

# ELECTRONIC AND OPTICAL PROPERTIES OF GRAPHENE



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Graphene has opened the way to investigate the behavior of a genuine two-dimensional material:

- very large mechanical strength, flexibility, transparency and conductivity
- electrons show remarkable properties from the theoretical point of view (relativisticlike behavior)



(J. C. Meyer et al., Nano Lett. 8, 3582 (2008))



From E. Stolyarova *et al.,* Proc. Natl. Acad. Sci. 104, 9209 (2007) But ... some challenges have to be faced:

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

#### PHYSICAL REVIEW

#### VOLUME 71, NUMBER 9

MAY 1, 1947

#### The Band Theory of Graphite

P. R. WALLACE\* National Research Council of Granda, Chalk River Laboratory, Chalk River, Ontario (Received December 19, 1946)

The structure of the electronic energy bands and Brillouin zones for graphite is developed using the "tight binding" approximation. Graphite is found to be a semi-conductor with zero activation energy, i.e., there are no free electrons at zero temperature, but they are created at higher temperatures by excitation to a band contiguous to the highest one which is normally filled. The electrical conductivity is treated with assumptions about the mean free path. It is found to be about 100 times as great parallel to as across crystal planes. A large and anisotropic diamagnetic susceptibility is predicted for the conduction electrons; this is greatest for fields across the layers. The volume optical absorption is accounted for.

#### PHYSICAL REVIEW

#### LETTERS

VOLUME 53

#### Condensed-Matter Simulation of a Three-Dimensional Anomaly

24 DECEMBER 1984

Gordon W. Semenoff The Institute for Advanced Study, Princeton, New Jersey 08540, and Department of Physics,<sup>(a)</sup> University of British Columbia, Vancouver, British Columbia V6T2A6, Canada (Received 4 September 1984)

A condensed-matter analog of (2+1)-dimensional electrodynamics is constructed, and the consequences of a recently discovered anomaly in such systems are discussed.

#### Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,<sup>1</sup> A. K. Geim,<sup>1</sup>\* S. V. Morozov,<sup>2</sup> D. Jiang,<sup>1</sup> Y. Zhang,<sup>1</sup> S. V. Dubonos,<sup>2</sup> I. V. Grigorieva,<sup>1</sup> A. A. Firsov<sup>2</sup>

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10<sup>13</sup> per square centimeter and with room-temperature mobilities of ~ 10,000 squae.

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 an electric current through it. As the

<sup>1</sup>Department of Physics, University of Manchester, Manchester M13 9PL, UK. <sup>2</sup>Institute for Microelectronics Technology, 142432 Chemogolovka, Russia. \*To whom correspondence should be addressed. E-mail: gen@man.ac.uk 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 allmetallic 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 atomically 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 insurroundable obstacle to metallic electronics, and no metal or semimetal has been shown to exhibit any notable (>1%) field effect (4).

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We report the observation of the electric field effect in a naturally occurring twodimensional (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 benzene-ring 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) (5-7). 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 (5-14).



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The electronic properties can be understood from a simple tight-binding model

$$H_{tb} = -t \sum \psi_{\circ}^{+}(\mathbf{r}') \ \psi_{\bullet}(\mathbf{r}) - t \sum \psi_{\bullet}^{+}(\mathbf{r}') \ \psi_{\circ}(\mathbf{r})$$

$$H = -t \begin{pmatrix} 0 & \sum_{j=1,2,3} e^{i\mathbf{K}\cdot\mathbf{v}_j} \\ \sum_{j=1,2,3} e^{-i\mathbf{K}\cdot\mathbf{v}_j} & 0 \end{pmatrix}$$

 $\varepsilon(\mathbf{K}) = \pm t \sqrt{1 + 4\cos^2(aK_y/2) + 4\cos(aK_y/2)\cos(\sqrt{3}aK_x/2)}$ 



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

$$H \approx \frac{3}{2} ta \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix}$$

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

 $\varepsilon(\mathbf{k}) \approx \pm v_F |\mathbf{k}| , \quad D(\varepsilon) \propto |\varepsilon|$ 

The scattering from disorder is very 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  $\pi$ 

$$W = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\phi/2} \\ \pm e^{i\phi/2} \end{pmatrix}$$

$$H = v_F \begin{pmatrix} 0 & |\mathbf{k}| e^{-i\phi} \\ |\mathbf{k}| e^{i\phi} & 0 \end{pmatrix} \longrightarrow \qquad \psi = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\phi/2} \\ \pm e^{i\phi/2} \end{pmatrix}$$

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)).

$$w \sim |A_{c} + A_{c}|^{2} = |A_{c}|^{2} + |A_{c}|^{2} + |A_{c} + A_{c} + A_{c}$$



$$A_{A_{a}}^{*} = e^{-i2\pi(\sigma_{z}/2)} |A_{a}|^{2} = -|A_{a}|^{2} < 0$$

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

 $\mathbf{r} \cdot \frac{\mathbf{k}}{|\mathbf{k}|}$ 



which commutes with the Dirac hamiltonian  $H = v_F \mathbf{\sigma} \cdot \mathbf{k}$ .

