Two-gap superconductivity in heavily n-doped graphene: ab initio Migdal-Eliashberg theory

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Graphene is the only member of the carbon family from zero- to three-dimensional materials for which superconductivity has not been observed yet. At this time, it is not clear whether the quest for superconducting graphene is hindered by technical challenges, or else by the fluctuation of the order parameter in two dimensions. In this area, ab initio calculations are useful to guide experimental efforts by narrowing down the search space. In this spirit, we investigate from first principles the possibility of inducing superconductivity in doped graphene using the fully anisotropic Migdal-Eliashberg theory powered by Wannier-Fourier interpolation. To address a best-case scenario, we consider both electron and hole doping at high carrier densities, so as to align the Fermi level to a van Hove singularity. In these conditions, we find superconducting gaps of $s$–wave symmetry, with a slight anisotropy induced by the trigonal warping, and, in the case of $n$-doped graphene, an unexpected two-gap structure reminiscent of MgB$_2$. Our Migdal-Eliashberg calculations suggest that the observation of superconductivity at low temperature should be possible for $n$-doped graphene at carrier densities exceeding $10^{15}$ cm$^{-2}$.

I. INTRODUCTION

Superconductivity in lightweight carbon-based materials was first discovered almost half a century ago in alkali-metal doped graphite$^{[1]}$. Since then, the intercalation of metal atoms into graphite and fullerene solids has led to superconducting critical temperatures $T_c$ above 11 K in CaC$_6$ at ambient pressure$^{[2]}$ and 38 K in C$_6$sC$_6$ at applied pressure$^{[3]}$. Substitutional doping of diamond with boron also induces a superconducting state, with a critical temperature in the range 4-10 K$^{[4,5]}$. The most recent breakthroughs within the family of carbon-based materials are the discoveries of superconductivity in doped polyaromatic hydrocarbons, namely [2,4]phenantren$^{[6]}$, [4,4]coronene$^{[7]}$, and dibenzopentalene$^{[8]}$ with critical temperatures up to 33 K$^{[9]}$.

The discovery of graphene$^{[10,11]}$ together with its unique properties$^{[12,13]}$ immediately raised the question of whether superconductivity could be achieved also in this two-dimensional material. Within this context, theoretical studies explored both conventional and unconventional pairing mechanisms$^{[14,15]}$. In the former case, it was suggested that phonon-mediated superconductivity could be induced by tailoring the electron-phonon coupling (EPC) via alkali-metal doping$^{[16]}$. In the latter case, it was proposed that chiral superconductivity should arise when graphene is doped near the van Hove singularity (VHS), as a result of strong electron-electron interaction$^{[15,16]}$. Chemical modifications of graphene were also predicted to lead to superconductivity. For example, in close analogy to B-doped diamond$^{[2]$, hole-doped graphite$^{[10]}$ was predicted to be a high-$T_c$ superconductor$^{[11]}$.

Despite such a variety of theoretical predictions, so far none has been confirmed experimentally. This raises the question of whether there exists a fundamental limitation preventing a superconducting phase transition in graphene, similar to the Mermin-Wagner theorem$^{[22]}$, or if inducing and observing superconductivity is indeed possible but technically very challenging.

On the experimental front, the study of possible pairing mechanisms is complicated by the sensitivity of the EPC to the character and location of the metal atoms, as well as the underlying substrates$^{[23-26]}$. For example, the EPC strength determined by angle-resolved photoelectron spectroscopy differs substantially in the cases of subsurface intercalation of potassium on graphene/Au$^{[27]}$ and potassium adsorption on graphene/Ir$^{[28]}$. This sensitivity may reflect the substrate-induced modification of the electronic structure in proximity of the Dirac point: for example, graphene on Ir or Cu exhibits a band gap$^{[29,30]}$, graphene grown on Au is gapless$^{[30]}$, and in the case of SiC both situations have been reported$^{[31,32]}$.

Given the lack of experimental confirmation of current theories, and the difficulty in extracting the relevant pairing parameters from experiment, in order to understand the potential of graphene for superconductivity it is important to carry out careful investigations using the most advanced tools available.

