

Velocity Renormalization and Carrier Lifetime in Graphene from the Electron-Phonon Interaction

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We present a first-principles investigation of the phonon-induced electron self-energy in graphene. The energy dependence of the self-energy reflects the peculiar linear band structure of graphene and deviates substantially from the usual metallic behavior. The effective band velocity of the Dirac fermions is found to be reduced by 4%–8%, depending on doping, by the interaction with lattice vibrations. Our results are consistent with the observed linear dependence of the electronic linewidth on the binding energy in photoemission spectra.

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The recent fabrication of single-layer graphene [1] has attracted considerable interest because low-energy charge carriers in this material have dispersion curves similar to Dirac fermions with a zero rest mass and a constant group velocity [2,3]. Because of the peculiar electronic structure of graphene, electrons and holes exhibit exceptionally large mobilities, and the density of states can be tuned over a wide range by applying a gate voltage [2,3]. These properties make graphene a promising candidate for new-generation electronic and spintronic devices.

Angle-resolved photoemission spectroscopy (ARPES) is used as a powerful tool for investigating quasiparticle behavior with extremely fine energy and momentum resolution [4]. The photoelectron intensity provides information about the energy versus momentum dispersions of the charge carriers and the associated lifetimes. Recent photoemission experiments performed on graphene showed a peculiar dependence of the hole lifetime on the binding energy, as well as a significant velocity renormalization [5]. The measured carrier lifetime has been discussed within a model including three different decay channels: electron-phonon (*e-ph*) scattering, electron-plasmon scattering, and electron-hole pair generation [5]. The linear dependence of the linewidth on the binding energy was attributed to the generation of electron-hole pairs. The phonon-induced lifetime was assumed to be energy-independent as found in conventional metallic systems [5]. A subsequent theoretical work analyzed the carrier lifetimes in graphene by adopting a two-dimensional electron-gas model, and it concluded that the experimental results could be explained without invoking the *e-ph* interaction [6].

In this work we investigate the *e-ph* interaction in graphene within a *first-principles* approach. We calculated the electron self-energy arising from the *e-ph* interaction using a dense sampling of the scattering processes in momentum space, and we extracted the velocity renormalization and the carrier lifetimes from the corresponding real and imaginary parts of the self-energy, respectively. Our analysis

shows that the self-energy associated with the *e-ph* interaction in graphene is qualitatively different from that found in conventional metals. The imaginary part of the self-energy shows a linear energy dependence above the phonon emission threshold, which directly reflects the band structure of graphene. The real part of the self-energy leads to a Fermi velocity renormalization of 4%–8% depending on doping. We further propose a simple analytical model of the electron self-energy capturing the main features of our first-principles calculations. Our calculation allows us to assign the low-energy kink in the measured photoemission spectrum and part of the linear energy-dependence of the electronic linewidths to the *e-ph* interaction.

The *e-ph* interaction in graphene is treated within the Migdal approximation [7]. The contribution to the electron self-energy $\Sigma_{nk}(E; T)$ arising from the *e-ph* interaction at the temperature T is [7,8]:

$$\begin{aligned} \Sigma_{nk}(E; T) = & \sum_{m,\nu} \int \frac{d\mathbf{q}}{A_{\text{BZ}}} |g_{mn,\nu}(\mathbf{k}, \mathbf{q})|^2 \\ & \times \left[\frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{E - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu} - i\delta} \right. \\ & \left. + \frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}}{E - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu} - i\delta} \right], \quad (1) \end{aligned}$$

where ε_{nk} is the energy of an electronic state with band index n and wave vector \mathbf{k} and $\hbar\omega_{\mathbf{q}\nu}$ the energy of a phonon with wave vector \mathbf{q} and branch index ν . $f_{n\mathbf{k}}$ and $n_{\mathbf{q}\nu}$ are the Fermi-Dirac and Bose-Einstein distribution functions, respectively. The integration extends over the Brillouin zone (BZ) of graphene of area A_{BZ} and the sum runs over both occupied and empty electronic states and all phonon branches. The *e-ph* matrix element is defined by $g_{mn,\nu}(\mathbf{k}, \mathbf{q}) = \langle m\mathbf{k} + \mathbf{q} | \Delta V_{\mathbf{q}\nu} | n\mathbf{k} \rangle$, $\Delta V_{\mathbf{q}\nu}$ being the change in the self-consistent potential due to a phonon with wave vector \mathbf{q} and branch index ν , while $|n\mathbf{k}\rangle$, $|m\mathbf{k} + \mathbf{q}\rangle$ indicate Bloch eigenstates. Equation (1) takes into account the anisotropy of the *e-ph* interaction in \mathbf{k} space, as well as

