Electron-phonon coupling and electron self-energy in electron-doped graphene: calculation of angular resolved photoemission spectra.

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We obtain analytical expressions for the electron self-energy and the electron-phonon coupling in electron-doped graphene using electron-phonon matrix elements extracted from density functional theory simulations. From the electron self-energies we calculate angle resolved photoemission spectra. We demonstrate that the measured jump at $\approx -0.2$ eV from the Fermi level is actually composed of two features, one at $\approx -0.195$ eV due to the twofold degenerate $E_{2g}$ mode, and a second one at $\approx -0.16$ eV due to the $A_1$ mode. The electron-phonon coupling extracted from the kink observed in ARPES experiments is roughly a factor of 5.5 larger than the calculated one. This disagreement can only be partially reconciled by the inclusion of resolution effects. Indeed we show that a finite resolution increases the apparent electron-phonon coupling by underestimating the renormalization of the electron velocity at energies larger than the kinks positions. The discrepancy between theory and experiments is thus reduced to a factor of $\approx 2.2$. From the linewidth of the calculated ARPES spectra we obtain the electron relaxation time. A comparison with available experimental data in graphene shows that the electron relaxation time detected in ARPES is almost two orders of magnitudes smaller than what measured by other experimental techniques.

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Despite the fact that the band structure of graphene is calculated in many solid-state textbooks\cite{1,2}, its experimental verification has been provided only recently by Angular Resolvent Photoemission (ARPES) measurements on a graphene monolayer deposited on a SiC substrate.\cite{3,4,5,6}. The experiments show that the peculiar features of the electronic structure predicted theoretically are qualitatively confirmed by experiments: the carbon $\pi$-bands (i) cross at the K-point in the Brillouin-zone (Dirac point) and (ii) depart linearly with a slope $v_F$ from the Dirac point. (iii) the Fermi velocity extracted from experiments\cite{3,5} is slightly larger (10-20\%) than that calculated theoretically using density functional theory (DFT).

Beside this encouraging agreement between theory and experience, recent angular photoemission (ARPES) experiments\cite{3,6} performed on graphene revealed remarkable surprises. Two kinks are seen in the ARPES dispersion: the first one is at energies of 0.2 eV below the Fermi level ($\epsilon_f$) and its energy position respect to $\epsilon_f$ is unchanged as a function of the doping level while the second one is closer to the Dirac point and its energy position respect to $\epsilon_f$ decreases rapidly as the doping level is increased (see Fig. 2 in Ref. \cite{6}). The first kink has been attributed to a phonon feature\cite{6}, while the second kink has been interpreted as due to a plasmon\cite{6,7}. In what follows we focus on the first kink.

The ARPES momentum distribution curves (MDCs) associated to the -0.2 eV kink display a puzzling behavior as a function of doping. Indeed it is observed that the magnitude of the jump associated to the MDC-linewidth in the $-0.5 eV < \epsilon - \epsilon_f < 0$ eV energy window decreases as a function of doping (see Fig. 3 in Ref. \cite{6}, where from top to bottom the jump increases). This is surpris-
In these definitions, \( \lambda \) is a small positive quantity. For \( \epsilon = \epsilon_f \), since we assume that the Fermi level is not too far from the Dirac point so that the \( \pi \) bands are linear, \( |k - K| \) or \( |k - K'| \) is a small but finite vector and \( \mathcal{F}_k(\epsilon_f) \cap \mathcal{F}_{k'}(\epsilon_f) \) is empty. The boundary of each region of space at \( \eta = 0 \) (circumference) is indicated as \( \partial \mathcal{F}_k(\epsilon_f) \) and \( \partial \mathcal{F}_{k'}(\epsilon_f) \).

In Eq. [2] the two \( \delta \)-functions restrict the \( k \) integrations to the region of space satisfying the conditions \( \epsilon_k = \epsilon_f \) and \( \epsilon_{k+q} = \epsilon_f \). The set of \( k \) points such that \( \epsilon_k = \epsilon_f \) is composed by the set \( \partial \mathcal{F}_k(\epsilon_f) \cup \partial \mathcal{F}_{k'}(\epsilon_f) \). Thus in the integral in Eq. [2] two cases are given (labeling \( k = k + q \)):

(i) \( k, k' \) \( \in \partial \mathcal{F}_k(\epsilon_f) \) or \( k, k' \) \( \in \partial \mathcal{F}_{k'}(\epsilon_f) \),

(ii) \( k \in \partial \mathcal{F}_k(\epsilon_f) \) , \( k' \in \partial \mathcal{F}_{k'}(\epsilon_f) \) or vice versa.

