Collective modes of massive Dirac fermions in armchair graphene nanoribbons

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Abstract
We report the plasmon dispersion characteristics of intrinsic and extrinsic armchair graphene nanoribbons of atomic width $N = 5$ using a $p_z$-orbital tight binding model with third-nearest-neighbor (3nn) coupling. The hopping parameters are obtained by fitting the 3nn dispersions to those of an extended Hückel theory. The resultant massive Dirac fermion system has a band gap $E_g \approx 64$ meV. The extrinsic plasmon dispersion relation is found to asymptotically approach a universal dispersion curve as the chemical potential $\mu$ increases, whereas the intrinsic plasmon dispersion relation is found to have both energy and momentum thresholds. We also report an analytical model for the extrinsic plasmon group velocity in the $q \to 0$ limit.

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene exhibits massless Dirac fermions [1–4] with semi-metallic behavior, for which the collective carrier modes in the form of plasmons have been a topic of study [5–10]. When graphene is patterned in the form of an armchair graphene nanoribbon (acGNR) [11–15], two important deviations occur. First, the acGNR develops a band gap and second the dispersions do not remain linear anymore and hence the electrons and holes behave as massive Dirac fermions.

While acGNRs with atomic widths $N$ of $\text{mod}(N, 3) = 0, 1$ exhibit significant band gap opening irrespective of the theoretical model, acGNRs with $\text{mod}(N, 3) = -1$ have zero band gap and massless dispersion within the continuum and the first nearest-neighbor $p_z$-orbital tight binding (1nn $p_z$TB) model [11, 12, 16, 17]. One has to use more detailed methods like density functional theory (DFT) [13], extended Hückel theory (EHT) [14, 15] or the beyond 1nn TB model to get a more detailed band structure. Although there are quantitative differences between these methods, nonetheless qualitatively these methods converge on massive Dirac fermions with a band gap opening for $\text{mod}(N, 3) = -1$ acGNRs. The band gaps predicted by EHT for these acGNRs are of the order of a few tens of meV for extremely narrow ribbons, and decrease as the width of the nanoribbon increases [15].

In this paper, we examine the plasmon dispersion in intrinsic and extrinsic acGNR with atomic width $N = 5$ (acGNR5) by using a third-nearest-neighbor (3nn) $p_z$TB model, benchmarked with EHT, within the random phase approximation (RPA), as discussed in section 2. We discuss the plasmon dispersion results in section 3 followed by the conclusions.

Although we focus on a specific geometry in this paper (acGNR5), we expect the results to be quite general. The energy gap in the acGNR gives rise to changes in the plasmon dispersion relation from that expected for a purely massless system. As the chemical potential $\mu$ moves into either the conduction or valence bands, and away from the curved region of the band, the dispersion relation asymptotically approaches what is expected in the massless limit. This effect is most pronounced for narrow acGNRs, due to their larger energy gap (and fermion mass). As the nanoribbon width increases, the gap decreases and this effect is diminished.
The carrier dispersion characteristics of the acGNR5 with the hopping parameters from table 1 is shown in figure 2. When compared with DFT results, the carrier dispersion for an acGNR5 calculated using the 3nn tight binding Hamiltonian with the hopping parameters given in table 1. Panel (a) shows the complete ten-band structure, and panels (b) and (c) show progressively more detail in the dispersion near the gap of $E_g \approx 64$ meV over two different ranges of momentum. In addition to the gap, asymmetry between the conduction and valence bands has been introduced by the non-zero 2nn and 3nn hopping parameters.

### 2. Theoretical model

The unit cell for a hydrogen passivated acGNR5 is highlighted in figure 1, and contains ten carbon and four hydrogen atoms. The unit vector is given as $\hat{a} = d_T = 3a_{cc}\hat{x}$, where $a_{cc} = 1.42$ Å is the carbon bond length. The pzTB Hamiltonian of the unit cell is a $10 \times 10$ matrix containing 3nn hopping parameters. We transform the real-space Hamiltonian to the reciprocal space $H(k)$ to calculate the eigenvalues $E_i(k)$ and eigenfunctions $c_\alpha^i(k)$ for the eigenstate $i = 1, 2, \ldots, 10$, where $i$ is the band index and $\alpha$ represents the atomic location. The band index ranges from $i = 1$ ($i = 1$) corresponding to the lowest-lying conduction (highest-lying valence) band to $i = 5$ ($i = 5$) corresponding to the lowest-lying conduction (lowest-lying valence) band. One finds that the electron–hole symmetry is broken due to finite 2nn and 3nn hopping parameters.

