Plasmon-phonon coupling in graphene

E. H. Hwang, Rajdeep Sensarma, and S. Das Sarma
Condensed Matter Theory Center, Department of Physics University of Maryland College Park, Maryland 20742-4111
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Collective excitations of coupled electron-phonon systems are calculated for both monolayer and bilayer graphene, taking into account the non-perturbative Coulomb coupling between electronic excitations in graphene and the substrate longitudinal optical phonon modes. We find that the plasmon-phonon coupling in monolayer graphene is strong at all densities, but in bilayer graphene the coupling is significant only at high densities satisfying the resonant condition \( \omega_p \approx \omega_{ph} \). The difference arises from the peculiar screening properties associated with chirality of graphene. Plasmon-phonon coupling explains the measured quasi-linear plasmon dispersion in the long wavelength limit, thus resolving a puzzle in the experimental observations.

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A plasmon is a collective mode of charge-density oscillation in the free-carrier system, which is present both in classical and quantum plasmas. Studying the collective plasmon excitation in the electron gas has been among the very first theoretical quantum mechanical many-body problems studied in solid-state physics. The collective plasmon modes of monolayer graphene (MLG) have been extensively studied theoretically\(^{12,13}\) and experimentally\(^{14,15}\). Recent discovery of bilayer graphene (BLG) has also led to a number of theoretical descriptions of plasmon modes in BLG\(^{12,13}\). Even though the long-wavelength plasmon frequency of MLG is explicitly nonclassical (i.e., the plasmon frequency is necessarily quantum with \( \hbar \) appearing manifestly in the long-wavelength plasmon frequency\(^{12,13}\)), its wave vector dispersion is given by classical electrodynamics, i.e., \( \omega_p(q) \propto \sqrt{q} \). Note that the quadratic band-dispersion of BLG and experimentally\(^{14,15}\), its wave vector dispersion is given by classical electrodynamics, i.e., \( \omega_p(q) \propto \sqrt{q} \). Note that the quadratic band-dispersion of BLG is explicitly nonclassical (i.e., the plasmon frequency is necessarily quantum with \( \hbar \) appearing manifestly in the long-wavelength plasmon frequency\(^{12,13}\)).

Since the plasmon dispersion relation is exactly known at long wavelengths \( (q \to 0) \) where the f-sum rule arising from particle conservation fixes the plasma frequency, it is surprising that the measured graphene plasmon dispersion in the long wavelength limit deviates from the classical dispersion \( (\omega_q \sim \sqrt{q}) \) and shows a rather linear dispersion\(^{8,10}\). In a recent experiment\(^{2}\), the strongly coupled plasmon-phonon mode dispersion has been measured by the angle-resolved reflection electron-energy-loss spectroscopy and it is found that the discrepancy arises from electron-phonon coupling. In epitaxial graphene the substrate (i.e. SiC) is a highly polar material. In general, carriers in polar materials couple with the longitudinal optical (LO) phonons of the system via the long-range Fröhlich interaction. However, the surface optical (SO) phonon is a well-characterized surface property of polar semiconductors, and it is possible that carriers in graphene layer couple to the SO-phonons of the underlying substrate lattice via the long-range polar Fröhlich coupling\(^{14,15}\). For isotropic media the frequency of SO phonons \( \omega_{SO} \) is related to the transverse optical (TO) bulk phonon \( \omega_{TO} \) as \( \omega_{SO}/\omega_{TO} = \sqrt{(\epsilon_0 + 1)/(\epsilon_{\infty} + 1)} \) where \( \epsilon_0 \) (\( \epsilon_{\infty} \)) is the static (high frequency) dielectric constant. Note that the bulk longitudinal optical phonons \( \omega_{LO} \) and \( \omega_{TO} \) are connected with the dielectric constants by the Lyddane-Sachs-Teller relation \( \omega_{LO}/\omega_{TO} = \sqrt{\epsilon_0/\epsilon_{\infty}} \).

The electron-phonon coupling is the macroscopic coupling of the electronic collective modes (plasmons) to the optical phonons. The mode coupling phenomenon, which hybridizes the collective plasmon modes of the electron gas with the optical-phonon modes of the lattice, gives rise to the coupled plasmon-phonon modes (the hybrid modes) which have been extensively studied\(^{12,22}\) both experimentally and theoretically in bulk and 2D electron systems. The electron-phonon interaction leads to many-body renormalization of the single-particle free carrier properties\(^{21,22}\) and also affects the transport properties\(^{23,24}\). A good understanding of electron-phonon coupling is thus important in developing quantitative theories for many different experimental studies in graphene.

