Kohn-Luttinger superconductivity in graphene

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We investigate the development of superconductivity in graphene when the Fermi level becomes close to one of the Van Hove singularities of the electron system. The origin of the pairing instability lies in the strong anisotropy of the e-e scattering at the Van Hove filling, which leads to a channel with attractive coupling when making the projection of the BCS vertex on the symmetry modes with nontrivial angular dependence along the Fermi line. We show that the scale of the superconducting instability may be pushed up to temperatures larger than 10 K, depending on the ability to tune the system to the proximity of the Van Hove singularity.

Since the fabrication in 2004 of single atomic layers of carbon, this new material (so-called graphene) has been attracting a lot of attention[1]. The undoped system has conical valence and conduction bands meeting at two different Fermi points (known as Dirac points)[2,3]. This peculiar dispersion has shown to be at the origin of a number of remarkable effects, like the existence of a minimum conductivity at the charge neutrality point[4,5,6,7].

From the point of view of possible applications, the interest in graphene has been driven by the large electron mobilities attained in typical experimental samples. Another remarkable property is that graphene can be used to build Josephson junctions when placed between superconducting contacts[8]. It becomes then quite intriguing whether graphene may support superconducting correlations on its own under suitable experimental conditions. On theoretical grounds, it is known that a model based on the conical dispersion requires a minimum strength of the pairing interaction for the development of a superconducting instability in the undoped system[5]. There have been already several proposals to drive graphene towards a pairing instability upon doping, placing the emphasis on the role of topological defects[10], the effect of a metallic coating[11], or the possibility of inducing superconductivity by electronic correlations[12,13].

In this paper we investigate a different route to superconductivity in graphene, when the Fermi level is close to one of the Van Hove singularities (VHSs) of the electron system. These are points characterized by a divergent density of states, one having the effect of enhancing the system. These are points characterized by a divergent density of states, which has the effect of enhancing the conductivity in graphene, when the Fermi level is close to the VHS. For this purpose, we have characterized the energy contour lines around the saddle points of the valence band by means of a tight-binding model, suited to fit the dispersion ε(k) known from angle-resolved photoemission spectroscopy (ARPES)[16]. In the model, we have considered the transfer integrals for first, second, and third neighbors of the graphene lattice, labelled respectively by t, d and t′, and the overlap integral s between first neighbors. In terms of these parameters, the Fermi velocity at the Dirac points is given by

\[ v_F = (3/2)(t - 2t' + 3d), \]

which must correspond to the value found in graphene, \( v_F \approx 2.7 \) eV. Moreover, the level of the saddle points relative to the Dirac points turns out to be \( 3d + (t - 3t' - 2d)/(1 + s) \), which must correspond to the value \( \approx 2.7 \) eV found in ARPES[16]. With this input, we arrive at the two conditions

\[ t' \approx d - 2.7s \]
\[ t \approx 2.7 + 2d - 5.4s - 3d \]

Finally, we can adjust the parameters to reproduce the curvature of the dispersion at the saddle points[16], arriving at a dependence of the hopping d which is linear on s to very high accuracy:

\[ d \approx 0.07 + 2.8s + O(s^2) \]

The ARPES dispersion around the saddle points can then be fitted leaving free the overlap integral s. The important point is that the hopping parameter t' remains always constrained to a very small value, \( t' \approx 0.1 \). This parameter controls the approximate nesting of the Fermi line, that is, the possibility of having regions in which the dispersion satisfies \( \varepsilon(k) \approx -\varepsilon(Q + k) \), with a fixed momentum Q. This is realized in the model with hopping parameters obtained from Eqs. [11, 12], as observed in a typical plot of energy contour lines shown in Fig. [1]. The measure of the nesting is given by the susceptibility \( \chi(Q, \omega) \) at the momentum Q connecting two inequivalent saddle points, which diverges in any event due to the singular density of states. We may approximate for

\[ \chi(Q, \omega) \approx \frac{1}{\omega} \int_{-\infty}^{\infty} d\epsilon \rho(\epsilon) \delta(\varepsilon) \delta(Q + k - Q - k) \]

where \( \rho(\epsilon) \) is the density of states and \( \delta(\varepsilon) \) the Dirac delta function.
instance the dispersion with the deviation $\delta k$ from the saddle point $(2\pi/3, 0)$ by

$$\varepsilon(k) \approx -\alpha \delta k_x^2 + \beta \delta k_y^2$$  \hfill (4)$$

Then we have

$$\chi(Q, \omega) \approx \frac{1}{2\sqrt{3\pi^2}} \frac{c'}{\alpha + \beta} \log(\omega)$$  \hfill (5)$$

where the nesting instability at $\alpha = 3\beta$ appears in the dependence

$$c' = \log \left( \frac{1 + \sqrt{3\beta/\alpha}}{1 - \sqrt{3\beta/\alpha}} \right)$$

This has to be confronted with the susceptibility at vanishing momentum transfer, which is

$$\chi(0, \omega) \approx \frac{1}{4\pi^2} \frac{1}{\sqrt{\alpha\beta}} \log(\omega)$$  \hfill (7)$$

For the lower VHS in graphene, sensible values of the parameters are $\alpha \approx 7.41$ and $\beta \approx 2.03$ (as obtained for $s = 0.1$), which gives $c' \approx 3.6$. We see therefore that the susceptibility at momentum $Q$ prevails over that at vanishing momentum.

