Carrier-density dependence of optical phonons in carbon nanotubes

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Abstract. The dependence of the frequency and broadening of optical phonons on the Fermi level is theoretically studied in carbon nanotubes. In metallic nanotubes, the frequency shift exhibits a logarithmic divergence and the broadening vanishes discontinuously when the Fermi level reaches the half of the optical-phonon frequency for the longitudinal mode, while the transverse mode is not affected. In semiconducting nanotubes, the frequency is raised for both transverse and longitudinal modes.

1. Introduction
In carbon nanotubes, optical phonons are strongly influenced by electron-phonon interactions [1, 2, 3]. In a previous work [4], the interaction effect was shown to cause characteristic diameter dependence of the frequency and broadening in metallic and semiconducting nanotubes within the continuum model for both electrons [5] and phonons [6]. Quite recently, a large change in the phonon spectra was experimentally observed for varying electron concentration by the application of a gate voltage [7, 8]. The purpose of this paper is to extend the previous work [4] and theoretically study the Fermi-level dependence of optical phonons.

2. Effective-mass description
A graphite sheet is a zero-gap semiconductor in the sense that the conduction and valence bands consisting of $\pi$ states cross at $K$ and $K'$ points in the wave-vector space [9]. Electronic states near the $K$ point are described by the $k \cdot p$ equation $\gamma(\hat{\sigma} \cdot \hat{k}) \mathbf{F}(\mathbf{r}) = \varepsilon \mathbf{F}(\mathbf{r})$, where $\gamma$ is the band parameter, $\hat{k} = (\hat{k}_x, \hat{k}_y) = -i \vec{\nabla}$, $\varepsilon$ is the energy, and $\sigma_x$ and $\sigma_y$ are the Pauli spin matrices [5]. Two components of the wave function $\mathbf{F}(\mathbf{r})$ correspond to the amplitude at two sites in a unit cell. This equation has the form of Weyl’s equation for neutrinos.

The structure of a nanotube is specified by a chiral vector $\mathbf{L}$ corresponding to the circumference (see Fig. 1). In the following, we choose the $x$ axis in the circumference direction and the $y$ axis in the tube-axis direction. The boundary conditions are given by $\mathbf{F}(\mathbf{r} + \mathbf{L}) = \mathbf{F}(\mathbf{r}) \exp[2\pi i(\varphi - \nu/3)]$, with $\nu = 0, \pm 1$ depending on the structure or $\mathbf{L}$ and $\varphi = \phi/\phi_0$, where $\phi$ is Aharonov-Bohm flux passing through the cross section and $\phi_0 = ch/e$ is the flux quantum. As a result the wave vector in the circumference direction is quantized into $k_x = k_{\nu\varphi}(n) \equiv (2\pi/L)(n+\varphi-\nu/3)$ with integer $n$ and $L = |\mathbf{L}|$. Corresponding results for the $K'$ point can be obtained by replacing $\hat{k}_y$ by $-\hat{k}_y$ and $\nu$ by $-\nu$.
3. Long wavelength optical phonon

The phonon modes are specified by the wave vector \( \mathbf{q} = (q_x, q_y) \). The wave vector in the circumference direction becomes discrete, i.e., \( q_x = (2\pi/L)j \) with integer \( j \), and that in the axis direction remains continuous, \( q_y = \mathbf{q} \). In the long-wavelength limit \( j = 0 \) and \( |q_s| \ll 1 \) with \( a \) being the lattice constant, both longitudinal and transverse phonons have the frequency \( \omega_0 \). The longitudinal mode \( \mu = l \) has lattice displacement along the \( y \) direction and the transverse mode \( \mu = t \) along the \( x \) direction. The phonon displacement \( \mathbf{u}(\mathbf{r}) \) is given by

\[
\mathbf{u}(\mathbf{r}) = \sum_{\mu \mathbf{q}} \sqrt{\frac{\hbar}{2NM\omega_0}} (b_{\mu \mathbf{q}} + b_{\mu \mathbf{q}}^\dagger) \mathbf{e}_\mu(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}},
\]

where \( N \) is the number of unit cells, \( \mu \) denotes \( t \) or \( l \), \( M \) is the mass of a carbon atom, \( \mathbf{e}_\mu(\mathbf{q}) \) is the normal coordinates, and \( b_{\mu \mathbf{q}} \) and \( b_{\mu \mathbf{q}}^\dagger \) are the creation and destruction operators, respectively.