The band structure for an acGNR5 is shown in figure 2. The 3nn tight binding hopping parameters ($E_0$, $t_0$, $t_1$, $t_2$) for the acGNR5 nanoribbon to the EHT [15] are reported in table 1. The parameters are obtained by fitting the top three valence bands and bottom three conduction bands of the EHT data to the 3nn pzTB band structure at 51 $k$-points uniformly spaced across the Brillouin zone. Fitting is accomplished using a least-squares algorithm and no geometric relaxation of the bond lengths is incorporated. This set of hopping parameters agrees well with [19] for the $t_0$ and $t_1$ parameters. However, the 3nn hopping parameter ($t_2$) we report is significantly smaller, due to the smaller gap predicted by EHT [14, 15] when compared with DFT results [13].

The band structure computed using the 3nn Hamiltonian with the hopping parameters from table 1 is shown in figure 2. The carrier dispersion characteristics of the $i = 1, 1$ (valence, conduction) bands in this system show a finite gap of $E_g \approx 64$ meV and represent a massive Dirac fermion system with a dispersion characterized by the relation

$$E_{\alpha} = \pm \sqrt{(m_0v_F)^2 + (hv_Fk)^2},$$  

where $v_F$ is the Fermi velocity for the $i = \bar{1}, 1$ (valence, conduction) bands, and the $+(-)$ sign is chosen for the conduction (valence) band. The band gap $E_g$ corresponds to a relativistic rest mass of the massive Dirac fermion system of $m_0 = E_g/2v_F^2$.

To compute the plasmon dispersion in the random phase approximation (RPA) for the nanoribbon with the 3nn Hamiltonian, we follow the procedure outlined in [17]. Due to large energy differences and small electronic wavefunction overlap integrals at $q \approx 0$ for both 1nn pzTB in [17] and 3nn pzTB in this paper, we use a two-band dielectric function including only the $i = 1$ conduction and $i = \bar{1}$ valence bands to study the plasmon dispersion relation. However, some of the details of the 3nn pzTB model are different, which we discuss next.

In the RPA expression for the interband polarizability, electronic wavefunction overlap integrals between states in the two bands at momenta $k$ and $k' = k + q$, where $q$ is the plasmon momentum, play a significant role. The polarizability is written as

$$\Pi_{mn}(q, \omega) = \lim_{\eta \to 0} \frac{g_s}{L_q} \sum_k \frac{f(E_{km}) - f(E_{k'n})}{E_{km} - E_{k'n} + i\omega + i\eta} \times |\langle n; k'|m; k \rangle|^2,$$

where $m$ and $n$ are band indices, $g_s = 2$ is the spin degeneracy, $L_q$ is the sample length, $k$ is the momentum of the initial state, $k' = k + q$ is the momentum of the final state, and $f(E) = 1/[1 + e^{(E-E_0)/k_BT}]$ is the Fermi–Dirac distribution function with chemical potential $\mu$ and Boltzmann constant $k_B$, where $T$ is the temperature in K. $\hbar$ is the reduced Planck’s constant and $\eta$ is a small number. We consider intrinsic acGNRs with the chemical potential $\mu = 0$. In figure 3, we illustrate several of these overlap integrals as functions of...
Intrinsic plasmons. In the two-band approximation for intrinsic acGNRs at $T = 0$, the self-polarizabilities of the $i = \bar{1}, \bar{1}$ bands are given as $\Pi_{\bar{1}\bar{1}}(q, \omega) = \Pi_{\bar{1}\bar{1}}(q, \omega) = 0$. Further, symmetries in the acGNRs require [21, 20] that the Coulomb matrix elements $v_{\bar{1}\bar{1},\bar{1}\bar{1}}(q) = v_{\bar{1}\bar{1},\bar{1}\bar{1}}(q) = v_{\bar{1},\bar{1},\bar{1}}(q)$. This result gives the dispersion relation of the collective (plasmon) state in the two-band approximation by simplifying equation (4) as follows:

$$1 - v_{\bar{1},\bar{1},\bar{1}}(q) [\Pi_{\bar{1}\bar{1}}(q, \omega) + \Pi_{\bar{1}\bar{1}}(q, \omega)] = 0.$$  

(5)

We compute the Coulomb matrix elements $v_{\bar{1},\bar{1},\bar{1}}(q)$ as described in [17] using the $p$-orbital wavefunction localization parameter $w = 1 \text{ Å}$ [22]. Solution of equation (5) gives the dispersion relation for the collective modes (plasmons) in the acGNR.

Extrinsic plasmons. The dispersion relation for plasmons in an extrinsic acGNR can also be obtained from equation (4) in the two-band approximation. For a chemical potential $\mu$ in the $i = \bar{1}$ conduction band at $T = 0$, states with momenta $-k_f \leq k \leq k_f$, where $E_{k_f} = \mu$, are filled, and states outside of this range are empty. For the extrinsic case $\Pi_{\bar{1}\bar{1}}(q, \omega)$ is no longer 0, and we write the plasmon dispersion relation as

$$(1 - v_{\bar{1},\bar{1},\bar{1}}(q) [\Pi_{\bar{1}\bar{1}}(q, \omega) + \Pi_{\bar{1}\bar{1}}(q, \omega)]) 	imes (1 - v_{\bar{1},\bar{1},\bar{1}}(q) \Pi_{\bar{1}\bar{1}}(q, \omega)) = 0.$$  

(6)

Plasmons for negative chemical potentials $\mu$ will exhibit similar behavior.

3. Discussion of results

Intrinsic plasmons. The intrinsic plasmon obtained using our formalism exhibits an onset threshold in both the $q$ and $E$ dimensions. The $q$ threshold can be understood from the data presented in figure 3(a). For small values of $q$, the overlap integral is nearly zero. Because the polarizabilities $\Pi_{\bar{1}\bar{1}}(q, \omega)$ and $\Pi_{\bar{1}\bar{1}}$ are proportional to this overlap, the dielectric function never crosses 0, and so no collective mode exists. As the overlap gets larger, the dielectric function eventually crosses zero and an intrinsic plasmon dispersion exists. The threshold in $E$ is a result of the fact that the polarizabilities are not large enough to cause a zero-crossing for small $E$. As the plasmon energy increases above the bottom of the conduction band, the resonant enhancement in the polarizabilities causes a zero-crossing. Because we are interested in plasmons in the $q \rightarrow 0$ limit, we do not consider the intrinsic case further.

Extrinsic plasmons. The dispersion relations for plasmons in an extrinsic acGNR computed using the tight binding formalism described above are also plotted in figure 4 for several values of the chemical potential $\mu > E_g/2$ corresponding to a geometric distribution of $k_f$. From these results, it can be readily observed that the dispersion curves have a $q^4\sqrt{\epsilon_{\bar{1}\bar{1},\bar{1},\bar{1}}(q)}$ character for values of the chemical potential within a few millielectronvolts of the band edge ($\mu \geq E_g/2$). Further, as the chemical potential increases, the dispersion relation is observed to asymptotically approach a limit that corresponds to the plasmon dispersion in a massless Dirac fermion system.