When the Fermi line becomes close to the saddle points, the large anisotropy of the $e$-$e$ scattering may actually induce a pairing instability. This can be understood within a renormalization group framework, by reclarifying the argument given by Kohn and Luttinger long time ago[1]. We will denote the interaction vertex by $V(\theta, \theta')$ for the particular case of BCS kinematics, in which the incoming (outgoing) particles collide with zero total spin and zero total momentum and the angle $\theta$ ($\theta'$) locates the position of the spin-up particle over the Fermi line. The BCS vertex gets corrections at low energies by the effect of the high-energy electron modes in slices between energy $\Lambda$ and $\Lambda + d\Lambda$ about the Fermi level[17]. The integration of these modes gives the variation

$$dV(\theta, \theta') = \frac{d\Lambda}{\Lambda} \int_0^{2\pi} \frac{d\theta''}{(2\pi)^2} \frac{\partial k_{||}}{\partial \theta''} \frac{1}{v(\theta'')} V(\theta, \theta'') V(\theta'', \theta')$$  \hfill (8)$$

where $v(\theta'')$ is the gradient of the dispersion and $\partial k_{||}/\partial \theta''$ is the variation of the momentum along the slice parametrized by the angle $\theta''$. We can write the above equation in more compact form by passing to the variable

$$\phi(\theta) = \frac{1}{2\pi n(\Lambda)} \int_0^\theta \frac{d\theta''}{\partial n(\Lambda)} \frac{\partial k_{||}}{\partial \theta''}$$  \hfill (9)$$

where the density of states $n(\Lambda)$ is introduced so that the new variable also ranges from 0 to $2\pi$ [18]. After defining the transformed vertex by $\tilde{V}(\phi, \phi') = V(\theta, \theta')$, we get

$$\frac{\partial \tilde{V}(\phi, \phi')}{\partial \log \Lambda} = \frac{n(\Lambda)}{2\pi} \int_0^{2\pi} d\phi'' \tilde{V}(\phi, \phi') \tilde{V}(\phi'', \phi')$$  \hfill (10)$$

We can further decompose the vertex $\tilde{V}(\phi, \phi')$ in terms of the eigenmodes $\Psi_m(\phi)$ for the different representations $\gamma$ of the point symmetry group,

$$\tilde{V}(\phi, \phi') = \sum_{\gamma, m, n} V_{\gamma, m, n} \Psi_m(\phi) \Psi_n(\phi')$$  \hfill (11)$$

We obtain then the set of coupled scaling equations

$$\frac{\partial V_{\gamma, m, n}}{\partial \log \Lambda} = n(\Lambda) \sum_s V_{\gamma, m, n} V_{s,\gamma, n}$$  \hfill (12)$$

In this framework, we recover the analogue of the Kohn-Luttinger mechanism when any of the couplings $V_{\gamma, m, n}$ turns out to be negative, in such a way that an unstable flow develops when the Fermi line is approached in the low-energy limit $\Lambda \to 0$.

We remark that the scaling equation (12) encodes the corrections to the BCS vertex that are logarithmically divergent at low energies in the particle-particle channel. If we start solving the scaling equation at an intermediate energy scale $\Lambda$, the initial values of the function $\tilde{V}(\phi, \phi')$ will be dictated by the bare interaction as well as by regular corrections to it, given in general by finite diagrams in the particle-hole channel. Previous scaling analyses of electrons near a VHS have shown that only the momentum-independent component of the interaction potential is not irrelevant at low energies[19], which is consistent with the large screening effects from the divergent density of states. For this reason, we may consider that a bare on-site repulsion $U$ between electron densities with opposite spin provides a sensible form of interaction close to the Van Hove filling. The relevant
point is that the bare short-range interaction gives rise to particle-hole corrections to the BCS vertex like those represented in Fig. 2. If we measure the angles \( \phi, \phi' \) with respect to the \( x \)-axis, we observe for instance that the value of \( \tilde{V}(0, \pi/3) \) will be enhanced by the particle-hole susceptibility \( (15) \) at momentum \( \mathbf{Q} \), while \( \tilde{V}(0, 0) \) is enhanced by the particle-hole susceptibility \( (1) \) at zero momentum. The prevalence of \( \chi(\mathbf{Q}, \Lambda) \) implies that

\[
\tilde{V}(0, 0) - \tilde{V}(0, \pi/3) \sim 3U^2\chi(0, \Lambda) - 2U^2\chi(\mathbf{Q}, \Lambda) < 0
\]