The interaction between optical phonons and an electron near the K point is given by [4]

\[
\mathcal{H}_{\text{int}}^K = -\sqrt{2} \frac{\beta \gamma}{\beta^2} \mathbf{\bar{\sigma}} \times \mathbf{u}(\mathbf{r}),
\]

where the vector product for \( \mathbf{a} = (a_x, a_y) \) and \( \mathbf{b} = (b_x, b_y) \) in two dimension is defined by \( \mathbf{a} \times \mathbf{b} = a_x b_y - a_y b_x \) and \( b = a/\sqrt{3} \) is the equilibrium bond length. The dimensionless parameter \( \beta \) is given by \( \beta = -d\ln \gamma_0/d\ln b \), where \( \gamma_0 \) is the hopping integral between nearest neighbor carbon atoms related to \( \gamma \) through \( \gamma = (\sqrt{3}a/2)\gamma_0 \). The corresponding Hamiltonian for the K’ point can be obtained by replacement of \( \mathbf{\bar{\sigma}} \) with \( \mathbf{\bar{\sigma}}^\ast \).

Effects of electron-phonon interactions on the phonon spectrum can be calculated using Green’s function. Because the coupling constant is sufficiently small, the phonon self-energy \( \Pi_{\mu}(\mathbf{q}, \omega) \) is calculated in the lowest order perturbation, and the shift of the phonon frequency \( \Delta \omega_\mu \) and the broadening \( \Gamma_\mu \) are given by \( \Delta \omega_\mu = \hbar^{-1}\text{Re} \Pi_\mu(\mathbf{q}, \omega_0) \) and \( \Gamma_\mu = -\hbar^{-1}\text{Im} \Pi_\mu(\mathbf{q}, \omega_0) \).

4. Frequency shift and broadening

The contribution of the states in the vicinity of the K point in the long-wavelength limit \( q \rightarrow 0 \) is written as [4]

\[
\Pi^K_\mu(\omega) = -g_s \sum_{s,s'} \sum_n \int \frac{dk}{2\pi} \left( \frac{\beta \gamma}{\beta^2} \right)^2 \frac{Ah}{NM\omega_0} \left( 1 \pm \frac{s s' \left( \kappa_{\nu \varphi}(n)^2 - k^2 \right)}{\kappa_{\nu \varphi}(n)^2 + k^2} \right) \frac{f[\varepsilon_{\nu \varphi}(n, k)] - f[\varepsilon'_{\nu \varphi}(n, k)]}{\hbar \omega - \varepsilon_{\nu \varphi}(n, k) + \varepsilon'_{\nu \varphi}(n, k) + i\delta},
\]

where \( f(\varepsilon) \) is the Fermi distribution function, \( g_s = 2 \) is the spin degeneracy, \( \delta \) represents a phenomenological broadening due to disorder, and the upper and lower signs correspond to \( \mu = l \) and \( t \), respectively. Because we start with the phonon mode with frequency \( \omega_0 \) in graphene, we have to subtract the corresponding contribution in the self-energy [4]. The contribution of states in the vicinity of the K’ point, \( \Pi^K_{\mu'}(\omega) \), is obtained by appropriate replacement of the wave vectors and the energies, and the total self-energy is given by the sum \( \Pi_\mu(\omega) = \Pi^K_\mu(\omega) + \Pi^K_{\mu'}(\omega) \).