Figure 3. The 3nn tight binding overlap integral computed for (a) the interband transition between the conduction and valence bands, and (b) the intraband transition of the conduction band along the line $q = k + q$. In each panel, a family of 12 curves is shown for $0 \leq q \leq q_{\text{max}}$, where $q_{\text{max}} = 11 \Delta q$, in steps of $\Delta q$, where $\Delta q = \pi/(800d)$. In (a) the overlap for $q = 0$ is identically 0, and the overlap for $q = q_{\text{max}}$ has a minimum of approximately 0.66, whereas in (b) the overlap for $q = 0$ is identically 1, and the overlap for $q = q_{\text{max}}$ has a minimum of approximately 0.76. The vertical bars show the bounds $-q_{\text{max}} \leq k < 0$, corresponding to the region where $|\{\bar{1}; k' = k + q_{\text{max}}|\}; k\rangle = 1$ in the continuum model. Outside of this range, $|\{\bar{1}; k' = k + q_{\text{max}}|\}; k\rangle = 0$ for the continuum model. The conduction–conduction band has the opposite symmetry in the continuum model.
where the integral is taken over the filled states between \( k \). The dispersion curves are calculated for a range of chemical potentials \( \mu \). It can be observed that as the chemical potential increases, the resultant dispersion curve asymptotically approaches a universal limiting curve. The universal limiting curve is that which would result from a purely massless Dirac fermion system with the same Fermi velocity.

Further, the intraband overlap integral becomes

\[
\langle \bar{\mathbf{q}} \rangle = \int d^2 k \langle \bar{\mathbf{q}} (\mathbf{k}) \rangle \langle \bar{\mathbf{q}} (\mathbf{k}) \rangle^*.
\]

It is interesting to analyze the behavior of the extrinsic plasmon group velocity in the \( q \rightarrow 0 \) limit as a function of the chemical potential \( \mu \). In this limit, the interband polarizabilities \( \Pi_{11}(q, \omega) = \Pi_{11}(q, 0) = 0 \) because the interband overlap integral \( \langle \bar{\mathbf{q}} (\mathbf{k}) \rangle = 0 \) (see figure 3(a)). Further, the intraband overlap integral \( \langle \bar{\mathbf{q}} (\mathbf{k}) \rangle = 1 \) in this limit (see figure 3(b)). As a result, the intraband polarizability becomes

\[
\Pi_{11}(q, \omega) = \frac{g_k}{E_k} \sum_k \frac{2\Delta E}{E_k^2 (\hbar \omega)^2}.
\]

Solving equation (8) for \( \omega \), the plasmon group velocity in the \( q \rightarrow 0 \) limit can then be written as

\[
v_g(k_F) = \left[ \left. \lim_{q \rightarrow 0} \left( \frac{2\Pi_{11}}{E_k^2 \hbar^2 q^2} \int_{-k_F}^{k_F} \Delta E \, dk \right) \right| \right]^{1/2},
\]

where \( \Delta E = E_{k+q,1} - E_{k,1} \). Thus, as \( q \rightarrow 0 \), the dielectric function becomes

\[
1 - v_{1,1,1}(q) \Pi_{11}(q, \omega) = 0.
\]

Solving equation (8) for \( \omega \), the group velocity of extrinsic plasmons as a function of the chemical potential \( \mu \) in the \( q \rightarrow 0 \) limit can be expected to occur from plasmon scattering to free electron states due to the nature of the relevant overlap integrals.

4. Conclusions

In summary, we have computed the plasmon dispersion for an acGNR5 nanoribbon using a 3nn tight binding model. This nanoribbon represents a massive Dirac fermion system. The hopping parameters for the model were obtained by fitting the 3nn band structure to band data obtained from an EHT calculation. The intrinsic plasmon dispersion relation obtained exhibits a threshold in both \( q \) and \( E \). The extrinsic plasmon dispersion relation obtained follows the \( q\sqrt{\mathbf{V}(q)} \) dependence expected in 1D systems for values of the chemical potential near the band edge (\( \mu \geq E_g/2 \), and the dispersion relation asymptotically approaches one corresponding to a massless Dirac fermion system as the chemical potential \( \mu \) increases. Good agreement between the group velocity of these plasmons in the \( q \rightarrow 0 \) limit and an analytic model based on the behavior of the polarizabilities as \( q \rightarrow 0 \) is obtained. Finally, we note that some damping of these plasmons may be expected to occur from plasmon scattering to free electron states due to the nature of the relevant overlap integrals.

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