In this paper we calculate the coupled plasmon-SO phonon modes of epitaxial graphene (or graphene on a polar substrate such as SiO\(_2\), SiC, or HfO\(_2\)). Our most significant finding is that in MLG plasmon-phonon mode coupling effect is strong at all electronic densities due to the singular behavior in the screening function arising from chirality\(^{4}\). By contrast, for BLG, the plasmon-phonon coupling is significant only at high carrier densities. We also find that at low densities, when the coupling is weak and the coupled phonon-like mode (gapped mode) lies in the interband electron-hole continuum, the energy of phonon-like mode decreases in the long wavelength limit due to the coupling of the phonon mode to the interband single particle excitation, which arises from the enhanced BLG backscattering\(^{25}\). However, at high densities, when the plasmon-phonon mode coupling is strong, the phonon-like mode frequency increases linearly.
with wavevector, as in MLG.

We first present our model for plasmon-phonon coupling, which consists of a two-dimensional electron gas coupled to dispersionless SO-phonons at zero temperature. For MLG, we have a system of Dirac fermions with linear dispersion, while BLG have a parabolic dispersion around the Dirac point. Due to the presence of the long range electron-phonon coupling, electrons interact among themselves through the Coulomb interaction and through virtual SO-phonon exchange via the Fröhlich interaction.

The electron-phonon interaction is given by

\[ H_{\text{e-ph}} = \sum_{kq} \sum_{ss'} M_{skq}^{ss'} c_{k+q+ss'}^\dagger c_{ks} (b_q + b_q^\dagger), \]

where \( c_{ks}^\dagger \) is the electron \( (s = +1) \) or hole \( (s = -1) \) creation operator, and \( b_q \) and \( b_q^\dagger \) are creation and destruction operators of surface phonon, and the interaction matrix element \( M_{skq}^{ss'} \) is defined by

\[ M_{skq}^{ss'} = M_0(q) F_{sk+q}^\dagger F_{s'k}, \]

where \( F_{sk} \) is the chiral spinor and given by \( F_{sk}^\dagger = (s, e^{-i\theta_k})/\sqrt{2} \) with \( s = \pm 1, \theta_k = \tan^{-1}(k_y/k_x) \) for MLG, and \( \theta_k = 2\tan^{-1}(k_y/k_x) \) for BLG. We also have

\[ [M_0(q)]^2 = \frac{2\pi e^2}{q} \frac{e^{-2qd\omega SO}}{2} \frac{1}{\epsilon_{\infty} + 1} \frac{1}{\epsilon_0 + 1}, \]

where \( d \) is the separation distance between graphene layer and substrate. Then the matrix element of SO-phonon mediated electron-electron interaction is dependent on both wave vector and frequency and give by

\[ v_{ph}(q, \omega) = [M_0(q)]^2 D_0(\omega), \]

where the unperturbed SO-phonon propagator is given by \( D_0(\omega) = 2\omega_{SO}/(\omega^2 - \omega_{SO}^2) \).

The total effective electron-electron interaction is obtained in RPA20 by summing all the bare bubble diagrams (see Fig. 1),

\[ v_{\text{eff}}(q, \omega) = \frac{v_c(q) + v_{ph}(q, \omega)}{1 - [v_c(q) + v_{ph}(q, \omega)] \Pi_0(q, \omega)} = \frac{v_c(q)}{\epsilon_\infty(q, \omega)}, \]

where \( v_c(q) = 2\pi e^2/\epsilon_\infty q \) is the electron-electron Coulomb interaction and \( \Pi_0(q, \omega) \) is the complex irreducible polarizability of either the monolayer or the bilayer system22 given by the bare bubble diagram. The total dielectric function within RPA contains contributions both from electrons and SO-phonons:

\[ \epsilon_\infty(q, \omega) = 1 + \frac{\epsilon_\infty q}{2} \frac{1}{\epsilon_{\infty} + 1} - \frac{1}{\epsilon_0 + 1}, \]

The collective mode dispersion is given by the zeros of the complex total dielectric function: \( \epsilon_\infty(q, \omega) = 0 \). Let us first focus on the collective modes of MLG. In the long wavelength limit \( (q \rightarrow 0) \) we get the following coupled \( \omega_\pm \) collective modes

\[ \omega_+(q) = \omega_{SO} + \frac{\alpha e^{-2qd} \omega_{SO}^2}{\omega_{SO}} \frac{1}{2}, \]

where \( \omega_{SO}^2 = 2e^2E_Fq/\epsilon_{\infty} \) \( (E_F = \text{Fermi energy}) \) is the plasmon mode dispersion of an uncoupled system in the long wavelength limit. As \( q \rightarrow 0 \) the phonon-like mode \( \omega_+ \) is located above \( \omega_{SO} \) and increases linearly, and the plasmon-like \( \omega_- \) is slightly less than the corresponding uncoupled monolayer graphene plasmon mode, \( \omega_q \).