retardation effects through the phonon frequency in the denominators.

The electronic structure was described within the local density approximation to density-functional theory [9]. Valence electronic wave functions were expanded in a plane-waves basis [10] with a kinetic energy cutoff of 60 Ry. The core-valence interaction was treated by means of norm-conserving pseudopotentials [11]. Lattice-dynamical properties were computed through density-functional perturbation theory [12]. We modeled an isolated graphene by a honeycomb lattice of carbon atoms within a periodic supercell. The graphene layers were separated by 8.0 Å of vacuum [13], and the relaxed C-C bond-length was 1.405 Å. Doped graphene was modeled by varying the electronic density and introducing a neutralizing background charge. We first calculated electronic and vibrational states and the associated e -ph matrix elements on 72×72 \mathbf{k} points and 12×12 \mathbf{q} points in the BZ of graphene. Then, we determined the quantities needed to evaluate the self-energy given by Eq. (1) on a significantly finer grid of 1000×1000 \mathbf{k} and $\mathbf{k} + \mathbf{q}$ points in the irreducible wedge of the BZ by using a first-principles interpolation based on electron and phonon Wannier functions [14–16]. The fine sampling of the BZ was found to be crucial for convergence of the self-energy. In the calculation of the self-energy we used a broadening parameter δ of 10 meV, comparable with the resolution of state-of-the-art photoemission experiments [4]. The calculations were performed with the electron and phonon occupations [Eq. (1)] corresponding to $T = 20$ K to make connection with the ARPES experiment [5]. In what follows, we discuss the computed electron self-energy by focusing on a straight segment perpendicular to the ΓK direction and centered at the K point in the BZ [Fig. 1].

We note here that within 2.5 eV from the Dirac point, the angular dependence of the self-energy is insignificant (at fixed energy E) [17]. As a consequence, the e -ph coupling parameter $\lambda_n(\hat{\mathbf{k}}) = -\partial \text{Re} \Sigma_{n\mathbf{k}}(E) / \partial E|_{E=E_F}$ is isotropic in \mathbf{k} space.

Figure 1 shows the calculated imaginary part of the self-energy (which is closely related to the linewidth) as a function of carrier energy, corresponding to three representative situations: intrinsic, electron-doped, and hole-doped graphene. We here considered doping levels corresponding to $4 \times 10^{13} \text{ cm}^{-2}$ electrons or holes. The corresponding Fermi levels were found to lie at +0.64 eV and -0.66 eV from the Dirac point, respectively. In the intrinsic system, we found that the electron linewidth due to e -ph interaction is negligible (< 1 meV) within an energy threshold $\hbar\omega_{\text{ph}}$ for the emission of optical phonons ($\hbar\omega_{\text{ph}} \approx 0.2$ eV being a characteristic optical phonon frequency), while it increases linearly beyond this threshold [Fig. 1(a)]. The scattering rate for electrons with energy below the optical phonon emission threshold is negligible because (i) only optical phonons are effective in e -ph scattering and (ii) Pauli's exclusion principle blocks tran-