In case (i) scattering occurs at \( q = \Gamma + \tilde{q} \), with small \( \tilde{q} \), and \( \pi \) bands can only couple to the twofold degenerate \( E_{2g} \) phonon mode. In case (ii) scattering occurs at \( q = K + \tilde{k} \) or at \( q = K' + \tilde{k} \), with small \( \tilde{k} \) and \( \pi \) bands can only couple to the \( A_1 \) phonon mode [11]. The electron-phonon matrix elements involved in the two scattering processes have been fitted to \textit{ab initio} data in Ref. [11] and are:

\[
\begin{align*}
|g_{E_{2g}}(K+k\pi^*,K+q\pi^*)|^2 &= \langle \phi^2 | 1 \pm \cos(\theta_{k,\tilde{q}} + \theta_{k,K+\tilde{q}}) \rangle |^5 \quad (5) \\
|g_{E_{2g}}(K+k\pi^*,K+q\pi^*)|^2 &= \langle \phi^2 | 1 + \cos(\theta_{K+k\tilde{q}}) \rangle |^6 \quad (6)
\end{align*}
\]

In Eq. [5] the \( \pm \) sign refers to the LO/TO \( E_{2g} \) modes respectively, \( \langle \phi^2 \rangle = 0.0405 \text{eV}^2 \) and \( \langle \phi^2 \rangle = 0.0994 \text{eV}^2 \), and \( \theta_{K+k\tilde{q}} \) is the minimal angle between the two vectors \( u, v \).

For case (i) one has

\[
\lambda_{\tilde{q}E_{2g}} = \frac{2 \times 2 \times 2 \langle \phi^2 \rangle F}{\hbar \omega_{\tilde{q}E_{2g}} N_\sigma(\epsilon_f)} \int \frac{d^2 \tilde{k}}{\Omega} \times
\delta(\epsilon_{K+k} - \epsilon_f) \delta(\epsilon_{K+k+\tilde{q}} - \epsilon_f) =
\frac{8 \langle \phi^2 \rangle F}{\hbar \omega_{\tilde{q}E_{2g}} N_\sigma(\epsilon_f)} I_{\tilde{q}} \quad (7)
\]

where

\[
\mathcal{F}_\Gamma(\epsilon) = \{ |\tilde{k}| |\beta| < \epsilon + \eta \}. \quad (8)
\]

The 8 prefactor is the results of having 2 \( E_{2g} \) modes and of having an identical integral over the second Fermi surface sheet at \( K' \). The integral \( I_{\tilde{q}} \) is the so-called nesting factor, defined as:

\[
I_{\tilde{q}} = \int_{\mathcal{F}_\Gamma(\epsilon_f)} \frac{d^2 \tilde{k}}{\Omega} \delta(\epsilon_{K+k} - \epsilon_f) \delta(\epsilon_{K+k+\tilde{q}} - \epsilon_f) \quad (9)
\]

The electron-phonon coupling due to \( E_{2g} \) modes is given by

\[
\lambda_{\Gamma}(\epsilon_f) = N(\epsilon_f) \int_{\mathcal{F}_\Gamma(2\epsilon_f)} \frac{d^2 \tilde{q}}{\Omega} \lambda_{\tilde{q}E_{2g}} = \frac{2N(\epsilon_f) \langle \phi^2 \rangle F}{\hbar \omega_{\Gamma E_{2g}}} \quad (10)
\]

where we have used that

\[
\int_{\mathcal{F}_\Gamma(2\epsilon_f)} \frac{d^2 \tilde{q}}{\Omega} I_{\tilde{q}} = N_\sigma^2(\epsilon_f)/4 \quad (11)
\]

and we have replaced the \( E_{2g} \) phonon frequency with its value at \( \Gamma \).

Similarly, case (ii) leads to

\[
\lambda_{K+qA_1'} = \frac{2 \times 2 \times 2 \langle \phi^2 \rangle F}{\hbar \omega_{K+qA_1'} N_\sigma(\epsilon_f)} \int_{\mathcal{F}_\Gamma(\epsilon_f)} \frac{d^2 \tilde{k}}{\Omega} \times \[1 - \cos(\theta_{K,k+\tilde{q}})] \times
\delta(\epsilon_{K'+k} - \epsilon_f) \delta(\epsilon_{K+k+\tilde{q}} - \epsilon_f) =
\frac{4 \langle \phi^2 \rangle F}{\hbar \omega_{K+qA_1'} N_\sigma(\epsilon_f)} J_{K+\tilde{q}} \quad (12)
\]

and the additional factor of 2 is a result of having scattering from \( \mathcal{F}_\Gamma(\epsilon_f) \) to \( \mathcal{F}_{k'}(\epsilon_f) \) and vice versa. The quantity

