GRAPHENE: A NANOSCALE QUANTUM PLAYING FIELD

by Tapash Chakraborty

Graphite, despite being a rather common material, whose properties are well established for many decades and has a wide range of industrial applications, is still capable of creating quite a sensation in the physics community [1-4] with recent reports that single layers of graphite, called graphene, have been isolated for the first time [5,6] and 'unusual' quantum properties were found in such systems [7-9].

Graphene layers have been created by mechanical exfoliation (repeated peeling) of small mesas of graphite [Fig. 1]. These layers exhibit a strong electric-field effect which promises their potential use in nanoelectronics. In addition, their much higher current densities and shorter screening lengths than doped semiconductors make them more attractive for future applications in novel carbon-based electric and magnetic field effect devices. Work on graphene is now progressing at a 'Mozartian speed' and more and more remarkable properties of graphene are discovered quite regularly. However, in order to understand those unusual electronic properties, we need to understand the crystal structures and importantly, the band structure calculations pioneered by P.R. Wallace, sixty years ago [10,11].

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FUNDAMENTALS

A single graphene layer has a honeycomb lattice structure with two atoms A and B per unit cell (*i.e.*, it is a two-dimensional triangular Bravais lattice with a basis of two atoms) [Fig. 2(a)]. Each atom is tied with its three nearest neighbours via strong σ bonds that act in the same plane with angles of 120°. The σ bond is a result of the sp^2 hybridization of the $2s$, $2p_x$, and $2p_y$ orbitals for the three valence electrons. The fourth valence electron is in the $2p_z$ orbital that is orthogonal to the graphene plane. A weak π bond is formed by the overlap of one half-filled $2p_z$ orbital with the other $2p_z$ orbitals. Transport properties of graphene are determined by these delocalized π electrons [12].

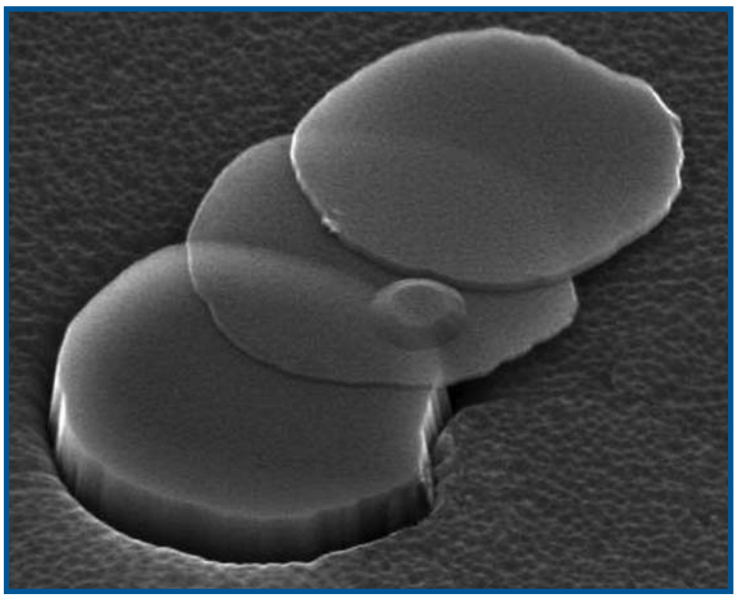

Fig. 1 Scanning electron micrograph of a fallen mesa of graphite. This is the way graphene molecules were "extracted" from bulk graphite. To be reasonably visible in SEM, a 10 nm carbon flake (30 layer thick) is shown. Courtesy of K. Novoselov, University of Manchester, http://onnes.ph.man.ac.uk/nano/Images.html