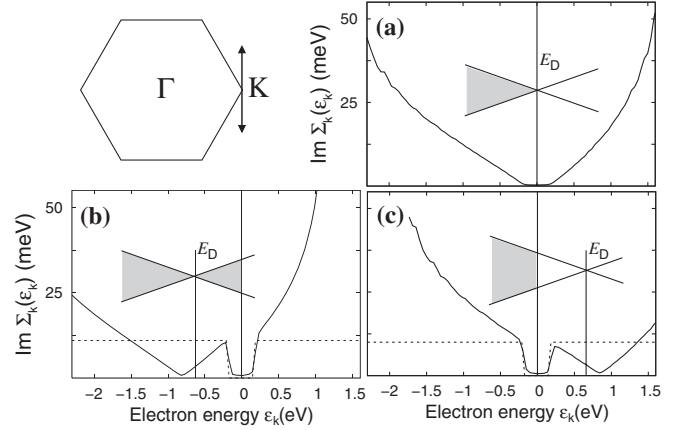


FIG. 1. Calculated imaginary part of the electron self-energy arising from the e -ph interaction at $T = 20$ K (solid lines) for (a) intrinsic, (b) electron-doped, and (c) hole-doped graphene. The self-energy $\Sigma_{\mathbf{k}}(\epsilon_{\mathbf{k}})$ was evaluated along the reciprocal space line segment shown in the upper-left corner. The Fermi level and the Dirac point are shown schematically in each case. We also show for comparison the imaginary part of the self-energy for a conventional metal (dashed lines) (Ref. [18]).

sitions into occupied states. On the other hand, the linear increase of the linewidth above the optical phonon energy relates to the phase-space availability for electronic transitions and reflects the linear variation of the density of states around the Dirac point in graphene. The energy dependence of the electron linewidths in the electron-doped and the hole-doped systems [Fig. 1(b) and 1(c), respectively] can be rationalized by a similar phase-space argument. We denote by E_D the energy of the Dirac point with respect to the Fermi level. For definiteness, we here consider the electron-doped situation ($E_D < 0$). When the energy of the hole is exactly equal to $|E_D| + \hbar\omega_{\text{ph}}$ (i.e., at $-|E_D| - \hbar\omega_{\text{ph}}$ in Fig. 1), there are no allowed final states for electronic transitions through optical phonon emission, resulting in a vanishing scattering rate at zero temperature. As the hole energy departs from $|E_D| + \hbar\omega_{\text{ph}}$, the linewidth increases linearly and exhibits a characteristic dip at the Fermi level. The latter feature corresponds to forbidden phonon emission processes, as discussed above for intrinsic graphene. The calculated energy dependence of the electron linewidth deviates substantially from the standard result which applies to conventional metals (Fig. 1, dashed line) [18]. The latter consists of a constant scattering rate above the phonon emission threshold and fails in reproducing the features revealed by our *ab initio* calculations.

Figure 2 shows the real part of the electron self-energy arising from the e -ph interaction, for intrinsic and for electron-doped graphene. The behavior of the hole-doped system is qualitatively similar to the electron-doped case. While in conventional metals the real part of the self-energy decays at large hole energies ($E < -\hbar\omega_{\text{ph}}$) [Fig. 2(b), dashed line], the self-energy in graphene shows a monotonic increase in the same energy range [Fig. 2(b), solid line]. Since the wave vector dependence of the self-

