by

$$H_C^S = \sum_q \sum_m \sqrt{\frac{4\pi e^2 \hbar L^{-2}}{\frac{\partial}{\partial \omega} [(\varepsilon_{1\perp} q^2 + \varepsilon_{1z} k_{1m}^2) d/2 - 2q f_S(\omega) \cos(k_{1m} d/2)]}} \left(a_q e^{i\mathbf{q}\cdot\mathbf{r}} + a_q^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} \right) \times \begin{cases} \cos(k_{1m} d/2) & |z| < d/2 \\ \cos(k_{1m} d/2) \exp[-\sqrt{\varepsilon_{2\perp}/\varepsilon_{2z}} q(|z| - d/2)] & |z| > d/2, \end{cases} \quad (2.127)$$

where $f_S(\omega) = \text{sgn}(\varepsilon_{1z}) \sqrt{\varepsilon_{1\perp} \varepsilon_{1z}} \sin(k_{1m} d/2) - \text{sgn}(\varepsilon_{2z}) \sqrt{\varepsilon_{2\perp} \varepsilon_{2z}} \cos(k_{1m} d/2)$. k_{1m} is determined from $\varepsilon_{1z} k_{1m} \sin(k_{1m} d/2) - \varepsilon_{2z} \sqrt{\varepsilon_{2\perp}/\varepsilon_{2z}} q \cos(k_{1m} d/2) = 0$ with $2m\pi/d < k_{1m} < (2m+1)\pi/d$, and the phonon frequencies may be determined from Eqs. (2.129) and (2.130). Likewise, for the antisymmetric mode

$$H_C^A = \sum_q \sum_m \sqrt{\frac{4\pi e^2 \hbar L^{-2}}{\frac{\partial}{\partial \omega} [(\varepsilon_{1\perp} q^2 + \varepsilon_{1z} k_{1m}^2) d/2 - 2q f_A(\omega) \sin(k_{1m} d/2)]}} \left(a_q e^{i\mathbf{q}\cdot\mathbf{r}} + a_q^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} \right) \times \begin{cases} \sin(k_{1m} d/2) & |z| < d/2 \\ \text{sgn}(z) \sin(k_{1m} d/2) \exp[-\sqrt{\varepsilon_{2\perp}/\varepsilon_{2z}} q(|z| - d/2)] & |z| > d/2, \end{cases} \quad (2.128)$$

where $f_A(\omega) = \text{sgn}(\varepsilon_{1z}) \sqrt{\varepsilon_{1\perp} \varepsilon_{1z}} \cos(k_{1m} d/2) - \text{sgn}(\varepsilon_{2z}) \sqrt{\varepsilon_{2\perp} \varepsilon_{2z}} \sin(k_{1m} d/2)$, k_{1m} is determined from $\varepsilon_{1z} k_{1m} \cos(k_{1m} d/2) - \varepsilon_{2z} \sqrt{\varepsilon_{2\perp}/\varepsilon_{2z}} q \sin(k_{1m} d/2) = 0$ with $(2m-1)\pi/d < k_{1m} < (2m+1)\pi/d$.

2.5.3 Phonons in Wurtzite Quantum Dots

In the case of polar wurtzite QDs, understanding the role of the confined (LO) and the surface optical (SO) phonon modes is essential [49, 50]. From Eq. (2.30), we obtain

$$\varepsilon \Delta\phi = 0, \quad (2.129)$$

where ϕ is the potential associated with the Fröhlich interaction discussed previously. The equation implies that $\varepsilon = 0$ or that $\Delta\phi = 0$. In the first case, $\varepsilon = 0$, which corresponds to the LO mode, the eigenfunctions, for a spherical QD, may be written as $B_k j_l(kr) Y_{lm}(\theta, \varphi)$, where $j_l(kr)$ is the spherical Bessel function of order l ($l = 0, 1, 2, 3 \dots$), and $Y_{lm}(\theta, \varphi)$ is the spherical harmonic function with $m = 0, \pm 1, \dots \pm l$. B_k is the normalization constant, given by

$$B_k^{-2} = R^3 j_{l+1}^2(kR)/2. \quad (2.130)$$

Here, R is the radius of QD. Accordingly, the potential, ϕ , may be expressed as

$$\phi(r) = \sum_{l,m} \sum_k B_k j_l(kr) Y_{lm}(\theta, \varphi). \quad (2.131)$$

The continuity of ϕ and the normal component of \mathbf{D} at the interface imply that ϕ vanishes outside the sphere and at its surface and can be expressed as $j_l(kR) = 0$ with $k = \alpha_{n,l}/R$, here $\alpha_{n,l}$ is the n th zero of the spherical Bessel function of order l .

