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PROPERTIES AND APPLICATIONS OF GRAPHENE

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Abstract. *The paper presents the properties and applications of graphene, focused on the results obtained by the author. Because in graphene the charge carriers satisfy a massless Dirac equation, it can serve as testing material for several predictions of high-energy physics. Graphene applications are based on its unique mechanical, optical and electrical properties, which generally lead to devices with superior performances compared to those fabricated with other materials. However, to fully benefit from the distinctive properties of graphene, novel device configurations should be searched for instead of implementing common devices*.

Keywords: graphene, charge transport, nanodevices

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1. Introduction

Graphene is a one-atom thick crystal containing carbon atoms in a hexagonal lattice, which can be obtained by peeling graphite [1]. Although the theory of graphene has been known for a long time [2], it was actually fabricated in 2004 [3] and has attracted interest ever since, being the first known two-dimensional material. The mechanical properties of graphene and of few-layer graphene materials are a consequence of the strong in-plane σ bond that forms between the sp^2 hybridized carbon orbitals, while the optical and electronic properties are determined by the π bonds, which form between the out-of-plane un-hybridized p orbitals. Although the mechanical properties of graphene are among the best [4], this material being characterized by an elastic limit of about 20%, the interest in graphene is mainly related to its particular bandstructure. Some properties of graphene are summarized in Table I. It should be mentioned that the actual properties of graphene flakes depend on the fabrication method [5].

Table 1) Properties of graphene

Property	*Value*	*Observation*
Young modulus	1 TPa	5 times higher than in steel
Breaking strength	42 N/m	100 times greater than in steel
Room-temperature mobility (in suspended graphene)	200,000 $cm^2V^{-1}s^{-1}$	100 times higher than in Si
Current density	> 108 A/cm	100 times larger than in Cu
Thermal conductivity	5000 $Wm^{-1}K^{-1}$	10 times higher than in Cu
Light absorption coefficient	2.3 %	50 times higher than in GaAs

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2. Low-energy charge carrier propagation in graphene

The hexagonal lattice of graphene can be considered as resulting from a superposition of two triangular lattices, represented by full and empty circles in Fig. 1(a), the unit cell being spanned by the vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$. The Brillouin zone, shown in Fig. 1(b), is also hexagonal, the two unequivalent corners being denoted by K and K'. These points are called Dirac points.

In the first approximation, if only hopping between neighboring C atoms that are part of different triangular lattices is taken into account, the Hamiltonian can be expressed as

$$H = -t\sum_{\boldsymbol{r}}[b^+(\boldsymbol{r})a(\boldsymbol{r}) + b^+(\boldsymbol{r}-\boldsymbol{a}_1)a(\boldsymbol{r}) + b^+(\boldsymbol{r}-\boldsymbol{a}_2)a(\boldsymbol{r}) + \text{h.c.}] \tag{1}$$

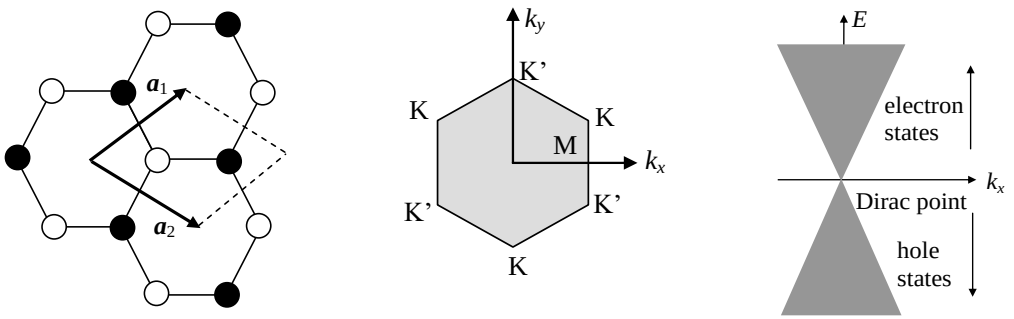
where $t \cong 2.8$ eV is the in-plane hopping energy, and the dispersion relation is given by

$$E_\pm(\boldsymbol{k}) = \pm t\sqrt{3 + 2\cos(\sqrt{3}k_y a) + 4\cos(\sqrt{3}k_y a/2)\cos(3k_x a/2)} \tag{2}$$

where a = 1.42 Å is the distance between two C atoms. This dispersion relation can be linearized in the neighborhood of the Dirac points (see Fig. 1(c)):

$$E_\pm(\boldsymbol{k}) = \pm\hbar v_F\,|\boldsymbol{k}| \tag{3}$$

where the wavevector $\boldsymbol{k}$ is measured from K or K', the plus and minus signs being associated to electron and hole states, respectively. Graphene is thus a material without bandgap, the upper and lower energy bands touching at the Dirac points. It is a gapless semiconductor, with dispersion relation in the form of Dirac cones.



a **b** **c**

Fig. 1. a. The honeycomb lattice structure, **b.** the first Brillouin zone and **c.** the linear dispersion relation in graphene

The linear dispersion relation in graphene in the low-energy limit has been confirmed by several experiments, in particular by ARPES [6]. It should be noted

that the dispersion relation of electrons and holes in graphene is similar to the ultrarelativistic limit of massive fermions propagating with a velocity $c = v_F$.