In this work we study from first principles the possibility of superconductivity in heavily doped graphene. We employ a recent ab initio implementation of the anisotropic Migdal-Eliashberg theory$^{[25,30]}$ based on electron-phonon Wannier-Fourier interpolation$^{[23,33]}$. This technique allows us to describe the electron-phonon pairing mechanism by taking fully into account the highly anisotropic nature of graphene, and by sampling the Brillouin zone with unprecedented accuracy. By considering high carrier densities, whereby the Fermi energy approaches a VHS, we show below that superconductivity should be attainable at least in $n$-doped graphene, due to the additional pairing channels associated with the free-electron-like (FEL) band.
FIG. 1: (Color online) Electronic-structure and phonon-dispersion relations of pristine and doped graphene. (a) Electronic density of states and (b) band structures of pristine graphene (black solid line), p-doped graphene (dashed red line), and n-doped graphene (dotted blue line). (c), (d) Fermi surfaces of p-doped and n-doped graphene, respectively. In both cases, the Fermi surface corresponds to the green region of the energy isosurface, as indicated by the small arrow in the colorbar. The long black arrows indicate the dominant electron-phonon scattering mechanisms at the Fermi surface. (e) Phonon-dispersion relations of pristine, p-doped, and n-doped graphene, using the same color code as in (a). The vibrational modes discussed in the text are indicated. (f) Phonon density of states corresponding to the dispersions in (e).

II. MODELING DOPED GRAPHENE AT HIGH CARRIER DENSITY

In conventional superconductors the critical temperature increases with the electronic density of states at the Fermi level. In the case of graphene, this means that a best-case scenario for superconductivity should correspond to situations in which the Fermi level matches a VHS, either in the valence or in the conduction band. From our calculations, we find that the carrier densities required to approach the VHS are $0.8 \cdot 10^{15}$ cm$^{-2}$ for p-doped graphene, and $1.2 \cdot 10^{15}$ cm$^{-2}$ for n-doped graphene, respectively. Carrier densities near the VHS have been achieved via two-sided alkali metal doping of graphene\cite{40,41} and densities up to $4 \cdot 10^{14}$ cm$^{-2}$ via electrolytic gating\cite{15}. While carrier densities up to $3.5 \cdot 10^{15}$ cm$^{-2}$ have been demonstrated recently by means of polymer/electrolyte gating of gold thin films\cite{33}, such values may not be easily attainable in graphene due to its quantum capacitance\cite{14,15}.

Here we simulate carrier doping using a jellium model, whereby the excess/defect electronic charge is compensated by a uniform neutralizing background. This approximation has been used in previous studies to examine the effect of doping on the electronic bands, phonon dispersions, and EPC strength in carbon nanotubes\cite{35,36}, graphite intercalation compounds\cite{15,16}, and graphene\cite{15,16,17}. Besides being computationally advantageous, the jellium model is expected to provide a realistic description of graphene doped via electrochemical gating\cite{18,19}. In fact, while doping is expected to modify the band structure in proximity of the Dirac points\cite{20,21}, at high carrier densities its effects on the Fermi surface and the EPC are expected not to be significant. In the related case of superconducting gated MoS$_2$\cite{22} first-principles calculations using the same jellium model were able to reproduce the measured trends in the superconducting transition temperature\cite{23}. The calculations were carried out within the local density approximation to density-functional theory, using the codes Quantum-ESPRESSO\cite{24}, EPW\cite{25}, and Wannier90\cite{26}. The technical details of these calculations are described in Sec. VII at the end of this paper.