In the second case, $\Delta\phi = 0$; this case corresponds to the SO modes. For this case, the solutions are

$$\begin{aligned} \phi(r) &= A_{l,m} r^l Y_{lm}(\theta, \varphi) \quad \text{for } r < R \\ \phi(r) &= B_{l,m} r^{-l-1} Y_{lm}(\theta, \varphi) \quad \text{for } r > R, \end{aligned} \quad (2.132)$$

where A_{lm} and B_{lm} are the normalization constants. The boundary conditions lead to the requirement that

$$\varepsilon_1/\varepsilon_2 = -(1+l)/l. \quad (2.133)$$

For the case of isotropic material, it follows that

$$\varepsilon_i(\omega_l) = \varepsilon_i^\infty (\omega_{\text{LO},i}^2 - \omega_l^2) / (\omega_{\text{TO},i}^2 - \omega_l^2) \quad (i = 1, 2), \quad (2.134)$$

where $i = 1$ denotes the dielectric constant of QDs with frequency ω_l , and $i = 2$ represents dielectric constant of the matrix element surrounding the dots with the same frequency. Thus, in the case where outside matrix is also a polar material, the frequency of the LO phonon follows upon solving Eq. (2.133)

$$\frac{\varepsilon_1^\infty (\omega_{\text{LO}1}^2 - \omega_l^2) (\omega_{\text{TO}2}^2 - \omega_l^2)}{\varepsilon_2^\infty (\omega_{\text{TO}1}^2 - \omega_l^2) (\omega_{\text{LO}2}^2 - \omega_l^2)} = -\frac{1+l}{l}, \quad (2.135)$$

For a non-polar surrounding material, the SO phonon frequency is

$$\omega_l = \omega_{\text{TO}} \left\{ [\varepsilon_g + (\varepsilon_g + \varepsilon_0)l] / [\varepsilon_g + (\varepsilon_g + \varepsilon_\infty)l] \right\}^{1/2} \quad (2.136)$$

where the subscript g labels the surrounding matrix material. There is only one SO mode in this case.

Upon using Green's first identity

$$\int_V \nabla \varphi \cdot \nabla \psi \, d\mathbf{r} = - \int_V \varphi \nabla^2 \psi \, d\mathbf{r} + \int_S \varphi \frac{\partial \psi}{\partial n} \, dS, \quad (2.137)$$

the surface integral vanishes for the confined phonon, while the volume integral vanishes for the surface phonon [in the present case $\varphi = \psi = B_k j_l(kr) Y_{lm}(\theta, \varphi)$]. The phonon modes outside the dots vanish for the case of polar dots in a non-polar matrix; accordingly, the integral is nonzero only inside the dots.

The interaction Hamiltonian for confined phonons may be written as [50]

$$H_{I-C} = e\phi = \sum_{l,m} f_{lm}^c(k) [a_{lm}(k) j_l(kr) Y_{lm}(\theta, \varphi) + \text{H.c.}] \quad (2.138)$$

where

$$f_{lm}^c(k) = \sqrt{4\pi \hbar \omega_{LO} e^2 / [j_{l+1}^2(kR) \varepsilon^* R^3 k^2]}, \quad (2.139)$$

with $1/\varepsilon^* = 1/\varepsilon_1^\infty - 1/\varepsilon_1^0$.

According to Eqs. (2.24), (2.25), (2.30), and (2.132), we can obtain

$$\nabla \phi = (1 - 4\pi/3) (\omega_1^2 - \omega_{TO}^2) \frac{\mu}{e} \mathbf{u}. \quad (2.140)$$

By using the normalization relationship Eq. (2.31), for any given l and m , the normalized displacement is found to be

$$\mathbf{u} = \sqrt{(2l+1) \hbar / (2n\mu\omega_l l R)} [\nabla r^l Y_{lm}(\theta, \varphi) + \text{H.c.}]. \quad (2.141)$$

Thus, the interaction Hamiltonian for SO phonons may be written as

$$H_{I-SO} = e\phi = \sum_{l,m} f_{lm}^s \left[b_{lm} \left(\frac{r}{R} \right)^l Y_{lm}(\theta, \varphi) + \text{H.c.} \right], \quad (2.142)$$

where

$$f_{lm}^s = \varepsilon_1^\infty \omega_{LO} \sqrt{2\pi e^2 \hbar l (2l+1) / \omega_l \varepsilon^* R} / [l \varepsilon_1^\infty + (l+1) \varepsilon_1^0], \quad (2.143)$$

where b_{lm} is the annihilation operator, and its conjugate is the creation operator.

The scattering rate is typically formulated by using Fermi's golden rule [1]

$$W = \left(\frac{2\pi}{\hbar} \right) |\langle \Psi_m | (H_{I-C} + H_{I-SO}) | \Psi_n \rangle|^2 \delta(E_m - E_n \mp \hbar\omega_l), \quad (2.144)$$

E_m , E_n are the energy eigenvalue of the final state Ψ_m and initial state Ψ_n , respectively. For phonon-assisted transitions, the energy difference between the final state and the initial state should be the energy of surface phonon energy. Clearly, in a quantum dot, this energy difference may be adjusted to be the surface phonon energy by simply selecting an appropriate radius for the dot. As discussed by Chen et al. [49], the three-dimensional confinement in the case of a QDs necessitates the estimation of a linewidth in estimating the transition rate. Numerical evaluation of the scattering rate for phonon associated transitions in QDs embedded in vacuum (Chen et al. [49]) reveals that rates as large as 10^{13} – 10^{14} s⁻¹ are possible for QDs with radii of 3.5 to 4.5 nm.

2.6 Summary

The review highlights selected advances of the last decade in the theory of acoustic and optical phonons in dimensionally confined structures. Among the structures considered are CNTs, graphene, graphite, and dimensionally confined wurtzite structures.

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