The unique properties of charge carriers in graphene compared to other solid state materials is revealed by the linear dispersion relation (3), which is different from the parabolic one in common semiconductors obeying the non-relativistic Schrödinger equation, and by the fact that electrons and holes in graphene obey a massless Dirac-like equation:

$$\hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = (E - V) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \tag{4}$$

The spinorial wavefunction $\psi^T = (\psi_1, \psi_2)$ is similar to that for ultrarelativistic fermions but with an important difference: the two components of the spinors do not correspond to different spin orientations (spin-up and spin-down), but to the contributions of the two triangular lattices of the hexagonal crystalline structure of graphene. As such, graphene, in the low-energy regime, can be used for testing high-energy theories.

It should be mentioned that bilayer graphene, formed from two graphene layers between which charge carrier hopping can occur, satisfies in the low-energy approximation the equation

$$\frac{\hbar^2}{2m} \begin{pmatrix} 0 & (k_x - ik_y)^2 \\ (k_x + ik_y)^2 & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = (E - V) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \tag{5}$$

which describes (otherwise, hypothetical) massive chiral fermions. The mass of charge carriers in bilayer graphene is related to the inter-layer hopping energy γ by $m = \gamma / 2v_F^2 \cong 0.054 m_0$.

Relation (3) for charge carriers is also similar to the linear dispersion relation for photons, the Fermi velocity $v_F \cong 10^6$ m/s being replaced in the last case by the light velocity in vacuum, $c \cong 3 \times 10^8$ m/s. However, this similarity cannot be extended further, although the spinorial wavefunction in graphene is formally analogous to the Jones vector of polarized light in optics [7], for example. Indeed, the Jones vector of a polarized electromagnetic radiation with electric field components E_x and E_y is defined as $J^T = (E_x, E_y)$, and propagation of ballistic charge carriers through a graphene region with constant potential energy can be mimicked in optics by a phase retarder. However, because the boundary conditions are different in the two cases, no optical system can be found that would be equivalent to a succession of regions with different potential energies in graphene. The same conclusion arises also if the spinorial wavefunction is put into correspondence with the electric and magnetic fields of the electromagnetic

radiation [8], and even when analogies with an electro-optic and gyrotropic optical medium is attempted. In the last case, the Jones vector of a monochromatic light field with frequency ω satisfies an equation very similar to that of charge carriers in graphene:

$$(c^2\kappa^2/\omega^2-\varepsilon)\begin{pmatrix}E_x\\E_y\end{pmatrix}=\begin{pmatrix}0 & \beta-i\gamma\\ \beta+i\gamma & 0\end{pmatrix}\begin{pmatrix}E_x\\E_y\end{pmatrix} \tag{6}$$

where ε, β and γ are the permittivity, electro-optic and gyrotropic coefficients of the medium, respectively, and κ is the propagation constant. However, since, again, the boundary conditions differ no exact optical analogy with charge carrier propagation in graphene can be established [9]; only structures with the same reflection or transmission coefficients can be found.

As mentioned before, graphene can be used to test several high-energy predictions, in particular the Klein paradox. According to Klein paradox, particles with mass m can be transmitted with a coefficient higher than 1 through an interface with a sufficiently high potential barrier (with a height higher than $2mc^2$) can occur, provided that particle-antiparticle pairs are created. This prediction has not been experimentally demonstrated in high-energy physics because potential barriers with very high heights are needed. However, in graphene, for which m = 0, this prediction can be tested for any potential barrier, that can be applied via a suitable gate potential. Indeed, both theory [10] and experiments [11] show that charge carriers are transmitted with unit coefficient at normal incidence on a *p-n* junction, suggesting that no particle-antiparticle pairs are created.

Graphene can thus be used to answer fundamental physical questions. However, charge carrier propagation through this material is not completely understood. In particular, the experimental existence of a finite minimum conductivity, with a value of $4e^2/h$, can be explained only by a measurement-induced energy-time uncertainty [12], any other theories (including mean-field theories, disordered-averaged propagators, etc.) being unable to reproduce this minimum conductivity value.