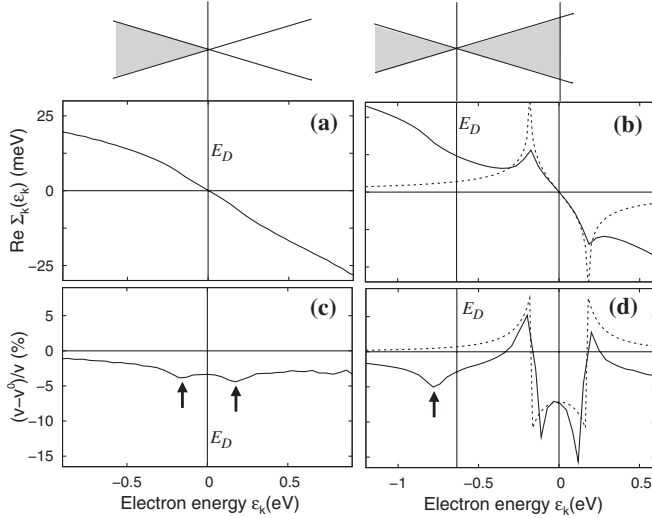


FIG. 2. Calculated real part of the electron self-energy arising from the e -ph interaction at $T = 20$ K (solid lines) for (a) intrinsic and (b) electron-doped graphene. The self-energy was evaluated along the reciprocal space line segment shown in Fig. 1. The corresponding velocity renormalization $(v_{nk} - v_{nk}^0)/v_{nk}$ is shown in panels (c) and (d), respectively. We also report, for comparison, the real part of the self-energy and the velocity renormalization for a conventional metal (dashed lines) (Ref. [18]). At variance with conventional metals, the group velocity in graphene shows additional dips when the carrier energy is $|E_D| + \omega_{ph}$ (arrows), reflecting the vanishing density of states at the Dirac point.

energy in graphene within a few eV from the Fermi level is negligible [i.e., $\Sigma_{nk}(E) \approx \Sigma_n(E)$] [17], we obtained the quasiparticle strength $Z_{nk} = (1 - \partial \text{Re} \Sigma_{nk} / \partial E)^{-1}$ by evaluating $(1 - d \text{Re} \Sigma_{nk}(\epsilon_k) / d \epsilon_k)^{-1}$. In all cases considered, the e -ph interaction was found to reduce the noninteracting quasiparticle strength down to at most $Z_{nk} = 0.93$ at the Fermi level. This suggests that a quasiparticle picture is still appropriate at low energy, the e -ph interaction largely preserving the weakly perturbed Fermi-liquid behavior. The quasiparticle strength is related to the velocity renormalization through $1 - Z_{nk}^{-1} = (v_{nk} - v_{nk}^0)/v_{nk}$, v_{nk}^0 and v_{nk} being the noninteracting and the interacting velocity, respectively. The velocity renormalization is plotted in Fig. 2(c) and 2(d) for the intrinsic and the electron-doped system, respectively. The velocity renormalization at the Fermi level was found to increase with the doping level, and it amounts to -4% , -8% , and -6% in the intrinsic, the electron-doped, and in the hole-doped system considered here. Our results indicate that the velocity of Dirac fermions in graphene is affected by the e -ph interaction. This bears important implications for the transport properties of graphene-based electronic devices.

In order to provide a simplified picture of the e -ph interaction in graphene, we analyzed the various e -ph scattering processes contributing to the electron lifetimes. We repeated our calculations by restricting either the en-

ergy $\hbar\omega_{qv}$ or the momentum transfer \mathbf{q} in Eq. (1) to limited ranges. When only the in-plane optical phonon modes between 174 and 204 meV are taken into account in Eq. (1), the electron linewidth is found to deviate from the full *ab initio* result by 15% at most. In contrast, when the momentum integration in Eq. (1) is restricted to small regions around the high-symmetry points Γ and K , the linewidth is found to deviate significantly from the full calculation, indicating that a proper account of the entire BZ is essential. Based on this analysis, we devised a simplified single-parameter model of the e -ph interaction in graphene. We assumed: (i) linear electronic dispersions up to a few eV away from the Dirac point [19], (ii) an Einstein model with the effective phonon energy $\hbar\omega_{ph}$ set to that of the highest degenerate zone-center mode, (iii) an effective e -ph vertex g , independent of the electron, and phonon momenta [17]. The e -ph matrix element g represents a free parameter in our simplified model and has been determined by matching the model self-energy with the full *ab initio* result. Within these assumptions, and with the Fermi level set to zero, the imaginary part of the self-energy reads

$$\text{Im} \Sigma(E) = \frac{\sqrt{3}a^2}{16} \alpha_G^2 g^2 |E - \text{sgn}(E)\hbar\omega_{ph} - E_D|, \quad (2)$$

whenever $|E|$ exceeds the characteristic phonon energy $\hbar\omega_{ph}$, and vanishes otherwise. In Eq. (2), a is the lattice parameter in Bohr units, $\alpha_G = e^2/\hbar v^0 = 2.53$ is the effective fine structure constant of graphene, and g is the average e -ph matrix element in Rydberg units. The fitting to our calculated *ab initio* self-energy gave $g = 3.5 \times 10^{-2}$ Ry. The real part of the model self-energy can be straightforwardly obtained from Eq. (2) through Kramers-Krönig relations. Figure 3 shows that this simplified model is in fairly good agreement with the full first-