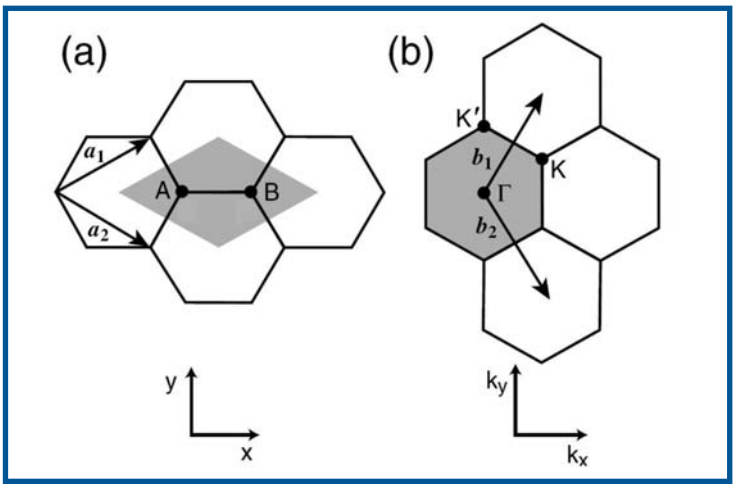

Fig. 2: (a) Graphene lattice in real space, and (b) the corresponding reciprocal lattice. The unit cell in the graphene lattice (shaded rhombus) contains two atoms A and B. The first Brillouin zone is drawn as shaded hexagon. The basis vectors of the direct lattice and the reciprocal lattice are a_i and b_i (i = 1,2) respectively.

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Band structure

The dispersion relation of the π electrons in graphene was first calculated by Wallace [10] in the tight-binding approximation, and is

$$\mathcal{E}(k_x, k_y) = \pm\gamma\left[1 + 4\cos\left(\sqrt{3}k_x a/2\right)\cos(k_y a/2) + 4\cos^2(k_y a/2)\right]^{\frac{1}{2}}$$

where γ is the overlap integral between the nearest neighbours. The + (–) term corresponds to the antibonding (bonding) band. They are degenerate at the K (K′) point, where the Fermi energy lies as well [Fig. 3]. As there are two π electrons per unit cell, they fully occupy the lower π band. The first Brillouin zone is hexagonal and at two of its inequivalent corners (the K and K′ points) [Fig. 2(b)], the conduction and valence bands meet [Fig. 3]. Graphene is often described as a two valley (K and K′) zero-gap semiconductor, or a semimetal. Near the K points, the energy dispersion is well approximated by $\mathcal{E}(\mathbf{k}) = \pm\hbar\upsilon_F|\mathbf{k}|$, where $\boldsymbol{k}$ is measured with respect to the K (or K′) point, and $\upsilon_F \approx 10^6$ m/s is the Fermi velocity. The *linear* dispersion near the K and K′ points [Fig. 3], in contrast to the parabolic dispersion of the conventional electron systems, plays a crucial role in various electronic and transport properties of graphene described below.

Dirac fermions

In the continuum limit, and in the effective-mass approximation, the Hamiltonian near the K point is written as $H_K(\boldsymbol{k}) = \hbar\upsilon_F\boldsymbol{\sigma}\cdot\boldsymbol{k}$, where $\boldsymbol{\sigma}$ are the 2 x 2 Pauli matrices. The Schrödinger equation then transforms into the relativistic Dirac equation with a zero rest mass that is known as the Weyl's equation for a neutrino [13]. We therefore have a unique case of Dirac fermions in condensed matter. The wave functions of these Dirac-Weyl particles have a spinor structure. For the K and K′ points, they are (without normalization)

$$\psi^{K}_{s,\boldsymbol{k}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\begin{pmatrix} s \\ e^{i\theta(\boldsymbol{k})} \end{pmatrix}; \psi^{K'}_{s,\boldsymbol{k}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\begin{pmatrix} e^{i\theta(\boldsymbol{k})} \\ s \end{pmatrix},$$

where s = +1 for the upper band and –1 for the lower band, $\tan\theta = k_y/k_x$, and the upper and lower terms correspond to the quantum mechanical amplitudes (or 'pseudospin') of finding the particle on one of the two sublattices, A and B. In graphene, the pseudospin direction is associated with the momentum of the particles. This means that the wave functions in the vicinity of the K and K′ points are 'chiral'. One consequence of this is that, any backscattering, *i.e.*, scattering of particles from the wave vector $\boldsymbol{k}$ to $-\boldsymbol{k}$ is suppressed [14]. Particles have opposite chirality in the K and K′ valleys or in the electron or hole bands [15]. The energy bands in the vicinity of these "Dirac points" (K and K′) are, $\mathcal{E} = \pm\hbar\upsilon_F|\boldsymbol{k}|$, where + (–) denotes the conduction (valence) band. They look like two cones with their pointed tips meeting at $k = 0$ [Fig. 3]. The charge carriers in graphene are usually described as 'massless Dirac fermions'.