In Fig. 2 we show the calculated coupled plasmon-phonon collective modes in MLG for two different densities. The following parameters are used throughout this paper: \( \omega_{TO} = 95.0 \text{ meV}, \omega_{SO} = 116.7 \text{ meV}, \epsilon_{\infty} = 6.4, \epsilon_0 = 10.0, \) and \( d = 5\text{Å} \). As shown in Fig. 2 the mode coupling in MLG is strong for all electron densities. In ordinary 2D systems or 3D systems the plasmon-phonon mode coupling is only significant at densities satisfying the resonant condition \( \omega_q \approx \omega_{SO} \). However, in MLG the plasmon mode exists for all wave vectors due to the singular behavior in the polarizability, which leads to strong plasmon-phonon coupling. Since the singular behavior of the polarizability arise from the suppression of the
The spectral weight of \( \omega \) carried by the phonon-like mode. In Fig. 3 the calculated function (loss function) and given by
tional to the imaginary part of the inverse dielectric func-
ction (loss function) and (b) \( n = 10^{12} \text{ cm}^{-2} \). Note that
the \( \omega_n \) mode of the high density result carries most spectral
weight and its dispersion is almost linear, which is observed in
the recent experiments. We use a phenomenological damping of 0.1\( E_F \) in these results.

back scattering due to the chirality of MLG the strong plasmon-phonon coupling is a direct consequence of its unique chiral property of MLG. Note that the plasmon-
like mode \( \omega_- \) in Fig. 2 vanishes at a finite critical wave
vector, \( q_c \simeq \omega_{SO}(1 - \alpha)/v_F \), and for \( q > q_c \) we find only
the phonon-like mode (\( \omega_+ \)) which approaches \( \omega_q \) for large \( q \).

The dynamical structure factor, \( S(q, \omega) \), which gives the spectral weight of the collective modes, is propor-
tional to the imaginary part of the inverse dielectric func-
tion (loss function) and given by

\[
S(q, \omega) = -\frac{1}{n_0 v_c(q)} \text{Im} \left[ \frac{1}{\epsilon(q, \omega)} \right]. \tag{9}
\]

For a true collective mode with zero Landau damping both Im[\( \epsilon(q, \omega) \)] and Re[\( \epsilon(q, \omega) \)] vanish, and the inverse
dielectric function becomes a delta function with weight

\[
W(q) = \frac{\pi}{n_0 v_c(q) \text{Re} \epsilon(q, \omega)_{\omega=\omega(q)}} \tag{10}
\]

where \( \epsilon(q) \) is the collective mode frequency at wave vec-
tor \( q \). In the long wavelength limit the weight of plasmon-
like mode can be calculated as

\[
W(q)|_{\omega_-} = \frac{\pi}{2} (1 - \alpha)^{3/2} \omega_q \tag{11}
\]

and the weight of phonon-like mode as

\[
W(q)|_{\omega_+} = \pi a \omega_{SO}/2. \tag{12}
\]

The spectral weight of \( \omega_- \) mode vanishes as \( \sqrt{q} \) in the
long wavelength limit, but the weight of \( \omega_+ \) mode is finite. Thus in the long wavelength limit all spectral weight is carried by the phonon-like mode. In Fig. 3 the calculated loss function \(-\text{Im}[1/\epsilon(q, \omega)]\) is shown in \((q, \omega)\) space for two different densities (a) \( n = 10^{13} \text{ cm}^{-2} \) and (b) \( n = 10^{12} \text{ cm}^{-2} \). In the long wavelength limit the phonon-like mode has most of the weight. In the intermediate wave

vector range, however, the plasmon-like mode becomes

stronger. The weight of the \( \omega_- \) mode vanishes again
when the plasmon-like mode merges with the electron-
hole continuum at a critical wave vector and \( \omega_- \) mode
becomes overdamped by Landau damping.