\[
J_{K+\tilde{q}} = \int_{\mathcal{F}_\Gamma(\epsilon_f)} \frac{d^2 \tilde{k}}{\Omega} \times \[1 - \cos(\theta_{K,k+\tilde{q}})] \times
\delta(\epsilon_{K'+k} - \epsilon_f) \delta(\epsilon_{K+k+\tilde{q}} - \epsilon_f) \quad (13)
\]
\[ \Sigma(\mathbf{k}, \omega) = \] FIG. 1: Lowest order contribution to the electron self-energy due to the electron-phonon interaction. The dotted (continuous) line represents the phonon (electron) self-energy.

and its integral over the momentum \( \mathbf{q} \) are evaluated in sec. VII A so that the contribution of the \( A_1 \) mode to the electron-phonon coupling is:

\[ \lambda_{\mathbf{k}}(\epsilon_f) = \int_{F \mathbf{k}(2\pi f)} \frac{d^2 \mathbf{q}}{\Omega} \lambda_{\mathbf{k}+\mathbf{q}A_1'} = \frac{(g_{2\mathbf{k}}^2)_{\epsilon}N_{\sigma}(\epsilon_f)}{\hbar \omega_{\mathbf{k}A_1'}} \] (14)

where we have approximated \( \omega_{\mathbf{k}+\mathbf{q}A_1'} \approx \omega_{\mathbf{k}A_1'} \).

The total electron phonon coupling is thus:

\[ \lambda(\epsilon_f) = N_{\sigma}(\epsilon_f) \left[ \frac{2(\gamma_{2\mathbf{k}}^2)_{\epsilon}}{\hbar \omega_{E_{2g}}} + \frac{(\gamma_{2\mathbf{k}}^2)_{\epsilon}}{\hbar \omega_{\mathbf{k}A_1'}} \right] \] (15)

which is eq. 1 in ref. [10].

II. ELECTRON SELF-ENERGY AND ANGLE RESOLVED PHOTOEMISSION

The lowest contribution to the retarded electron self-energy due to coupling of \( \pi^* \) electrons to a phonon mode \( \nu \) is illustrated in Fig. 1. At zero temperature direct calculation [12] of the diagram gives:

\[ \Sigma_{\nu}(\mathbf{k}, \epsilon) = \sum_{\alpha\{\pm,1\}} \int_{BZ} \frac{d^2 \mathbf{q}}{\Omega} |g_{\mathbf{k},\mathbf{q}A_{1'}}|^2 \times \frac{\Theta(\alpha \epsilon_f - \alpha \epsilon_{\mathbf{k}+\mathbf{q}})}{\epsilon + i \delta - \epsilon_{\mathbf{k}+\mathbf{q}} + \alpha \hbar \omega_{\mathbf{q}A_{1'}}} \] (16)

where \( \Theta(x) \) is the Heaviside function. The imaginary part of eq. 16 is

\[ \Sigma'_{\nu}(\mathbf{k}, \epsilon) = -\pi \sum_{\alpha\{\pm,1\}} \int_{BZ} \frac{d^2 \mathbf{q}}{\Omega} |g_{\mathbf{k},\mathbf{q}A_{1'}}|^2 \times \Theta(\alpha \epsilon_f - \alpha \epsilon_{\mathbf{k}+\mathbf{q}}) \delta(\epsilon - \epsilon_{\mathbf{k}+\mathbf{q}} + \alpha \hbar \omega_{\mathbf{q}A_{1'}}) = \]

\[ = -\pi \sum_{\alpha\{\pm,1\}} \Theta(\alpha \epsilon_f - \alpha \epsilon - \hbar \omega_{\mathbf{q}A_{1'}}) \times \int_{BZ} \frac{d^2 \mathbf{k}}{\Omega} |g_{\mathbf{q},\mathbf{k}A_{1'}}|^2 \delta(\epsilon - \epsilon_{\mathbf{k}+\mathbf{q}} + \alpha \hbar \omega_{\mathbf{q}A_{1'}}) \] (17)

In angular resolved photoemission (ARPES) experiments the graphene is electron-doped, so the Fermi level is larger than the Dirac point but it is still in the region where \( \epsilon_{\mathbf{k}} \) can be considered linear. For a given mode \( \nu \) and a given value of \( \alpha \), the \( \delta \)-function in eq. 17 restricts the BZ integration to two regions, close to \( \mathbf{K} \) and to \( \mathbf{K}' \). The restriction to these regions of k-space and the fact that we are interested in the region of energy-momentum close to the Dirac point, namely \( \mathbf{k} = \mathbf{K} + \mathbf{q} \) with \( \mathbf{q} \) small, restricts furthermore the integration region. Indeed it implies that for small \( \mathbf{q} \): (i) \( \mathbf{q} = \mathbf{q} \) and (ii) \( \mathbf{q} = \mathbf{K} + \mathbf{q} \). Case (i) represents scattering to phonons close to the \( \Gamma \) point while (ii) to phonons close to the \( \mathbf{K} \) point. So the situation is similar to the previous electron-phonon calculation.