Graphene has a particular behavior also in magnetic fields. Unlike materials in which charge carriers obey the Schrödinger equation, and in which the discrete Landau levels are given by $E_n=\hbar\omega_c(n+1/2)$ with $\omega_c=eB/m$, in graphene the Landau levels have a different expression: $E_n=\pm\hbar\omega_c\sqrt{|n|}$, with a cyclotronic frequency $\omega_c=v_F\sqrt{2eB/\hbar c}$. Thus, graphene differs from other materials in practically any respect.

3. Graphene applications

As mentioned previously, the interest in graphene is related to its unique bandstructure. Both optical and electronic properties of graphene are determined by its unique dispersion relation.

In particular, each graphene layer is characterized by a linear absorption coefficient of $\pi e^2 / \hbar c \cong 2.3\%$, which has only weak wavelength dependence [13]. The value of the absorption coefficient is remarkably high for such a thin material, but its wavelength-independence is not encountered in any other material. Therefore, graphene, and in particular graphene ink, placed above an interdigitated electrode, can act as photodetector in a wide range of wavelengths, from UV up to NIR [14]. The responsivity of the detector can be enhanced by functionalizing the graphene ink with Ag nanoparticles, with a diameter of about 55 nm. As expected, if the fingers of the interdigitated electrode are made from different metals, Au and Pt, for example, a photovoltaic response is obtained over the same wide range of frequencies [15].

The nonlinear optical properties of graphene are also influenced by its unique band structure, which determines a distinctive nonlinear response to an excitation with frequency f_0, such that the intensities of higher-order harmonics are comparable. More precisely, the intensity of the *n*th harmonic is predicted to depend as $1/n$ [16], such that harmonics up to the 7^{th} order can be easily obtained from an input signal with a frequency of 1 GHz and a power of 1.4 dBm [17].

Because of its extreme thinness and large conductivity, graphene has found numerous applications in nanoelectronics. The first field-effect transistor (FET) was demonstrated in 2007 [18], the main objective being to enhance the density of graphene FETs, up to values of the order of 40,000 GFET/cm^2 [19], as well as to increase their operating frequencies. The cut-off frequencies of graphene FETs are reaching today some hundreds of GHz [20], other devices such as graphene-based switches integrated on coplanar lines operating also in the GHz range [21].

One of the principal issues to be solved in graphene electronics, which is a direct consequence of the massless Dirac equation, is the impossibility to modulate the transmission of normally incident charge carriers by electrostatic potentials only. This is a disadvantage because nanodevices are based on transmission modulation, but can be avoided by fabricating heterostructures comprising other two-dimensional materials, with bandgap. For example, graphene-BN [22], graphene-MoS_2 FETs [23] or even graphene-BN-MoS_2 FETs [24] have been demonstrated. Alternatively, bandgaps in graphene can be opened by cutting the flake in very narrow nanoribbons [25], or by employing heterostructures containing flakes with a different number of graphene layers [26]. Thus, the future of graphene nanoelectronics is not impeded by apparent disadvantages. The

advantages of graphene devices are even more evident when their conduction properties are combined with their unique optical and/or mechanical characteristics. The thinness, flexibility, and almost total optical transmission of graphene make it suitable for transparent and flexible electronics [27], artificial retina [28] being recently fabricated using such circuits.

All the above mentioned graphene-based electronic devices mimic, often with better performances, devices that can be implemented with other materials. However, there are also devices specifically conceived taking into account he unique charge carrier transport in graphene. Among these, a single oblique gate on graphene acts as a negative differential resistance [29], the maximum in current being due to a forbidden region for conductance, while the same effect is obtained in usual negative differential resistance devices by resonant tunneling in a structure containing a quantum well surrounded by two barriers. The possibility of miniaturizing such devices is evident; a graphene-based negative differential resistance device was recently demonstrated on high-quality graphene at wafer scale [30].

The possibility to modulate charge carrier transmission via one, two or several oblique gates can also be used to implement reversible logic gates [31] and circuits containing a small number of gates, diodes with ideality factors lower than 1 (impossible to obtain otherwise) [32], or to generate ultrashort pulses [33]. Nevertheless, there are technological difficulties to fabricate oblique gates in a reproducible manner in miniaturized devices.

On the other hand, graphene superlattices containing periodic successions of regions with different potential energies, which can be tuned using gate electrodes, have considerable applications as thermoelectric devices [34], or as switches, beam-splitters, beam-shapers and steerers of ballistic electrons [35]. It should be mentioned that the periodicity of the superlattice affects the linear dispersion relation in graphene, the structure becoming actually equivalent to bilayer-like graphene, in which the mass is determined by the periodicity-induced curvature of the dispersion relation [36]. Another feasible method to control charge carrier transport in graphene via introducing a controllable bandgap is to fabricate arrays of nanoholes. Indeed, e-beam fabrication/patterning of nanoholes with a diameter of 100 nm and distance between holes of 100 nm is able to open a bandgap of about 0.18 eV [37]. Such a value is large enough to be of use in electronic devices, the graphene field-effect transistors with nanopatterned channels showing an on/off ratio of at least 10^3 at room temperature.