Let us now turn our attention to BLG. Just like MLG, we
again get two hybridized plasmon-phonon modes, one
\((\omega_-)\) having a \( \sim \sqrt{q} \) dispersion and the other \((\omega_+)\) ex-
hibiting a gap equal to the SO phonon frequency \( \omega_{SO} \)
in the long wavelength limit. The \( \omega_- \) mode has the same
dispersion as in MLG, \( \omega_-(q) = (1 - \alpha e^{-2qd})\omega_q \), which lies in the gap between the intraband and interband continua and has a spectral weight which goes as \( \sim \sqrt{q} \). Thus, in the long wavelength limit, all the oscillator strength lies in the gapped mode \( \omega_+ \).

However, there are two main differences from MLG, i.e.,
the quadratic energy dispersion and the enhanced
backscattering due to chirality in BLG\(^{22}\), which lead to non-trivial differences in the collective mode spectrum. These two effects lead to very different behaviour in the low and high density limits. To illustrate these effects, we plot the collective mode spectrum of bilayer graphene at two different densities, (a) \( n = 10^{13} \text{ cm}^{-2} \) (high density, \( E_F > \omega_{SO} \)) and (b) \( n = 10^{12} \text{ cm}^{-2} \) (low density, \( E_F < \omega_{SO} \)) in Fig. 4. Here, \( \omega_q \) is the uncoupled plasmon frequency
and the shaded regions represent the intraband and interband particle-hole continuum. The correspond-
ing loss functions are plotted in Fig. 5.

In the high density limit where \( w_q \sim \omega_{SO} \), there is a
strong plasmon-phonon coupling as evidenced by the deviations of \( \omega_- \) from \( \omega_{SO} \) and of \( \omega_+ \) from \( \omega_q \), which gives rise to the gapped mode \( \omega_+ \) having a linear dispersion with a positive slope in the low \( q \) limit. At larger \( q \) values, it approaches the uncoupled plasmon dispersion, as seen
in Fig. 5(a). The \( \omega_- \) mode merges into the continuum
at a critical wavevector \( q_c \), which is much smaller than
that of the uncoupled mode indicating strong electron-phonon coupling. Furthermore, as seen from Fig. 5(a), the phonon-like mode \( \omega_+ \) carries a much larger spectral

![FIG. 3. The density plots of energy loss function (−Im[1/\epsilon(q, \omega)]) of MLG in (q, \omega) space for two different densities (a) n = 10^{13} \text{ cm}^{-2} and (b) n = 10^{12} \text{ cm}^{-2}. Note that the \( \omega_n \) mode of the high density result carries most spectral weight and its dispersion is almost linear, which is observed in the recent experiments. We use a phenomenological damping of 0.1\( E_F \) in these results.](image)

![FIG. 4. Calculated plasmon-phonon coupled mode \( \omega_{\pm} \) dispersions in bilayer graphene as a function of the wave vector \( q \) for two different densities (a) \( n = 10^{13} \text{ cm}^{-2} \) and (b) \( n = 10^{12} \text{ cm}^{-2} \). The plasmon dispersion \( \omega_+ \) without the electron-phonon coupling is shown by the dashed line. The dotted horizontal line represent the frequency of the uncoupled SO phonon mode.](image)
SO phonon mode is pushed into the interband electron-hole continuum, the coupled $\omega_+$ mode is always Landau-damped due to the presence of the interband continuum and carries little spectral weight beyond a very small range of low $q$ values. The deviation of the plasmon-like mode $\omega_-$ from the uncoupled dispersion is much smaller than in the high density limit, further showing that the plasmon-phonon coupling is weak in this limit. From Fig. 5(b), we find that beyond a small range of low $q$ values, the plasmon-like mode carries much more spectral weight than the phonon-like mode and hence, at low densities, the plasmon mode should be easier to detect in BLG.

In summary, we have calculated the dispersion and the spectral weight of the coupled plasmon-phonon mode of 2D graphene. We find that the mode-coupling effect is strong in monolayer graphene at all densities in contrast to the corresponding bilayer graphene, where the coupling is only significant at high densities. Since the carriers in graphene are strongly coupled to the surface optical phone of a polar substrate it is important to understand the many-body renormalization of the single-particle properties and the transport properties in the presence of electron-SO phonon coupling.

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FIG. 5. The density plots of energy loss function $(-\text{Im} [1/e(q, \omega)])$ of bilayer graphene in $(q, \omega)$ space for two different densities (a) $n = 10^{13}$cm$^{-2}$ and (b) $n = 10^{12}$cm$^{-2}$.