The total self-energy, \( \Sigma'' = \sum_{\nu \{E_{2g}A_1\}} \Sigma''_{\nu} \), due to the two \( E_{2g} \) phonon modes at \( \Gamma \) and to the \( A_1 \) phonon mode at \( \mathbf{K} \) is obtained substituting Eqs. 4 and 6 in Eq. 17 assuming a constant phonon dispersion around \( \Gamma \) and \( \mathbf{K} \) and performing the integration over the BZ, as

\[ \Sigma''(\mathbf{k}, \epsilon) = -\frac{\pi}{2} \sum_{\alpha\{\pm,1\}} \left[ \hbar \omega_{E_{2g}} \lambda_{\mathbf{F}}(\epsilon - \alpha \hbar \omega_{E_{2g}}) \times \Theta(\alpha \epsilon_f - \alpha \epsilon - \hbar \omega_{E_{2g}}) + \hbar \omega_{\mathbf{K}A_1} \lambda_{\mathbf{K}}(\epsilon - \alpha \hbar \omega_{\mathbf{K}A_1}) \times \Theta(\alpha \epsilon_f - \alpha \epsilon - \hbar \omega_{\mathbf{K}A_1}) \right] \] (18)

where \( \lambda_{\mathbf{F}}(\epsilon - \hbar \omega_{E_{2g}}) \) and \( \lambda_{\mathbf{K}}(\epsilon - \hbar \omega_{\mathbf{K}A_1}) \) are defined in Eq. 10 and in Eq. 13 respectively. From Eq. 18 we note that for small \( \mathbf{k} \) the imaginary part of the phonon self-energy is momentum-independent, so in what follows we drop the \( \mathbf{k} \)-label. Using numerical values of \( \hbar \omega_{E_{2g}} = 0.195eV \) and \( \hbar \omega_{\mathbf{K}A_1} = 0.16eV \), the \( \Sigma''(\epsilon) \) is illustrated in Fig. 2 (black lines).

The imaginary part in eq. 18 has to be compared with the square well model which is obtained from Eq. 18...
assuming a constant density of states. This is the commonly used approximation to interpret ARPES spectra \[13, 14\]. The square well model is illustrated in fig. 2 (red-dashed). In graphene this approximation is in principle not allowed due to the behavior of the density of states proportional to $|\epsilon|$ (see eq. 1). The difference between the two models becomes relevant for energies smaller than or closer to the Dirac point.

The real part of the electron self-energy can be obtained using the Kramers-Kronig relations, namely:

$$\Sigma' (\epsilon) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Sigma'' (\epsilon')}{\epsilon' - \epsilon} \, d\epsilon$$

(19)

If the self-energy in Eq. 18 is used then $\Sigma' (\epsilon)$ diverges at large $|\epsilon|$ due to the $|\epsilon|$ dependence of the density of states. However this divergence is unphysical since in real graphene the linearity of the $\pi^+$ bands and the consequent behavior of the density of states is only up to energies of $\approx 1.5$ eV from the Dirac point. Thus for large $|\epsilon|$ the imaginary part of the phonon self-energy should be regularized. We adopted the following regularization:

$$\Sigma''_{\text{Reg}} (\epsilon) = \begin{cases} \Sigma'' (\epsilon) & \text{if } |\epsilon| < \epsilon_M \\ \frac{1}{\epsilon} \times \frac{\epsilon}{\epsilon - \epsilon_M} & \text{if } \epsilon_M < |\epsilon| \end{cases}$$

(20)

