ELECTRONIC PROPERTIES OF GRAPHENE

J. González
Instituto de Estructura de la Materia, CSIC, Spain

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Condensed-Matter Simulation of a Three-Dimensional Anomaly
Gordon W. Semenoff
The Institute for Advanced Study, Princeton, New Jersey 08540, and Department of Physics, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada
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A condensed-matter analog of (2 + 1)-dimensional superconductors is constructed, and the consequences of a recently discovered anomaly in such systems are discussed.

Electric Field Effect in Atomically Thin Carbon Films

The ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. In many cases, it is the electric field effect that allows one to vary the carrier concentration in a semiconductor device, and, consequently, change its electric current. As the semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nontraditional materials whose properties can be controlled by the electric field. The most notable recent examples of such materials are organic conductors (1) and carbon nanotubes (2). It has long been tempting to extend the use of the field effect to metals (e.g., to develop all-metallic transistors that could be scaled down to much smaller sizes and would consume less energy and operate at higher frequencies than traditional semiconducting devices (3)). However, this would require electronically thin metal films, because the electric field is screened at extremely short distances (~1 nm) and bulk carrier concentrations in metals are large compared to the surface charge that can be induced by the field effect. Films so thin tend to be thermodynamically unstable, becoming discontinuous at thicknesses of several nanometers; so far, this has proved to be an insurmountable obstacle to metallic electronics, and no metal or semiconductor has been shown to exhibit any notable (~5%) field effect (4).

We report the observation of the electric field effect in a naturally occurring two-dimensional (2D) material referred to as few-layer graphene (FLG). Graphene is the name given to a single layer of carbon atoms densely packed into a honeycomb structure, and is widely used to describe properties of many carbon-based materials, including graphite, large fullerenes, nanotubes, etc. (e.g., carbon nanotubes are usually thought of as graphene sheets rolled up into nanometer-sized cylinders (~5 nm). Planar graphene itself has been presumed not to exist in the free state, being unstable with respect to the formation of curved structures such as soot, fullerenes, and nanotubes (~1 nm).
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Graphene has opened the way to investigate the behavior of a genuine electron system in $D = 2$:

- it shows remarkable properties from the theoretical point of view (relativistic-like behavior)
- it has raised expectations of reaching very large electron mobilities

But … some challenges have to be faced:

- samples have significant corrugation
- the interaction with the substrate and boundary conditions modify significantly the transport properties

From E. Stolyarova et al.,
The observed properties were actually consistent with the dispersion expected for electrons in a honeycomb lattice.

\[
H_{tb} = -t \sum_{r,r'} \psi^+ (r') \psi (r) \quad \Rightarrow \quad H = -t \begin{pmatrix}
0 & \sum_{j=1,2,3} e^{i k_v j} \\
\sum_{j=1,2,3} e^{-i k_v j} & 0
\end{pmatrix}
\]

\[
\epsilon (k) = \pm t \sqrt{1 + 4 \cos^2 (ak_y / 2) + 4 \cos (ak_y / 2) \cos (\sqrt{3}ak_x / 2)}
\]

Expanding around each corner of the Brillouin zone, we obtain the Hamiltonian for a two-component fermion (Dirac Hamiltonian).

We have to introduce a Dirac fermion for each independent Fermi point, at which

\[
\epsilon (k) \approx \pm v_F |k|, \quad D(\epsilon) \propto |\epsilon|
\]
The first experimental observations and measurement of unusual transport properties pointed at the existence of a conical dispersion of electron quasiparticles in graphene.

- the electric field effect shows that a substantial concentration of electrons (holes) can be induced by changes in the gate voltage

\[ n \propto V_g \]

- the response to a magnetic field is also unusual, as observed in particular in the quantum Hall effect

\[ \sigma_{xy} = \frac{4e^2}{h} (N + 1/2) \]

From K. S. Novoselov et al., Nature 438, 197 (2005)

(see also Y. Zhang et al., Nature 438, 201 (2005))
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The peculiar quantization of the Hall conductivity can be explained satisfactorily by the coupling of the Dirac fermions to gauge fields:

\[ H_{tb} = -t \sum_{r,r'} \psi^+(r') \exp(i e / c) \int_{r'} A \cdot dl \psi(r) \]

which corresponds to the gauge prescription

\[ H = v_F \sigma \cdot k \rightarrow v_F \sigma \cdot (k - \frac{e}{c} A) \]