Figure 1 shows the calculated band structures, Fermi surfaces, and phonon-dispersion relations of pristine as well as doped graphene. In analogy with the interlayer state of graphite intercalation compounds, the FEL band crosses the Fermi level for n-doped graphene as shown in Fig. 1(b) (blue dotted lines). Upon doping, the highest optical phonon branches corresponding to the $E_{2g}$ modes at $\Gamma$ and the $B_{3u}$, $B_{2u}$, and $A_g$ modes at $M$ become softer, while the $A'_1$ mode at $K$ hardens [Fig. 1(e)]. This behavior can be rationalized in terms of the changes intervening in the Fermi surface upon doping. In fact, it is well known that in pristine graphene the scattering of electrons around $\Gamma$ and between $\Gamma$ and $K$ leads to two Kohn anomalies in the phonon dispersions at $\Gamma$ and $K$\cite{27}. When graphene is doped until the Fermi level matches one of the VHS [Fig. [1b]], the topology of the Fermi surface is dramatically altered and we obtain a hexagon connecting adjacent $M$ points [Figs. 1(c) and 1(d)]. As a result, the $\Gamma$ to $K$ scattering channel is suppressed, while scattering between flat parallel sheets of the Fermi surface becomes possible, as shown schematically in Fig. 1(c) and (d). As a consequence, the original Kohn anomaly at $K$ is lifted, and significant phonon softening is observed at $\Gamma$ and $M$, corresponding with $\Gamma$-$\Gamma'$ and $\Gamma$-$M'$ scattering across adjacent Brillouin zones, respectively. We also
III. ELECTRON-PHONON INTERACTION IN HEAVILY DOPED GRAPHENE

Within the framework of conventional superconductivity, Cooper pairing arises from the interaction between electrons and phonons. In order to analyze the strength of this interaction, in Fig. 2 we show the isotropic Eliashberg spectral function, $\alpha^2 F(\omega)$, the cumulative EPC, $\lambda(\omega)$, and the momentum-resolved EPC of each electronic state at the Fermi surface, $\lambda_k$. Here $\omega$ and $k$ represent the vibrational frequency and the electron momentum, respectively, and explicit expressions for $\alpha^2 F(\omega)$, $\lambda(\omega)$, and $\lambda_k$ are provided in Sec. VII.

Starting from $p$-doped graphene, $\lambda(\omega)$ displays a smooth increase as a function of phonon frequency, and the sharp peaks in $\alpha^2 F(\omega)$ above 140 meV, corresponding to the optical modes, account for more than half of the total EPC, $\lambda = 0.27$ [Fig. 2(a)]. Fig. 2(c) shows that the momentum-resolved EPC is rather uniform across the Fermi surface at various temperatures (shown in black), for $p$-doped and $n$-doped graphene, respectively. The isotropic superconducting gap is shown as blue filled dots. The dotted lines are BCS fits to the calculated data. Panels (g) and (h) show the corresponding superconducting gap at zero temperature on the Fermi surface (in meV). In the case of $n$-doped graphene, there are two superconducting gaps, one for the $\pi^*$ band and one for the FEL band (h).

note that the softening of the lowest acoustic branch in $p$-doped graphene leads to a dynamical instability. This instability is expected to be mitigated by the coupling with a substrate; in any event, the soft mode does not contribute to the electron-phonon coupling in the following analysis.

In principle, the electron-hole symmetry around the Dirac point should result into similar Fermi surfaces for $p$-doping and $n$-doping. However, in the latter case the presence of a FEL band introduces an additional Fermi-surface sheet centered at $\Gamma$, as shown in Fig. 1(d). This extra sheet opens an additional $\Gamma-\Gamma'$ scattering channel, and it is responsible for the more pronounced phonon softening near $\Gamma$ in the case of $n$-doping. The details of the phonon softening/hardening upon doping are expected to change slightly when the lattice constant of doped graphene, non-adiabatic corrections, or the presence of dopant atoms are explicitly taken into account. Nevertheless the general trends should be insensitive to these effects.
graphene we show in Fig. 2(b) the contributions to $\lambda(\omega)$ associated with intraband scattering within the $\pi^*$ sheet, and interband scattering between the $\pi^*$ and FEL sheets. From this plot and the decomposition of $\lambda(\omega)$ into the contributions from each phonon mode, we deduce that the optical in-plane C-C stretching phonons are responsible for intraband scattering in the $\pi^*$ sheet, while the out-of-plane buckling modes give rise to $\pi^*$-FEL interband scattering. The intraband scattering within the FEL sheet is found to be negligible. This phenomenology is similar to that of graphite-intercalation compounds, however in the present case the $\pi^*$-FEL coupling is much smaller, due to the fact that the FEL wavefunction is located farther away from the graphene layer.