With this assumption, the calculation of the integral in eq. 19 leads to:

$$\Sigma' (\epsilon) = -N_\sigma (\epsilon_f) (g_0^2) \left\{ (\epsilon + \hbar \omega_{E2g}) \left[ -2 \log |\epsilon + \hbar \omega_{E2g}| + \log \left| (\epsilon_M + \epsilon) (\epsilon_f - \hbar \omega_{E2g}) \right| + \left( \epsilon - \hbar \omega_{E2g} \right) \log \left| \frac{\epsilon_M - \epsilon}{\epsilon_f - \hbar \omega_{E2g}} \right| \right] + \frac{N_\sigma (\epsilon_f) (g_0^2)}{2} \left\{ (\epsilon + \hbar \omega_{A1'}) \left[ -2 \log |\epsilon + \hbar \omega_{A1'}| + \log \left| (\epsilon_M + \epsilon) (\epsilon_f - \hbar \omega_{A1'}) \right| + \left( \epsilon - \hbar \omega_{A1'} \right) \log \left| \frac{\epsilon_M - \epsilon}{\epsilon_f - \hbar \omega_{A1'}} \right| \right] + \frac{N_\sigma (\epsilon_f)}{2} \left\{ (\epsilon - \hbar \omega_{E2g}) \left[ -2 \log |\epsilon - \hbar \omega_{E2g}| + \log \left| (\epsilon_M - \epsilon) (\epsilon_f + \hbar \omega_{E2g}) \right| + \left( \epsilon - \hbar \omega_{E2g} \right) \log \left| \frac{\epsilon_M - \epsilon}{\epsilon_f + \hbar \omega_{E2g}} \right| \right] + \frac{N_\sigma (\epsilon_f)}{2} \left\{ (\epsilon - \hbar \omega_{A1'}) \left[ -2 \log |\epsilon - \hbar \omega_{A1'}| + \log \left| (\epsilon_M - \epsilon) (\epsilon_f + \hbar \omega_{A1'}) \right| + \left( \epsilon - \hbar \omega_{A1'} \right) \log \left| \frac{\epsilon_M - \epsilon}{\epsilon_f + \hbar \omega_{A1'}} \right| \right] \right\} \times \left[ \frac{\epsilon_M + \epsilon}{\epsilon_M - \epsilon} \right] \right\}$$

(21)

In practical calculations we choose $\epsilon_M = 1.5$ eV.

The real part of the electron self-energy is illustrated in Fig. 2 and is compared with the real part obtained from the Kramers-Kronig transformation of $\Sigma^\prime (\omega)$ with a constant density of states.

In ARPES experiment the spectral weight is measured, namely

$$A(k, \epsilon) = \frac{-2[\Sigma'' (\epsilon) + \eta]}{[\epsilon - \epsilon_k - \Sigma' (\epsilon)]^2 + [\Sigma'' (\epsilon) + \eta]^2}$$

(22)

where we allowed for a small constant imaginary part $\eta$ to eliminate numerical instabilities. Typically $\eta = 10^{-4}$ eV

### III. RESULTS

In this section we consider a Fermi level of $\epsilon_f = 0.4$ eV measured from the Dirac point. Neglecting resolution effects, the spectral function (Eq. 22) is shown in figure 8 (left). The scans presented are fixed photoelectron energy scans (the energy value is given on the left of Fig. 3 (left) ) while the photoelectron momentum is varied (MDC scans). In the MDC scans two kinks are present (compare scans g and h for the first kink and scans e and d for the second), both in the spectral-weight maximum-position and linewidth.

The behavior of the MDC-maximum-position as a function of energy and momentum is illustrated in fig. 4. Notice that, in absence of resolution effects, the linewidth is equal to $-\beta \Delta \epsilon'' (\epsilon)$. The behavior of the linewidth is compared with that of square well model typically used to interpret ARPES data. The differences are negligible at energies larger than -0.2 eV, but they are significative at lower energies and in particular at the Dirac point.

To test the robustness of the phonon features against experimental resolution we introduce the following convoluted spectral weight:

$$A_{\text{exp}} (k, \epsilon) = f (\epsilon) \int_{-\infty}^{\epsilon} \int d^3k' \left[ \frac{1}{\exp[(\epsilon - \epsilon_f)/k_B T] + 1} \right]$$

(23)

This form of the experimental resolution assumes to have decoupled momentum and energy resolutions.

We chose $\eta_e = 25$ meV and $\eta_k = 0.1 \AA^{-1}$, as in recent ARPES experiments \[4, 6\]. The maximum position in $A_{\text{exp}} (k, \epsilon)$ is plotted in Fig. 5.