The corresponding density of states varies linearly as a function of the energy and vanishes at $\mathcal{E} = 0$. This is in contrast to the conventional two-dimensional electrons, where the density of states is independent of the energy.

MAGNETIC ENERGY LEVELS

When a magnetic field $\boldsymbol{B}$ is applied perpendicular to a conventional two-dimensional electron gas, the energy levels quantize into the Landau levels with energies $\mathcal{E}_n = (n+\frac{1}{2})\,\hbar eB/m^*c$, where $n \geq 0$ is an integer, m^* is the effective mass and c is the speed of light. Due to the relativistic nature of electrons in graphene the energy spectrum of the Landau levels now are very different from the above expression. The energy of the nth Landau level (for the K valley) in graphene has the form [16-18], $\mathcal{E}_n = sgn(n)\sqrt{2e\hbar\upsilon_F^2|n|B/c}$, where $n = 0, \pm1, \pm2, \ldots$, and $sgn\,(j)$ denotes the signature of j, *i.e.*, $sgn\,(j) = +1$ for $j > 0$ and –1 for $j < 0$ and $sgn\,(n = 0) = 0$. One can derive similar expressions for the K' point. In addition to the Landau levels being unequally spaced in energy, the presence of a Landau level at $\mathcal{E} = 0$ that is independent of the magnetic field strength is a unique feature of the Dirac-Weyl electrons.

Quantum Hall effects

The discovery of the quantum Hall effect in a conventional (*i.e.*, non-relativistic) two-dimensional electron gas created at the interface of the semiconductor heterojunctions [19,20] has been a remarkable achievement in condensed matter physics, where two Nobel prizes (for the integer and fractional effects) were awarded. The basic features of these effects are that at low temperatures and in a strong magnetic field applied perpendicular to the electron plane, the Hall resistance R_H (inverse of the Hall conductance σ_{xy}) exhibits plateaus as a function of the magnetic field as $R_H = 1/\sigma_{xy} = h/ie^2$, where i can be an integer in the case of the integer quantum Hall effect or a small rational fraction in the case of the fractional quantum Hall effect [21]. When the Fermi energy lies in a Landau level gap, the filling factor $\nu = i$ corresponds to the number of filled Landau levels. The extremely accurate quantization of the Hall resistance to approximately one part in 10^8 resulted in the use of the integer effect as the international standard of resistance.

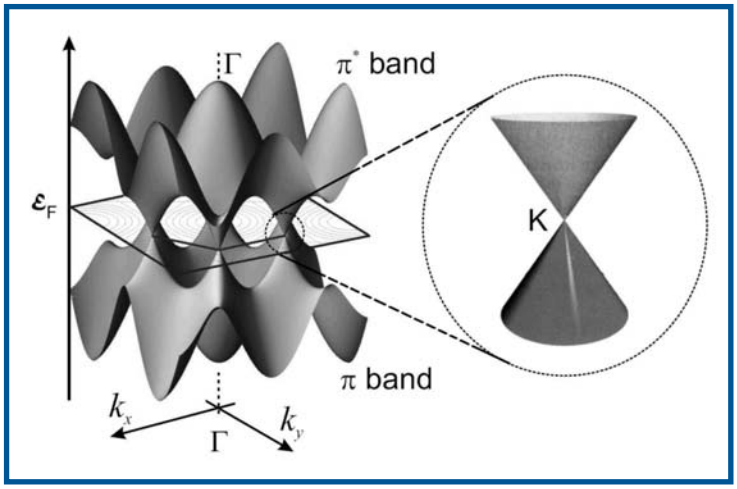

Fig. 3 **Band structure of graphene. Since we ignore the coupling between the graphene sheets, the bands depend only on k_x and k_y. The π band is completely filled and meets the totally empty π* band at the K and K′ points (Dirac points). Near these points both the bands have linear dispersion as described in the text.**