The strength of the electron-phonon interaction is specified by the dimensionless coupling parameter

\[
\alpha(L) = \frac{27}{\pi} \beta^2 \gamma_0 \frac{\hbar^2}{2Ma^2} \left( \frac{1}{\hbar \omega_0} \right)^2 \frac{a}{L},
\]

For \( \hbar \omega_0 = 0.196 \text{ eV} \) corresponding to 1583 cm\(^{-1}\), \( \gamma_0 = 2.63 \text{ eV} \), and \( 2 < \beta < 3 \), we have \( 0.08 \times (a/L) < \alpha(L) < 0.17 \times (a/L) \), which is small for typical nanotubes with \( L/a \sim 10\sqrt{3} \).

In semiconducting nanotubes, the imaginary part vanishes identically. The frequency of the longitudinal and transverse modes is both shifted to higher frequency side and the shift is smaller.
Figure 1. (a) A schematic illustration of the lattice structure of the two-dimensional graphite and the lattice displacement for transverse and longitudinal optical phonons. (b) The coordinate system in the nanotube. (c) The first Brillouin zone and K and K’ points.

The frequency shift in a semiconducting nanotube as a function of the Fermi wave vector $k_F$. The solid and dashed lines represent the longitudinal and transverse modes, respectively.

for the longitudinal mode for small $k_F$. Figure 2 shows the shifts. It is interesting to note that the behavior of two modes as a function of $k_F$ is similar to that of a “level crossing.”

In metallic nanotubes, the transverse mode is not affected by the doping at all. This is to be expected because the band $n = 0$ does not give any contribution to the phonon self-energy due to the vanishing matrix element. For the longitudinal mode, the self-energy becomes nonzero even for $k_F=0$

$$\Pi^K(\omega) = \frac{\alpha}{2} \omega \hbar \omega_0 \left( \ln[2\pi e^{-1} \hbar \omega_0(2\pi \gamma/L)^{-1}] - i\pi \right).$$

The result for the K’ point is the same. This gives a downward frequency shift and considerable broadening obtained previously [4]. Figure 3 shows the frequency shift relative to that given by (5) and the broadening as a function of the Fermi energy $E_F \equiv \gamma k_F$. For nonzero $k_F$, the self-energy has a logarithmic divergence at $\gamma k_F = \hbar \omega_0/2$ and increases logarithmically with $k_F$ for $\gamma k_F > \hbar \omega_0/2$ for vanishing $\delta$, where $\delta$ is a phenomenological broadening due to disorder. This behavior of the logarithmic singularity at $\gamma k_F = \hbar \omega_0/2$ and the reduction of the broadening is essentially the same as that predicted theoretically [10, 11, 12, 13] and observed experimentally in graphene [14, 15]. Figure 4 shows the spectral function with varying $k_F$ for $\delta/\hbar \omega = 0.1$.

5. Summary
The self-energy of long-wavelength optical phonons has been calculated in nanotubes for nonzero carrier concentrations. In metallic nanotubes, the frequency shift of the longitudinal mode exhibits a logarithmic divergence and the broadening vanishes discontinuously when the Fermi level reaches the half of the optical-phonon frequency, while the transverse mode is not affected. In semiconducting nanotubes, the frequency is raised for both transverse and longitudinal modes, although the details of the dependence on the Fermi level is different. The results are in qualitative agreement with recent experiments [7, 8] and can be quite useful for quantitative analysis of Raman experiments, in particular, the $G^+$ and $G^-$ peaks.
Figure 3. The frequency shift (solid lines) and the broadening (dashed lines) of the longitudinal mode in metallic nanotubes as a function of the Fermi energy. δ is phenomenological broadening due to disorder.

Figure 4. The spectral function of the longitudinal mode for varying Fermi energy γkF. The downward shift at γkF = ℏω0/2 and the sharpening for γkF > ℏω0/2 are quite noteworthy.

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