As it can be seen the experimental resolution substantially smears out the two kinks so that a very weak kink is visible at -0.2 eV while the second one is almost invisible. The kink is substantially smaller than what detected in experiments \[6\]. The mass enhancement parameter is defined as \[12, 13\]:

$$\lambda = \frac{\partial \Sigma' (\epsilon)}{\partial \epsilon} \bigg|_{\epsilon = \epsilon_f}$$

(25)
Linearizing $\Sigma'(\epsilon) \approx -\lambda \epsilon$, the spectral-weight becomes (for $\eta = 0$):

$$A(k, \epsilon) \approx -\frac{2\Sigma''(\epsilon)Z^2}{[\epsilon - Z\epsilon_k]^2 + [\Sigma''(\epsilon)Z]^2}$$

(26)

where

$$Z = \frac{1}{1 + \lambda}$$

(27)

is the quasiparticle weight. From Eq. 26 one sees that the quasiparticle state has quasiparticle energy $Z\epsilon_k$ and linewidth $\Sigma'(\epsilon)Z/2$. In graphene the bands are linear, with $\epsilon_k = \beta k$, so that the maximum position in the spectral weight at energies higher than the kink is given by the relation

$$\epsilon_{\text{max}}^k = \frac{\beta k}{1 + \lambda}$$

(28)

Assuming linear renormalized bands, $\epsilon_k = \beta_{\text{ph}}k$, for energies larger than the kink then the following expression for $\lambda$ is obtained:

$$\lambda = \frac{\beta}{\beta_{\text{ph}}} - 1$$

(29)

Typically $\beta$ is obtained from a linear fit to maximum position in MDC curves at energies below the kink (in our case $\beta = 5.52eV\text{A}$ within DFT), while $\beta_{\text{ph}}$ is obtained from a linear fit at energies higher than the kink but enough below $\epsilon_f$ so that the effects of the Fermi function in eq. 23 are absent.

When a finite resolution is used, the result is substantially affected. Indeed, we find that a linear fit in the energy window from $-0.195\text{eV} < \epsilon - \epsilon_f < -0.04\text{eV}$ leads to values of the electron-phonon coupling which are a factor 2.5 than Eq. 15 as shown in Fig. 6. A similar fitting procedure is used in experiments (note that in experiments only the kink due to the $E_{2g}$ phonon is visible). A comparison with available experimental data (see fig. 5 in Ref. 9) is shown in fig. 6. A clear disagreement between theory and experiments is still present, even if it is reduced by resolution effects.

For this reason, we believe, the determination of $\lambda$ using Eq. 29 is affected by a large error. The error is due to the difficulties in the determination of $\beta_{\text{ph}}$ generated by the non-linearity in $\Sigma'(\epsilon)$ near the kink. The non-linearity, when convoluted with a finite resolutions, results in a quasi-linear behavior with an “apparent” enhanced electron-phonon coupling.

### IV. ELECTRON RELAXATION TIMES IN GRAPHITE AND GRAPHENE

#### A. Electron-doped graphene

It is interesting to compare the ARPES-measured self-energy imaginary part with what detected by alternative experimental techniques. In electron-doped graphene the
The electron relaxation time has been determined experimentally by conductivity/mobility data \cite{16} and by angular resolved photoemission measurements \cite{6}. The mobility measurement detect the scattering time of electrons at energies $|\epsilon - \epsilon_f| < k_BT$, where $k_B$ is the Boltzmann constant and $T$ is the temperature at which the experiment is performed ($T \approx 300$ K). As shown in appendix VII B, this leads to electron scattering time of the order of

$$\tau = 0.35\text{ps} \quad \text{(from mobility)}$$

for $\epsilon_f > 0.2$ eV. Since the Debye temperature of the optical phonon in graphene is much larger than 300 K, the scattering in the mobility measurements is mainly due to defects and acoustic phonons.

ARPES measures the electron self-energy at photoemitted electron-energies $\epsilon$. The imaginary part of the electron self-energy is related to the electron scattering-time by the relation $\tau(\epsilon) = \hbar/2\zeta''(\epsilon)$. From the data in Refs. \cite{6, 7} for $|\epsilon - \epsilon_f| \approx k_BT$ we obtain

$$\tau \approx 3.5\text{fs} \quad \text{(from ARPES)}$$

which is two order of magnitudes smaller than Eq. \ref{eq:30}.

### B. Graphite

In graphite the electron scattering time has been measured by two different experimental techniques; (i) Femtoseconds time-resolved spectroscopy \cite{17} and (ii) ARPES.

![FIG. 4: (Color online) MDC - linewidth (HWMH) for the two model self-energy. The curve in upper panel is obtained using a finite resolution, while that in the lower one is without resolution effects. In the absence of resolution effects the linewidth is equal to $-\beta\zeta''(\epsilon)$ (see fig. 1). The Fermi level is $\epsilon_f = 0.4$ eV.](image)

![FIG. 5: Position of the maximum in MDC curves using a finite resolution. The Fermi level is $\epsilon_f = 0.4$ eV.](image)