(13)

In general, we can anticipate the dominant terms in the modulation of the BCS vertex complying with the symmetry of the Fermi line:

\[
\tilde{V}(\phi, \phi') \approx c_0 + c_{6}\cos(6\phi) + \ldots
\]

(14)

\[
\tilde{V}(0, 0) \approx c'_0 + c'_2\cos(2\phi) + c'_4\cos(4\phi) + c''_6\cos(6\phi) + \ldots
\]

(15)

\[
\tilde{V}(\phi, \pi - \phi) \approx c''_0 + c''_2\cos(2\phi) + c''_4\cos(4\phi) + c''_6\cos(6\phi) + \ldots
\]

(16)

As we will see, several relations can be obtained between the coefficients in \( (14)-(16) \) by estimating the strength of the different scattering processes around the Fermi line.

The Fourier expansions \( (14)-(16) \) match well with the decomposition \( (11) \) of the BCS vertex in terms of the basis functions \( \Psi_{6n}(\phi) \). The point symmetry group is \( C_{6v} \), which has 6 irreducible representations. Four of them are one-dimensional, with respective sets of basis functions given by \( \{ \cos(6n\phi) \}, \{ \sin(6n\phi) \}, \{ \cos((6n + 3)\phi) \}, \{ \sin((6n + 3)\phi) \} \) \( n \) being always an integer. The other two representations are two-dimensional and have sets of basis functions which can be represented by \( \{ \cos(m\phi), \sin(m\phi) \} \), with the integer \( m \) running over all values that are not multiple of 3 and which are odd for one of the representations and even for the other. We can write therefore an expansion of the BCS vertex following \( (11) \) and matching the modulations in \( (14)-(16) \):

\[
\tilde{V}(\phi, \phi') = V_{0,0} + 2V_{0,6}(\cos(6\phi) + \cos(6\phi')) + 2V_{0,2}(\cos(2\phi) + \cos(2\phi')) + 2V_{0,4}(\cos(2\phi) - \sin(2\phi) + \phi \leftrightarrow \phi') + 2V_{3,3}\cos(3\phi)\cos(3\phi') + 2V_{3,3}\sin(3\phi)\sin(3\phi') + \ldots
\]

(17)

One can check that the terms displayed in \( (17) \) account for the dependence of the BCS vertex in Eqs. \( (13)-(16) \). We identify actually the different coefficients \( c_2'' = 2V_{2,2} + 2V_{2,4}, c'_2 = 2V_{2,4}, c''_6 = 2V_{0,6}, \) on the one hand, and \( c_2'' = 4V_{2,4}, c''_6 = 2V_{2,2}, c''_6 = 4V_{0,6} + V_{0,3}, \) on the other hand. The constraint \( (13) \) can be translated then to these couplings, since \( \tilde{V}(0, 0) - \tilde{V}(0, \pi/3) \) is given by the combination \( 3(c_2'' + c_4''/2) = 3(c_2'' + c_4'')/2 \). We find

\[
3(V_{2,2} + V_{2,4}) \sim 3U^2\chi(0, \Lambda) - 2U^2\chi(\mathbf{Q}, \Lambda)
\]

(18)

This already points at the existence of an unstable flow in the channel corresponding to the representation with \( d \)-wave symmetry as long as \( \chi(0, \Lambda) < \chi(\mathbf{Q}, \Lambda) \). A closer inspection reveals actually that both couplings \( V_{2,2} \) and \( V_{2,4} \) must be negative. To show this, one more constraint can be enforced by noticing that \( \tilde{V}(\pi/6, -\pi/6) - \tilde{V}(\pi/2, -\pi/2) = 3(c_2'' - c_4'')/2 \). The relevant point is that the corrections to the BCS vertex at those angles are not singular at low energy \( \Lambda \), as they involve scattering by particle-hole processes that scale at most as \( \sim \sqrt{\Lambda} \) \( (20) \). Therefore, the dominant contribution to both couplings \( V_{2,2} \) and \( V_{2,4} \) arises from the logarithmic dependence on \( \Lambda \) at the right-hand-side of Eq. \( (18) \).