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





M. I. Katsnelson, K. S. Novoselov, and A. K. Geim, Nature Physics 2, 620 (2006)

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, moving the Fermi level with the gate voltage, a substantial concentration of electrons (or holes) can be induced



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



 $n \propto V_{g}$ 



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

$$\sigma_{xy} = \frac{4e^2}{h} \left( n + \frac{1}{2} \right)$$

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, that is,  $\sigma \propto \varepsilon_F^2$ 

This requires a particular type of scatterers for which  $\tau \propto \epsilon$ 

- > in the case of short-range scatterers,  $\tau \propto 1/k \Rightarrow \sigma = \text{const.}$
- > in the case of charged Coulomb scatterers,  $\tau \propto k \Rightarrow \sigma \propto \varepsilon^2$











The nonvanishing conductivity at the Dirac point can be also understood starting from the linear quasiparticle dispersion  $\varepsilon = \pm v_F k$ .

The conductivity can be computed from the Kubo formula

$$\sigma(\omega) = \frac{ie^2}{\omega} \lim_{\mathbf{q} \to 0} \langle \mathbf{j}(\mathbf{q}, \omega) \mathbf{j}(-\mathbf{q}, -\omega) \rangle$$

which, using the continuity equation  $\partial_t \rho = \partial \cdot \mathbf{j}$ , can be converted into

$$\sigma(\omega) = ie^2 \lim_{\mathbf{q}\to 0} \frac{\omega}{\mathbf{q}^2} \langle \rho(\mathbf{q},\omega) \rho(-\mathbf{q},-\omega) \rangle$$

The density-density correlator corresponds to the charge susceptibility



$$\chi(\mathbf{q},\omega) = \frac{\mathbf{q}^2}{4\hbar\sqrt{v_F^2\mathbf{q}^2 - \omega^2}}$$



and leads to a nonvanishing DC conductivity

$$F(\omega=0) = \frac{e^2}{4\hbar}$$

However, the question of the minimum conductivity of undoped graphene is not so simple, and there has been a long controversy regarding whether it should be given by a "universal" value.

The experimental measures were pointing at a value equal to four times the quantum of conductance  $\sigma \approx 4e^2/h$ , in disagreement with the theoretical prediction for clean graphene

$$\sigma(\omega=0) = \frac{\pi}{2} \frac{e^2}{h}$$



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

and above the more realistic result obtained after including the effect of disorder

$$\sigma(\omega=0) = \frac{4}{\pi} \frac{e^2}{h}$$

(the mystery of the missing  $\pi$ ).

Nowadays we know that the interaction with some substrates may give rise to a minimum value of  $\sigma$ . Thus, charged impurities in SiO<sub>2</sub> lead to the formation of electron-hole puddles in graphene, and percolation of the electron current is what produces a value  $\sigma \approx 4e^2/h$ .



J. Martin et al., Nat. Phys. 4, 144 (2008)

Away from zero frequency and  $\varepsilon_F \neq 0$ , we can also test the ac conductivity

$$\sigma'(\omega) = \frac{e^2}{4\hbar} \Theta(\hbar\omega - 2\varepsilon_F)$$

which, with more generality, becomes for nonvanishing temperature

$$\sigma'(\omega) = \frac{e^2}{4\hbar} \frac{\sinh\left(\frac{\hbar\omega}{2k_BT}\right)}{\cosh\left(\frac{\varepsilon_F}{k_BT}\right) + \cosh\left(\frac{\hbar\omega}{2k_BT}\right)}$$





This behavior is consistent with the results of the experiments carried out with infrared spectroscopy:



Z. Q. Li *et al.*, Nature Phys. 4, 532 (2008)

The knowledge of the optical conductivity allows also to obtain the transmission of light, by solving the Maxwell equations

$$\nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = \frac{\omega^2}{c^2} \mathbf{E} + \frac{i\omega}{c^2} \mathbf{j}$$

with the current  $j_x = \sigma(\omega) \,\delta(z) \, E_x$ 

The optical transmittance turns out to be given by

$$T = \frac{1}{\left(1 + \frac{\sigma}{2c}\right)^2} \approx 1 - \pi\alpha \quad (\approx 0.977)$$



which is in agreement with the experimental observations



R. R. Nair *et al.*, Science 320, 1308 (2008)



# A direct evidence of the conical dispersion has been obtained with angle-resolved photoemission spectroscopy





A. Bostwick et al., Nature Phys. 3, 36 (2007)

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



A. Bostwick et al., Nature Phys. 3, 36 (2007)

The quasiparticle properties are anyhow significantly renormalized due to the strong Coulomb interaction, which has a coupling  $\lambda \equiv e^2/4\pi v_F$ :



 $Z(\omega) \approx 1 - c \lambda^2 \log(\Lambda/\omega)$  $Z_{\nu}(\omega) \approx 1 + c' \lambda \log(\Lambda/\omega)$ 

The effective coupling  $\lambda \equiv e^2/4\pi v_F$  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  $\langle \Psi(\mathbf{r},t) \Psi^{+}(\mathbf{r}',t') \rangle = iG(\mathbf{r}-\mathbf{r}',t-t')$ 

$$G(\mathbf{k},\omega) = \frac{Z}{\omega - Z_{\nu} v_F \mathbf{\sigma} \cdot \mathbf{k} + i\Gamma}$$

(J. G., F. Guinea and M. A. H. Vozmediano, Phys. Rev. B 59, R2474 (1999))



(D. C. Elias et al., Nature Phys. 7, 701 (2011))

Turning now to the imaginary part  $\Gamma$ , we can analyze the way in which the scattering of electrons gives rise to a finite lifetime for the electron quasiparticles.

In the undoped system, the electron quasiparticles cannot decay into electron-hole pairs



$$\varepsilon(\mathbf{q},\omega) = 1 + \frac{e^2}{2|\mathbf{q}|} \frac{\mathbf{q}^2}{4\sqrt{v_F^2 \mathbf{q}^2 - \omega^2}}$$

$$\tau^{-1} = \Gamma(\mathbf{k}, \omega = v_F |\mathbf{k}|) = 0$$

$$G(\mathbf{k},\omega) = \frac{Z}{\omega - Z_v v_F \mathbf{\sigma} \cdot \mathbf{k} + i\Gamma}$$



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



The quasiparticle decay rate becomes

$$\tau^{-1} \propto (k - k_F)^2 \log \left( \left| k - k_F \right| \right)$$



E. H. Hwang, Ben Yu-Kuang Hu and S. Das Sarma, Phys. Rev. B **76**, 115434 (2007)

We can also compute the electronic response to an external potential  $V_{\text{ex}}(\mathbf{q},\omega)$ , expressing the screening effects in terms of the dielectric function

$$V(\mathbf{q}, \omega) = V_{\text{ex}}(\mathbf{q}, \omega) + V_{\text{scr}}(\mathbf{q}, \omega)$$
$$= \frac{1}{\varepsilon(\mathbf{q}, \omega)} V_{\text{ex}}(\mathbf{q}, \omega)$$

The poles in  $1/\varepsilon(\mathbf{q},\omega)$  account for the existence of collective excitations of electrons (plasmons)

$$\varepsilon(\mathbf{q},\omega) = 1 + \frac{e^2}{2|\mathbf{q}|} \chi(\mathbf{q},\omega) = 0$$

But plasmons can only arise in the case of doped graphene, with dispersion

$$\omega_P(\mathbf{q}) \propto \sqrt{\varepsilon_F |\mathbf{q}|}$$





The plasmon dispersion has been measured with great accuracy in experiments with infrared nanoscopy

> Z. Fei *et al.,* Nano Lett. 11, 4701 (2011)



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



 $\tau^{-1} = \Gamma(\mathbf{k}, v_F | \mathbf{k} |) \propto g^2 \varepsilon(\mathbf{k}) k_B T$ 



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 lineraly proportional to temperature

$$\sigma_{ph}(\varepsilon_F) = \frac{1}{2} e^2 v_F^2 D(\varepsilon_F) \tau(\varepsilon_F)$$
$$\propto \frac{e^2}{h} \frac{1}{g^2} \frac{1}{k_B T}$$



S. Das Sarma and E. H. Hwang, Phys. Rev. B **87**, 035415 (2013)

The theoretical results have to 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

$$\rho(V_g,T) = \rho_{\rm imp}(V_g) + \rho_{\rm ph}(T) + \rho_{\rm nl}(V_g,T)$$







$$u(T) = \frac{\sigma_{ph}(T)}{e n}$$



J.-H. Chen et al., Nature Nanotech. 3, 206 (2008)

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