Although nanopatterning of graphene is expected to reduce the mobility of charge carriers by generating holes in the material, which can be assimilated with defects, the opposite occurs. Indeed, experiments have shown that in graphene transistors

with channels consisting of periodic arrays of nanoholes with period of 100 nm and hole diameter of 200 nm, the mobility of charge carriers at room temperature attains values over 10000 $cm^2V^{-1}s^{-1}$ for channel lengths of 1 μm, value that is still very high, of 550 $cm^2V^{-1}s^{-1}$ in transistors with 8 μm-long channels [38]. These experimental findings, although explainable by theory, emphasize the need to further investigate graphene and graphene-based configurations both theoretically and experimentally.

It should be mentioned that transmission modulation of charge carriers in graphene can also be achieved via applied magnetic fields, the discrete Landau levels being used to filter electrons with different energies [39], for example. Such a spectrometer for ballistic electrons can be miniaturized by using magnetic nanowires as the source of the magnetic field.

4. Perspectives of graphene-based devices

The previous section presented the basic devices based on graphene. The advantage of this material resides in its unique electronic, optical and mechanical properties. Most graphene-based devices have either better performances or are smaller than similar devices fabricated with usual materials, in which charge carriers satisfy a Schrödinger equation. Thus, it seems that there is just a matter of time until mechanical, electronic, or optoelectronic devices based on graphene will supersede other similar devices. However, there are also several problems that need to be solved first. One of them regards the fabrication of large-enough high-quality graphene flakes. Although advances are continuously made, this issue is not yet solved. Paradoxically, the best quality graphene flakes are still obtained by the original mechanical peeling method, in which scotch tapes are used to peel monolayers from high-quality graphite. Another, more interesting problem from a physical point of view, deals with charge carrier propagation at graphene-metal contacts.

This last problem has two components. The first one is a material-related issue. It is known that the quality and the type (ohmic or Schottky) of contacts depend on the metal [40,41]. In particular the Dirac points can disappear at contacts with chemisorbed materials such as Co, Ni, Pd. However, the quality of graphene/ metal interface depends very much on the fabrication conditions of electrodes. In particular, carbon atoms can penetrate into the metal, the roughness influences the interface quality, etc., so that there is no well established agreement between theoretical simulations (by whatever methood/computational tool) and experimental results regarding charge carrier transport at the graphene/metal interface. The second problem is of a fundamental nature. It deals with the transformation of Schrödinger-like electrons in contacts to Dirac-like electrons in graphene and back again. The boundary conditions at such Dirac-Schrödinger

interfaces are not unique. From similar interfaces in optics we know that the only condition that can be required is the conservation of the probability current density, which is, however, not enough to define the appropriate continuity condition at the interfaces. A whole class of boundary conditions can be envisaged [42], future experiments on optical analogues (much easier to control) being probably required to settle this problem. Here, again, we deal with the sensitive problem of the validity of optics/ballistic charge carriers analogy and with the experimental difficulties in assuring ballistic transport over large enough distances. It should be noted that these different boundary conditions affect measurable quantities such as transmission and traversal time [43].

5. Conclusions

Since its discovery, graphene was referred to as a "wonder material". It is a justified description. Graphene is unique in its properties because it is the only known material in which charge carriers behave as massless Dirac-like electrons. Several other two-dimensional materials have been discovered recently. None of them has the same properties. Silicene and germanene, which are hexagonal honeycomb crystals from Si and Ge atoms, respectively, are thought to be similar to graphene, in the sense that Dirac cones can be observed, but this similarity is not exact. More precisely, graphene is a truly two-dimensional, planar material, whereas silicene and germanene have buckled structures, since the Si and Ge atoms tend to form sp^3 bonds rather than sp^2 bonds, as in graphene. Therefore, the wondrous mechanical, electrical and optical properties of graphene are likely to not be found in these materials, at least not all of them.

As a result of its unique properties, graphene has spurred an unprecedented interest in fundamental and applied physics. Many high-energy theories could be tested in graphene provided that proper identification of analogous parameters can be made. On the other hand, faster and smaller devices can be fabricated using this material, as long as it is grown with high-enough quality. Moreover, innovative configurations could be imagined, which use the peculiar physics of graphene. Both graphene-related fundamental and applied physics has attracted interest in recent years, and there are still many challenges that must be overcome in order to better understand and exploit this truly wonder material.

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