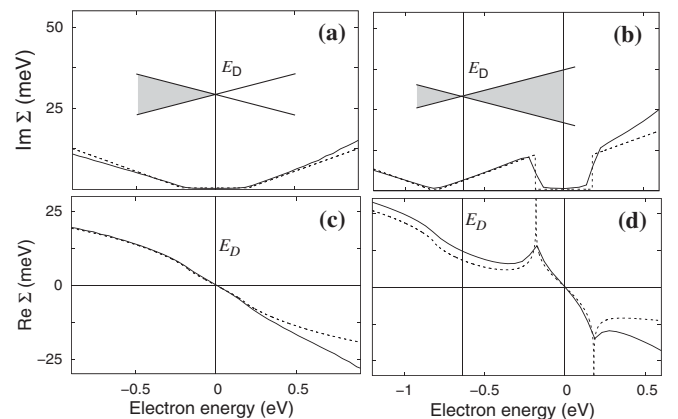


FIG. 3. Comparison between the electron self-energy obtained from a first-principles calculation (solid lines) and a single-parameter model (dashed lines): imaginary (upper panels) and real (lower panels) part for the intrinsic system (left) as well as for the electron-doped system (right). Note that the horizontal energy ranges differ from those shown in Fig. 1.

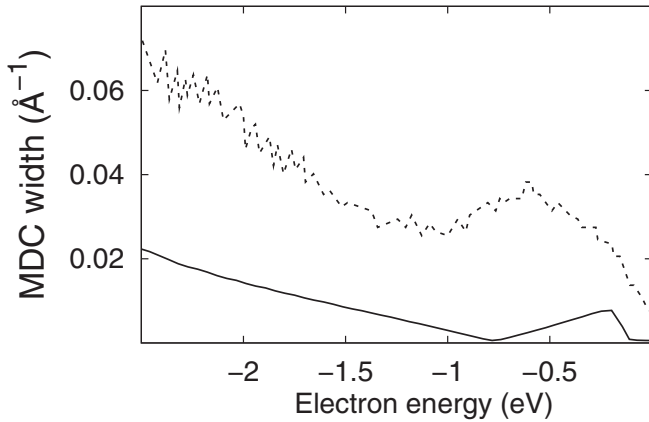


FIG. 4. Calculated width of the ARPES momentum distribution curve for electron-doped graphene (solid line) compared to the experimental result of Ref. [5] (dashed line). In our calculation, the Fermi level was set in order to simulate the sample with 2.1×10^{13} electrons/cm² in Fig. 3 of Ref. [5].

principles calculation. Therefore, despite its simplicity, our single-parameter model captures the qualitative features of the e -ph interaction in graphene.

In Fig. 4 we compare our first-principles calculations with the width of the momentum distribution curve (MDC) measured by ARPES experiments at 20 K on graphene with a similar doping [5]. The width Δk_{nk} of the MDC was calculated taking into account renormalization effects through $\Delta k_{nk} = Z_{nk} 2\text{Im}\Sigma_{nk}/\hbar v_{nk}$ [7]. Figure 4 shows that, contrary to previous findings [6], the e -ph interaction plays a significant role in reducing the carrier lifetime in graphene, as it accounts for about a third of the measured linewidth at large binding energies. The e -ph contribution to the width of the MDC is found to increase linearly at large binding energy, in agreement with experiment.

In conclusion, we have computed from first-principles the velocity renormalization and the carrier lifetimes in graphene arising from the e -ph interaction and we have reproduced these results with a simplified model. The calculated energy dependence of the phonon-induced electronic linewidths is shown to originate from the linear electronic dispersions. The renormalization of the Fermi velocity was found to be -4% for intrinsic graphene and -8% for an electron doping of 4×10^{13} cm⁻², and it is expected to affect the mobility of graphene-based electronic and spintronic devices.

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Note added.—After submission of this manuscript we became aware of a related work whose results are in agreement with our conclusions [22].

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