In graphene, a somewhat unusual quantum Hall effect was discovered which in fact, confirmed the Dirac nature of the electrons in that system [7-9]. From magnetoresistance measurements in the quantum Hall

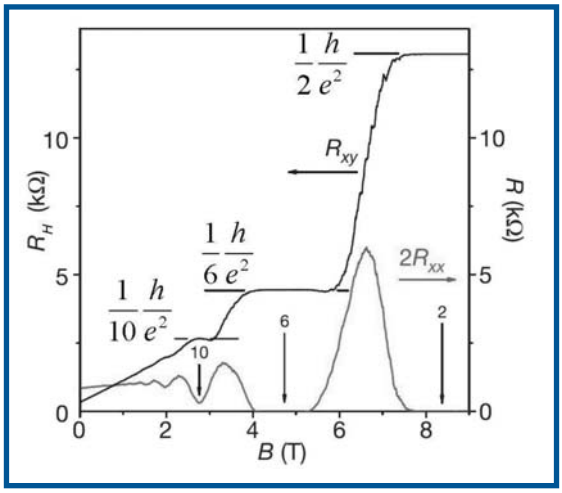

Fig. 4 Quantum Hall effect in graphene. The Hall resistance plateaus appear at the filling factors ν = 2,6, and 10 (adapted from Ref. [8]).

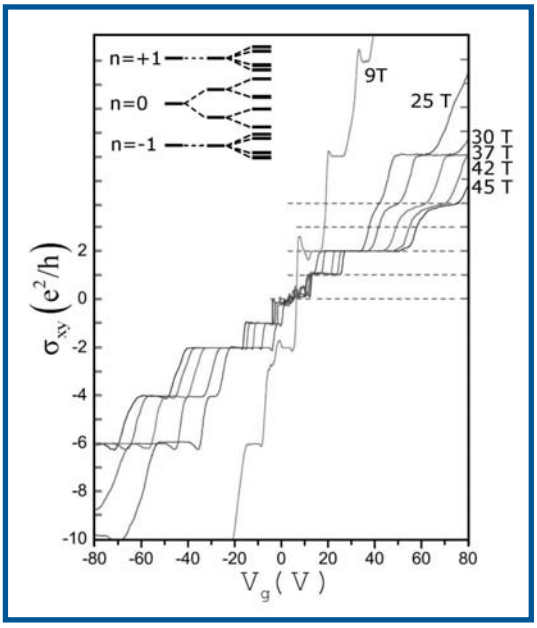

Fig. 5 Quantum Hall effect in graphene at high magnetic fields. The plateaus at ν = 0, ±1, ±4 are resolved at these fields. Inset: Landau levels (schematic) at low (left) and high (right) magnetic fields (adapted from Ref. [9]).

limit, it was found that in graphene the Hall conductivity follows the relation: $\sigma_{xy} = \nu e^2/h = 2(2n+1)\, e^2/h$, where n is an integer [Fig. 4]. This result has been explained as an outcome of four times the quantum Hall conductivity $(n+½)e^2/h$ for each Dirac fermion, that is quite consistent with the four-fold degeneracy (two spins and two valleys, or flavours) of the Landau levels for the Dirac fermions [22].