![FIG. 6: Electron-phonon coupling in electron-doped graphene. The continuous line labeled DFT refers to Eq. \ref{eq:15} the empty squares are experimental data from Fig. 5 in ref. \cite{9}, while the empty circles represents the “apparent” electron-phonon coupling extracted from fits to the calculated ARPES spectra using Eq. \ref{eq:29} and including resolution effects. The curves DFT × 5.5 and DFT × 2.5 indicates Eq. \ref{eq:29} with multiplied by the prefactors 5.5 and 2.5 respectively.](image)
From femtoseconds time-resolved spectroscopy [17]:
\[ \tau \approx 0.2 \text{ps for } |\epsilon - \epsilon_f| = 0.25 \text{ eV} \]
\[ \tau \approx 0.1 \text{ps for } |\epsilon - \epsilon_f| = 0.50 \text{ eV} \]
(from femtoseconds time-resolved spectroscopy) (32)

Similar to what happens in graphene, ARPES measurements [4, 5, 13, 19] lead to a relaxation time which are two order of magnitudes times smaller than what obtained from the femtoseconds photoemission spectroscopy. For example, from the measured ARPES linewidth in Ref. [19] (see Fig. 10 c), we obtain:
\[ \tau \approx 4.75 \text{s for } |\epsilon - \epsilon_f| = 0.25 \text{ eV} \]
\[ \tau \approx 3.46 \text{s for } |\epsilon - \epsilon_f| = 0.50 \text{ eV} \]
(from ARPES) (33)

V. CONCLUSIONS

In this work we calculated the electron-phonon coupling parameter and the electron-phonon coupling contribution to the electron self-energy in doped graphene. From the electron self-energy we obtained the spectral-weight function and the ARPES spectra.

The ARPES spectra as a function of momentum and energy displays two kinks. The kinks are at energies \( \epsilon - \epsilon_f \approx -0.195 \text{ eV} \) and \( \epsilon - \epsilon_f \approx -0.16 \text{ eV} \), where \( \epsilon_f \) is the Fermi level. The two kinks are due to coupling to the twofold degenerate \( \text{E}_{2g} \) mode and to the \( \text{A}_1 \) mode respectively. The MDC-linewidth as a function of energy is discontinuous (jump) at \( \text{E}_{2g} \) and \( \text{A}_1 \) phonon energies.

Comparing the calculated electron-phonon coupling with that extracted from ARPES experiments we found that, for large enough electron-doping, the latter is roughly a factor 5.5 larger than the former, as suggested in ref. [14]. We partially solved this contradiction by including finite resolution effects. Indeed, in experiments the electron-phonon coupling is determined from the ratio of the electron-velocities at higher and lower energies respect to the kink. The velocities are obtained from the slopes of the maximum position of the ARPES spectra as a function of energy and momentum. We find that the slope above the kink is substantially affected by the presence of a finite resolution and the extracted values of the electron-phonon coupling are \( \approx 2.5 \) larger than what obtained without any resolution effect. Thus when comparing calculated spectra with the inclusion of finite resolution effects to ARPES experiments [6, 9] we remark that the measured electron-phonon coupling is still a factor of 2.2 larger than the calculated one [14]. Thus this work shows once more [20] the importance of including resolution effects to correctly describe ARPES data.

Finally, from the imaginary part of the electron self-energy we obtain the electron-relaxation time. The calculated electron relaxation time is in good agreement with mobility data on electron-doped graphene and is of the same order of magnitude of the electron relaxation time obtained from conductivity and femtoseconds time-resolved spectroscopy measurements in graphite. However this is in strong disagreement with ARPES measurements, being the ARPES relaxation times, both in graphene and graphite, almost two order of magnitudes smaller. This discrepancy essentially reflects the disagreement in the measured and calculated electron-phonon coupling. The aforementioned disagreement in the electron self-energies is even more surprising when considering that previous DFT calculations of the phonon self-energy in graphene, graphite and nanotubes were found to be in perfect agreement with experimental data for what concerns phonon dispersion and phonon lifetimes, [21 22 23]. Since the electron and phonon self-energies involve the same vertex, and thus the same matrix elements, a good agreement would be expected even for the electron self-energies too.