This leads to Landau levels quantized according to the expression

\[ \varepsilon(N) = \text{sgn}(N) \sqrt{2ev_F^2|N|B} \]
The quantum Hall effect is actually quite robust and should persist even in the presence of curvature of the samples. In the case of the shells of MWNTs with radius $R = 20 \text{ nm}$, for instance, we can predict the sequence of band structures for magnetic field strength $B = 0, 5, 10, 20 \text{ T}$:

**ELECTRONIC PROPERTIES OF GRAPHENE**

The scattering due to disorder is quite unconventional in graphene, due to the chirality of electrons. When a quasiparticle encircles a closed path in momentum space, it picks up a Berry phase of $\pi$.

\[
H = v_f \begin{pmatrix}
0 & |k| e^{-i\phi} \\
|k| e^{i\phi} & 0
\end{pmatrix} \quad \rightarrow \quad \psi = \frac{1}{\sqrt{2}} \begin{pmatrix}
e^{-i\phi/2} \\
\pm e^{i\phi/2}
\end{pmatrix}
\]

In the absence of scatterers that may induce a large momentum-transfer, backscattering is then suppressed (H. Suzuura and T. Ando, Phys. Rev. Lett. 89, 266603 (2002)).

\[
w \sim |A_\subset + A_\supset|^2 = |A_\subset|^2 + |A_\supset|^2 + [A_\subset^* A_\supset + A_\subset A_\supset^*]
\]

\[
A_\subset A_\supset^* = e^{-i2\pi(\sigma_z/2)} |A_\subset|^2 = -|A_\subset|^2 < 0
\]
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Another way of explaining the suppression of backscattering is by considering that, for the massless Dirac fermions, the pseudospin gives rise to the conserved quantity

\[ \mathbf{\sigma} \cdot \frac{\mathbf{p}}{|\mathbf{p}|} \]

that changes sign upon the inversion of the momentum.

This also explains the peculiar properties of electrons when tunneling across potential barriers: the transmission probability is equal to 1 at normal incidence, and 0 for backscattering.

ELECTRONIC TRANSPORT IN GRAPHENE

Coming back to the conductivity, this can be computed in Boltzmann transport theory in terms of the density of states \( D \) as

\[
\sigma(\varepsilon_F) = e^2 v_F^2 D(\varepsilon_F) \tau(\varepsilon_F) \propto e^2 v_F^2 \varepsilon_F \tau(\varepsilon_F)
\]

The linear dependence observed experimentally on gate voltage implies that \( \sigma \) should be proportional to the electron density.

- in the case of short-range scatterers, \( \tau \propto 1/k \), implies that \( \sigma = \text{const} \).
- in the case of charged Coulomb scatterers, \( \tau \propto k \), implies that \( \sigma \propto \varepsilon^2 \)

The relevance of the Coulomb scatterers is also in agreement with other experiments where the influence of the background dielectric constant is shown. The best fit to the resistivity is given by

\[
\frac{1}{\sigma(\varepsilon_F)} = \frac{1}{en(\varepsilon_F) \mu_i} + \frac{1}{\sigma_i}
\]

ELECTRONIC TRANSPORT IN GRAPHENE

There is also the question of the minimum conductivity of undoped graphene. There has been some controversy, regarding whether it should be given by a “universal” value. In fact, the conductivity can be computed from the charge susceptibility

\[ \Pi_0(q, \omega) = \frac{q^2}{4 \hbar \sqrt{v_F^2 q^2 - \omega^2}} \]

By using particle conservation, we can obtain the conductivity as

\[ \sigma(\omega) = e^2 \lim_{q \to 0} \frac{i \omega}{q^2} \Pi_0(q, \omega) = \frac{\pi e^2}{2 \hbar} \]

Including the effect of impurities, it turns out to be \( \sigma(\omega) = 4e^2/\pi \hbar \), still below the claimed universal value (the mystery of the missing \( \pi \)).

Nowadays there is some consensus that the impurities in the substrate may give rise to a minimum value of \( \sigma \). Charged impurities lead to the formation of electron-hole puddles in undoped graphene, and percolation of the electron current is what produces a value \( \sigma \approx 4e^2/\hbar \).