In agreement with these observations, Fig. 2(d) shows that the momentum-resolved coupling $\lambda_{k\pi}$ is relatively uniform on each Fermi surface sheet, but it differs considerably between the $\pi^*$ sheet (0.46-0.57) and the FEL sheet (0.24-0.30).

IV. SUPERCONDUCTING PAIRING

Having examined the EPC in doped graphene we now move on to investigate its effect on the superconducting pairing. We solve the anisotropic Migdal-Eliashberg (ME) equations using the method described in Ref. 29. The solution to the ME equations, which are given explicitly in Sec. VII, provides the complete superconducting gap function $\Delta(k, \omega)$ across the Fermi surface. From this quantity, the leading edge of the superconducting gap for electron momenta $k$ on the Fermi surface is obtained by solving for $\omega$ in $\Re \Delta(k, \omega) = 0$.

Since in the ME theory the Coulomb repulsion between electrons typically counters the electron-phonon pairing, as a best-case scenario we consider first the case of vanishing Coulomb pseudopotential, $\mu^* = 0$ (see Sec. VII). Figure 2 shows the calculated distribution of the leading edge $\Delta_0$ of the superconducting gap. In the case of $p$-doped graphene, the gap function is slightly anisotropic [anisotropy ratio $(\Delta^\text{min}_0 - \Delta^\text{max}_0)/\Delta^\text{av}_0 = 11\%$], however the symmetry is clearly $s$-wave as can be seen in Fig. 2(g). For a carrier density corresponding to 0.4 holes/cell we obtain a critical temperature $T_c(\mu^*_c = 0) = 9.5$ K and a ratio $2\Delta_0/k_BT_c = 3.44$, very close to the ideal BCS value of 3.53. The temperature dependence of the superconducting gap is well described by a BCS model, as obtained by solving numerically the BCS gap equation using $\Delta_0$ and $T_c$ from our first-principles calculations. This is shown by the dotted black line in Fig. 2(c).

In the case of $n$-doped graphene, the presence of two Fermi surface sheets leads naturally to a two-gap structure, similar to the case of MgB$_2$. As shown by Figs. 2(f) and 2(h), also in this case the gaps have $s$-wave symmetry and are slightly anisotropic. The calculated superconducting critical temperature is $T_c(\mu^*_c = 0) = 51$ K for a carrier density of 0.6 electrons/cell. In this case, the ratios between the gap and the critical temperature are $2\Delta^\text{FEL}_0/k_BT_c = 1.76$ and $2\Delta^\text{B}_0/k_BT_c = 3.57$, therefore it appears that the gap on the FEL sheet deviates substantially from the standard BCS behavior. Despite such a deviation our calculated distributions of superconducting gaps are described nicely by BCS curves, as shown by the dotted black lines in Fig. 2(f).

Interestingly, as we show in Fig. 2(e) and (f), if we neglect the anisotropy of the electron-phonon interaction, and solve instead the Eliashberg equations using the isotropic average of the Eliashberg function, then the resulting critical temperatures are severely underestimated, by up to a factor of 2. This finding indicates that the standard approach based on the Allen-Dynes equation, employed in all previous studies on graphene, is inadequate for studying superconductivity in this material. This observation is in line with similar analyses performed for superconducting MgB$_2$. 