As long as \( V_{2,2} \) and \( V_{2,4} \) are negative, we have a pairing instability in the system, whose critical scale can be estimated by solving the coupled scaling equations \( (19) \) in the relevant symmetry channel. We can truncate the set of equations to

\[
\frac{\partial}{\partial \log \Lambda} \begin{pmatrix} V_{2,2} \\ V_{4,2} \\ V_{4,4} \end{pmatrix} \approx n(\Lambda) \begin{pmatrix} V_{2,2} & V_{2,4} & V_{4,2} \\ V_{4,2} & V_{4,4} & V_{4,4} \end{pmatrix} \begin{pmatrix} V_{2,2} \\ V_{2,4} \\ V_{4,4} \end{pmatrix}
\]

(19)

Eq. \( (19) \) can be easily solved by passing to the eigenvalues \( \lambda_1, \lambda_2 \) of the matrix of couplings. The scaling equations read for them

\[
\frac{\partial}{\partial \log \Lambda} \lambda_j = n(\Lambda)\lambda_j^2
\]

(20)

We remark that \( V_{4,4} \) does not appear at the dominant level in the expansion of the BCS vertex, implying that such a coupling must be much smaller than those displayed in \( (17) \). The two eigenvalues can be approximated then by \( \lambda_{1,2} = (V_{2,2} \pm \sqrt{V_{2,2}^2 + 4V_{2,4}^2})/2 \). It is clear that the positive eigenvalue \( \lambda_1 \) will vanish in the low-energy limit, while the signature of the pairing instability will be given by the growth of \( \lambda_2 \) towards very large negative values as \( \Lambda \to 0 \).

To find the behavior of the negative eigenvalue, we take for \( n(\Lambda) \) the density of states about a VHS at an energy \( \mu \) from the Fermi level:

\[
n(\varepsilon) \approx \frac{3}{4\pi^2} \frac{1}{\sqrt{\alpha\beta}} \log \left( \frac{\Lambda_0 - \varepsilon}{|\varepsilon - \mu|} \right)
\]

(21)

In the above expression, \( \Lambda_0 \) is an upper bound for the cutoff in our model of the VHS, that we take as 1 eV. The other important factor in the resolution of \( (20) \) is the
choice of initial conditions for $V_{2.2}$ and $V_{2.4}$ at the upper cutoff $\Lambda_0$. In this respect, we have taken a value of $U = 4$ eV for the bare on-site repulsion, which is between the estimates made for graphite and carbon nanotubes. In order to go beyond the perturbative particle-hole corrections to the BCS vertex, we have summed up the series of leading logarithms obtained by iteration of the particle-hole susceptibilities in the diagrams of Fig. 2. Thus, we have constrained the initial couplings by the condition

$$3(V_{2.2} + 2V_{2.4}) = \frac{U}{1 - 3U\chi(0, \mu)} - \frac{U}{1 - 2U\chi(Q, \mu)}$$  \hspace{1cm} (22)$$

The precise values of $V_{2.2}$ and $V_{2.4}$ have been obtained by adding the other constraint mentioned below Eq. [15], which reads $3(2V_{2.4} - V_{2.2}) = \tilde{V}(\pi/6, -\pi/6) - \tilde{V}(\pi/2, -\pi/2)$. In these conditions, we have determined the position of the pairing instability in terms of the energy $\Lambda$ at which the solution of Eq. (20) diverges, marking the position of a pole in the BCS vertex. The results are shown in Fig. 3, where we have represented the critical point in a temperature scale after trading the energy variable $\Lambda$ by the thermal energy $k_BT$.

We observe that the scale of the pairing instability depends drastically on the value of the chemical potential $\mu$ measuring the deviation of the VHS from the Fermi level. The plot of Fig. 3 shows anyhow that the instability exists irrespective of the value of $\mu$. We recall in this respect that the Kohn-Luttinger mechanism was proposed to put forward the idea that any Fermi liquid is unstable at sufficiently low temperature. On the other hand, an inflection point can be seen in the plot of Fig. 3 for a value of $\mu$ slightly below 0.2 meV. That feature corresponds to the case in which the energy scale of the instability (and the scale of the gap) coincides with the deviation of $\mu$ of the VHS from the Fermi level. Values of $\mu$ to the left of the inflection point correspond therefore to the regime where the pairing instability is driven all the way by the VHS.

The possibility of finding a pairing instability in graphene at temperatures of the order of $\sim 10$ K may rely on the ability to make a fine tuning of the Fermi level to the VHS. This may be feasible as long as the proximity to the divergent density of states corresponds to a situation with a very large compressibility, which is energetically very favorable. It has been actually shown that the VHS may pin the Fermi level over a range of doping levels, forcing the breakdown of the uniform charge distribution into patches with uneven electron density (phase separation) so that the Van Hove filling is reached in one of the phases.

In conclusion, we have seen that placing graphene in the proximity of the VHS of its valence band may be a good instance to induce a superconducting instability in the electron system. The origin of this effect lies on the large anisotropy of the $e-e$ scattering along the Fermi line, which leads to an attractive coupling in a channel with $d$-wave symmetry. We have shown that the scale of the pairing instability may be pushed up to temperatures larger than 10 K, depending on the ability to tune the system to the proximity of the VHS.

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