K. S. Novoselov et al., Nature 438, 197 (2005)

J. Martin et al., Nat. Phys. 4, 144 (2008)
JOSEPHSON EFFECT IN GRAPHENE

There have been also observations of supercurrents, when graphene is contacted with superconducting electrodes

From H. B. Heersche et al.,
Nature 446, 56 (2007)

The reason why supercurrents may exist at the charge neutrality point is that Cooper pairs have a nonvanishing susceptibility even in undoped graphene

From J. G. and E. Perfetto,
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A direct evidence of the conical dispersion has been obtained with angle-resolved photoemission spectroscopy


These experiments are also useful to provide a measure of the interaction effects in graphene

MANY-BODY EFFECTS IN GRAPHENE

Graphene is a system with remarkable many-body properties. The electron-hole susceptibility is

\[ \Pi_0(q, \omega) = \frac{q^2}{4\sqrt{v_F^2 q^2 - \omega^2}} \]

This leads to a behavior of the electron self-energy \( \Sigma(k, \omega) \)

\[
\text{Im} \, \Sigma(k, v_F|k| + \delta) \propto v_F |k|
\]

\[
\text{Im} \, \Sigma(k, v_F|k| - \delta) = 0
\]

In the doped system, the decay of electron quasiparticles comes from intraband electron-hole excitations:

The quasiparticle decay rate becomes

\[
\tau^{-1} \propto (k - k_F)^2 \log|k - k_F|
\]

MANY-BODY EFFECTS IN GRAPHENE

The quasiparticle properties are anyhow significantly renormalized due to the strong Coulomb interaction:

\[
\frac{1}{G} = \frac{1}{G_0} - \Sigma
\]

\[
G(k, \omega) = \frac{Z}{\omega - Z v_F \sigma \cdot k + i \Gamma(\omega)}
\]

\[
\Sigma(k, \omega) = \sum_{n=1}^{\infty} \frac{1}{n^2}
\]

\[
Z(\omega) \approx 1 + c \alpha^2 \log(\Lambda / \omega)
\]

\[
Z_v(\omega) \approx 1 + c' \alpha \log(\Lambda / \omega)
\]

\[
\Gamma(\omega) \sim \alpha^2 \omega
\]

The effective coupling \( \alpha \equiv e^2/4\pi v_F \) flows to zero at low energies due to the enhancement of the Fermi velocity, leading the system towards the non-interacting regime. This behavior has been observed in experiments carried out in graphene at very low electronic densities

\[
\]
MANY-BODY EFFECTS IN GRAPHENE

We now turn to phonons as the relevant source of scattering at low carrier densities. At low temperatures we have the contribution of acoustic phonons

\[
\tau^{-1} = - \text{Im} \Sigma(k, v_F | k|) \propto g^2 \varepsilon(k) k_B T
\]

This gives rise to a decay rate linearly proportional to the quasiparticle energy. Using Boltzmann transport theory, we obtain a resistivity that does not depend on carrier density and is linearly proportional to temperature

\[
\sigma_{ac}(\varepsilon_F) = \frac{1}{2} e^2 v_F^2 D(\varepsilon_F) \tau(\varepsilon_F)
\]

\[
= \frac{e^2}{h} \frac{8 \rho_m \hbar^2 v_{ph}^2}{g^2} \frac{1}{k_B T}
\]

RESISTIVITY AND MOBILITY IN GRAPHENE

The theoretical results have to be matched with the experimental measures of the resistivity.

It is assumed that the resistivity has a contribution from impurities, another from acoustic phonon scattering, and some extra contributions accounting for $T$-dependent nonlinear behavior

$$\rho(V_g, T) = \rho_{\text{imp}}(V_g) + \rho_{\text{ac}}(T) + \rho_{\text{nl}}(V_g, T)$$

The hope is to be able to remove the contribution from impurities, in order to remain with the intrinsic source of resistivity (phonons). In that case the mobility would be enhanced at low carrier density as

$$\mu(T) = \frac{\sigma_{\text{ac}}(T)}{e n}$$

Graphene seems therefore a quite exciting material from the experimental as well as from the theoretical point of view, with many other aspects besides those covered here:

- electronic properties of bilayer and multilayer graphene, leading in particular to the possibility of opening a gap in bilayer graphene with a transverse electric field

- influence of the strain in the carbon layer, and the ability to mimic the effect of magnetic fields with appropriate engineering of the applied stress

- role of the adsorbates in graphene, with the development of a metal-insulator transition at sufficiently large concentration of adsorbed molecules

- effect of vacancies and impurities in the formation of local magnetic moments in the carbon layer