FIG. 3: (Color online) Superconducting critical temperature in doped graphene vs. Coulomb parameter. (a), (b) Calculated superconducting critical temperature as a function of the Coulomb pseudopotential $\mu^*_c$, for $p$-doped graphene and $n$-doped graphene, respectively. The filled black squares are from anisotropic Migdal-Eliashberg calculations, the filled blue circles correspond to the isotropic approximation, and the filled green triangles are estimates based on the Allen-Dynes equation. The lines are guides to the eye. The vertical red line in (b) indicates the Coulomb parameter estimated here using the model dielectric function of Ref. 28 and the small arrow indicates our best estimate for the $T_c$ of $n$-doped graphene. The schematic band-structure plots illustrate the two doping scenarios considered in this work.
V. COULOMB EFFECTS

The results presented so far correspond to an ideal scenario whereby the electron-electron Coulomb interaction is assumed to have no effect on the superconducting pairing. To explore more realistic situations, we show in Fig. 3 the critical temperatures calculated for several values of the Coulomb pseudopotential $\mu^*_c$ in the typical range used for carbon materials. As a direct consequence of the weak EPC in graphene, $T_c$ varies strongly with $\mu^*_c$. The trends shown in Fig. 3 are consistent with a simple analysis based on the Allen-Dynes equation at variable $\mu^*_c$ (filled green triangles in Fig. 3). Since typical values for $\mu^*_c$ are in the range 0.10-0.20, we expect only n-doped graphene to exhibit superconductivity upon doping, with $T_c$ of the order of 10 K.

It would be desirable to perform first principles calculations of the superconducting gap including electron-electron effects as in the density functional theory for superconductors (SCDFT); however the incorporation of such effects in the ME theory is nontrivial. As a simpler alternative we estimate $\mu^*_c$ using the model screened Coulomb interaction proposed in Ref. and the double Fermi surface average of Ref. Using this approach we estimate $\mu^*_c \simeq 0.16$, in good agreement with previous results. The corresponding critical temperature for n-doped graphene is $T_c = 13$ K, as indicated by the vertical red line in Fig. 3(b). A detailed discussion of the parameter $\mu^*_c$ in a related system was given in Ref., where the Coulomb parameter of CaC$_6$ was determined by comparing the superconducting gap obtained from the ME theory and that from the SCDFT.

From this analysis it is clear that electron-electron interactions are important for the superconducting pairing in graphene. However, while in the context of the Eliashberg theory such interactions always tend to weaken the pairing, it is also possible that in proximity of a VHS novel Coulomb effects may emerge and co-operate with the electron-phonon mechanism investigated here.

VI. CONCLUSIONS

In conclusion, we report the calculations of the superconducting properties of heavily doped graphene within the ab initio anisotropic Migdal-Eliashberg theory. Our work highlights the delicate interplay between electron-phonon interactions, anisotropy, and Coulomb effects in this material, and it demonstrates that simplified approaches based on isotropic approximations, such as the Allen-Dynes equation, are inadequate in this context.

Our main finding is that, when enough carriers are injected into graphene so that the Fermi level is aligned with the VHS in the $\pi^*$ manifold, it should be possible to observe conventional superconductivity at low temperature, due to the extra pairing associated with the FEL band. In this case, two distinct superconducting gaps should be clearly observable in tunneling experiments. Given the role of the FEL state in the superconductivity of n-doped graphene, and the well-known sensitivity of the FEL energetics to dielectric screening and quantum confinement, the superconducting state of graphene is expected to be rather delicate, and sensitive to device design and materials preparation.

We hope that this work will serve as a guideline to experimental research in the quest for a superconducting state that remains, to date, elusive.

VII. METHODS

The calculations are performed within the local density approximation (LDA) to density-functional theory and norm-conserving pseudopotentials using Quantum Espresso. The valence electronic wavefunctions are expanded in a plane-wave basis set with a kinetic energy cutoff of 60 Ry. A graphene layer in isolation is described using a supercell geometry. The optimized lattice parameter is $a = 2.434$ Å and periodic replicas are 10 Å apart. The electron charge density is computed using a $\Gamma$-centered Brillouin-zone mesh with 72×72×1 k-points and a Methfessel-Paxton smearing of 0.10 eV. The dynamical matrices and the linear variation of the self-consistent potential are calculated within density-functional perturbation theory on the irreducible set of a regular 12×12×1 q-point mesh. The electronic wavefunctions required for the Wannier-Fourier interpolation within the EPW code are calculated on a uniform and $\Gamma$-centered k-points mesh of size 12×12×1. We considered seven maximally-localized Wannier functions in order to describe the electronic band structure up to 1 eV above the VHS in the conduction band. Two Wannier functions are $p_z$-like states (one per C atom), three functions are $\sigma$-like states localized in the middle of C-C bonds, and two correspond to $\pi$-like states located directly above and below the center of the C$_6$ hexagon. We consider two doping scenarios where the Fermi energy matches either one of the two VHS in the $\pi$ or $\pi^*$ manifolds. This is achieved by using 0.4 electrons per unit cell (0.8·10$^{-15}$ cm$^{-2}$) for p-doped graphene, and 0.6 electrons per unit cell (1.2·10$^{-15}$ cm$^{-2}$) for n-doped graphene. The isotropic Eliashberg spectral function is defined as:

$$\alpha^2 F(\omega) = \frac{1}{N_F N_k N_q \sum_{k,k',\nu} |\delta_{kk'}^{\nu}|^2 \delta(\epsilon_k) \delta(\epsilon_{k'}) \delta(\omega - \omega_{qv})},$$

the cumulative EPC is calculated as

$$\lambda(\omega) = 2 \int_0^\omega \omega' \alpha^2 F(\omega') d\omega',$$

and the momentum-resolved EPC of each electronic state at the Fermi surface is given by

$$\lambda_k = \sum_{k',\nu} \delta(\epsilon_k) |g_{kk'}^{\nu}|^2 / \omega_{qv}.$$
In these expressions \( N_F \) represents the density of electronic states per spin at the Fermi level, \( N_k \) and \( N_q \) are the total numbers of \( k \) and \( q \) points, \( \epsilon_k \) is the Kohn-Sham eigenvalue referred to the Fermi level, and \( \phi_{k'k}^{\gamma} \) is the screened electron-phonon matrix element for the scattering between the electronic states \( k \) and \( k' \) through a phonon with wave vector \( q = k' - k \), frequency \( \omega_{\gamma q} \), and branch index \( \nu \). Here \( k \) and \( k' \) indicate both the electron wavevector and the band index. The anisotropic Migdal-Eliashberg equations\(^\text{[22,23,25,26]}\) are given by:

\[
Z(k, i\omega_n) = 1 + \frac{nT}{N_F\omega_n} \sum_{k'\nu'} \frac{i\omega_n}{\sqrt{\omega_n'^2 + \Delta^2(k', i\omega_n')}} \delta(\epsilon_{k'}) \lambda(k, k'_{n-n'}, \nu
\]

\[
Z(k, i\omega_n)\Delta(k, i\omega_n) = \frac{nT}{N_F} \sum_{k'\nu'} \Delta(k', i\omega_n') \delta(\epsilon_{k'}) \left[ \lambda(k, k'_{n-n'}, \nu) - \mu^*_k \right].
\]

Here \( \omega_n = (2n + 1)\pi T \) with \( n \) integer are fermion Matsubara frequencies, and \( T \) is the absolute temperature. \( Z(k, i\omega_n) \) is the mass renormalization function, \( \Delta(k, i\omega_n) \) is the superconducting gap function, \( \lambda(k, k'_{n-n'}) \) is the momentum- and energy-dependent EPC, and \( \mu^*_k \) is the semiempirical Coulomb parameter. From the superconducting gap function \( \Delta(k, i\omega_n) \) we obtain the gap at real-valued frequencies via Padé approximant.\(^\text{[21,22]}\) A detailed discussion of the formalism can be found in Ref.\(^\text{[22]}\). For the solution of the Eliashberg equations it is absolutely critical to use extremely fine Brillouin-zone grids.\(^\text{[23]}\) In this study we use grids containing \( 400 \times 400 \times 1 \) \( k \)-points and \( 200 \times 200 \times 1 \) \( q \)-points, respectively. The frequency cutoff in the Migdal-Eliashberg equations is set to five times the maximum phonon frequency, and the Dirac delta functions are smeared using Lorentzian broadenings of 100 meV and 0.5 meV for electrons and phonons, respectively. All the technical details of the Migdal-Eliashberg calculations are described extensively in Ref.\(^\text{[23]}\).

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