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VII. APPENDIX

A. Evaluation of the integral \( J_{\text{K+q}} \)

In Eq. [12] \( \theta_{k+q} = 2 \theta_{kq} - \pi \), so that \( 1 - \cos(\theta_{k+q}) = 2 \cos^2(\theta_{kq}) \) and the integral \( J_{\text{K+q}} \) (see Eq. [12]) can be evaluated as:

\[
J_{\text{K+q}} = \int_0^{2\pi} d\theta_{kq} \int \frac{d\tilde{k}}{\Omega} 2\tilde{k} \cos^2(\theta_{kq}) \delta(\beta\tilde{k} - \beta f) \times \delta(\beta\tilde{k} + \tilde{q} - \beta f) =
\]
\[
\frac{2\epsilon_f}{\Omega f^2} \int_0^{2\pi} d\theta_{kq} \cos^2(\theta_{kq}) \times \delta(\sqrt{k_f^2 + q^2 + 2k_fq\cos(\theta_{kq})} - \beta f) =
\]
\[
\frac{2k_f}{\Omega f^2} \sum_{\alpha=1,2} \int_{-1}^{1} d(\cos(\theta_{kq}^\alpha)) \delta(\cos(\theta_{kq}^\alpha) + \frac{\tilde{q}}{2k_f}) \times \frac{\cos^2(\theta_{kq}^\alpha)}{k_f|\sin(\theta_{kq}^\alpha)|} =
\]
\[
\frac{2}{\Omega f^2} \sqrt{1 - \frac{\tilde{q}^2}{4k_f^2}} \times
\]
(34)
Furthermore, the integral of such a quantity is:

\[
A = \frac{\Omega^2}{\beta^2} \int_{\mathcal{F}_K(2\pi)} \frac{d^2q}{\Omega} J_{K+\bar{q}} =
\frac{2}{\Omega^2\beta^2} \int_{\mathcal{F}_K(2\pi)} d^2q \frac{q/2k_f}{\sqrt{1 - \frac{q^2}{4k_f^2}}} =
\frac{8k_f^2}{\Omega^2\beta^2} \int_0^{2\pi} d\theta \int_0^1 dy \frac{y^2}{\sqrt{1 - y^2}} =
\frac{2\pi k_f^2}{\Omega^2\beta^2} \left[ \frac{y\sqrt{1 - y^2}}{2} + \frac{1}{2} \arcsin(y) \right]_0^1 =
\frac{16\pi k_f^2}{\Omega^2\beta^2} \frac{\pi}{4} = \frac{16\pi^2 e^2}{\Omega^2\beta^2} N_e^2(\epsilon_f) \frac{\pi}{4}.
\]

(35)

B. From mobility to electron relaxation time

The conductivity tensor is [24]

\[
\sigma = 2e^2 N_e^2 \sum_{\nu} \int \frac{d^2k}{(2\pi)^2} \tau_{\nu}(k) \mathbf{v}_{\nu}(k) \cdot \mathbf{v}_{\nu}(k) \left( -\frac{\partial f}{\partial \epsilon} \right)_{\epsilon = \epsilon_f(k)}
\]

(36)

Eq. [36] should then be divided by two since we are interested in only one component of the conductivity tensor. Moreover, we only consider intraband transition since they are the only relevant at low temperature. The graphite bands are linear so that \( \epsilon_k = \pm \beta k = \pm h v_f k \) where \( k \) measure the distance from the \( K \)-point. At zero temperature only electrons on the Fermi surface contribute to the integral thus, assuming a constant relaxation time, one gets:

\[
\sigma \approx 2e^2 \sum_{\nu} v_f^2 \tau \int_{\mathcal{F}_K} \frac{dk}{(2\pi)^2} \frac{d^2q}{\Omega} \frac{\epsilon_f - \epsilon_{\nu}}{\epsilon^2 \epsilon_f} =
\frac{2e^2 v_f^2 \tau}{h^2} \int_0^{2\pi} d\theta \epsilon_f =
\frac{2e^2 v_f^2 \tau}{h^2} \frac{\epsilon_f}{\epsilon_f}
\]

(37)

so that

\[
\tau = \frac{h^2 \pi \sigma}{2e^2 \epsilon_f}
\]

(38)

The conductivity can be written as a function of the mobility as \( \sigma = \delta e \mu \), where \( \delta \) is the number of electrons participating in conduction per surface area. Using Eq. 1 in Ref. [22] \( \delta = \epsilon_f^2/(\pi \beta^2) \) and \( \sigma = \epsilon_f^2 e \mu/(\pi \beta^2) \). Thus the relaxation time becomes:

\[
\tau = \frac{h^2 \pi \delta \mu}{2e^2 \epsilon_f} = \frac{h^2 \epsilon_f \mu}{e \beta^2}
\]

(39)

where \( \epsilon_f \) is expressed in eV and \( \mu \) in cm\(^2\)/(Volt \times sec). Expressing the mobility in m\(^2\)/(Volt \times sec) one gets

\[
\tau = 1.47 \times 10^{-12} \epsilon_f \mu = 1.47 \times \epsilon_f \mu \text{ ps}
\]

(40)

Using the values of Ref. [16] for mobility one gets at large doping (\( \epsilon_f > 0.18 \) eV) values of the order of 0.35 ps.

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