Interestingly, for an ideal graphene system, the wave functions for an electron in the valleys K and K′ are described by the vectors

$$\Psi_{K,n} = C_n \begin{pmatrix} \mathrm{sgn}(n)\, i^{|n|-1}\phi_{|n|-1} \\ i^{|n|}\phi_{|n|} \\ 0 \\ 0 \end{pmatrix}, \quad \Psi_{K',n} = C_n \begin{pmatrix} 0 \\ 0 \\ i^{|n|}\phi_{|n|} \\ \mathrm{sgn}(n)\, i^{|n|-1}\phi_{|n|-1} \end{pmatrix},$$

where $C_n = 1$ for $n=0$ and $C_n = 1/\sqrt{2}$ for $n \neq 0$. The two non-zero elements in $\Psi_{K,n}$ ($\Psi_{K',n}$) correspond to the occupation of the sublattice A (upper term) and sublattice B (the lower term). Here ϕ_n is the Landau wave function for a particle with non-relativistic (*i.e.*, conventional) parabolic dispersion relation in the n-th Landau level [21]. Clearly, a specific feature of the relativistic dispersion law is the "mixture" of the non-relativistic Landau levels [23]. This mixture is present only for $n \neq 0$. For $n = 0$ the electron in the valley K or K′ occupies only the sublattice A or B, respectively. For higher Landau levels the electron in each valley occupies both sublattices. The wave functions in the sublattices A and B are the wave functions of the non-relativistic electrons with different Landau level indices. This property of the relativistic electrons strongly modifies the inter-electron interaction within a single relativistic Landau level and influences the Dirac counterpart of the fractional quantum Hall states in graphene [23].

Extreme quantum limit

In the very high magnetic field regime (up to 45 Tesla), Zhang *et al.* [9] discovered a new set of quantum Hall states at filling factors ν = 0, ±1, ±4 [Fig. 5]. Observation of these states clearly indicated that the four-fold degeneracy of the observed states at ν = ±4 $(n+½)$ discussed in the previous section, is now lifted. Different mechanisms have been proposed to explain the possible origin of the appearence of these new plateaus. Clearly, electron-electron interactions are important at these fields and the system is regarded as a quantum Hall ferromagnet [24,25], where the Coulomb exchange interactions strongly stabilize the ν = 1 state, even in the absence of the Zeeman coupling. Other proposals involve a valley splitting mechanism based on the on-site electron repulsion and the neglect of the exchange interaction in the dirty graphene sample [26] or magnetic field induced out of plane lattice distortion [27]. A definite answer to this puzzling observation is yet to emerge.

OTHER PROPERTIES

As we mentioned above, research on graphene is progressing at a furious pace. Some of these unique properties that are found only recently, are briefly described below. In contrast to the massless Dirac fermions in a single layer of graphene, charge carriers in bilayer graphene are `massive chiral fermions' [28] and have the usual parabolic energy dispersion of the conventional electrons. By selectively adjusting the carrier concentration in each layer, a gap could be opened at the Dirac crossing point and can be manipulated. This could be particularly important in future nanoelectronic devices. The edge states in graphene in the presence of a perpendicular magnetic field also exhibit unusual properties, such as counterpropagating spin-polarized modes [29]. Confinement of the charge carriers in graphene turns out to be an interesting endeavour. Theoretical studies have indicated that the relativistic nature of the carriers in graphene allows for the observation of Klein's paradox [30], *i.e.*, perfect transmission of relativistic particles through high and wide potential barriers. In the case of the non-relativistic electrons, in contrast, the transmission probability decays exponentially with increasing height of the barrier. It has been proposed that confinement of Dirac fermions can be explored in graphene if one applies a transverse magnetic field [31]. The confinement would actually modify the fermion energy spectrum as a function of the magnetic field and perhaps could be observed experimentally. Recently, electron confinement has been reported in an epitaxially-grown patterned graphene structure [32].

To summarize: In the past two years, there has been an unprecedented outburst of activities to discover the unusual electronic properties of graphene. Although the band structure of the system is known for about sixty years, it was realized only recently that the low-energy dynamics of the two-dimensional electrons in graphene is governed, not by the Schrödinger equation as one expects, but by the Dirac-Weyl equation. Experimental confirmation of the existence of Dirac fermions in a condensed matter system has opened new avenues of research which is expected to broaden our understanding of the rich physics of quantum electrodynamics in a two-dimensional electron system, that was never imagined before. However, most importantly, the unusual properties of the charge carriers in graphene may provide a totally novel way of making nanoscale devices that are not attainable in conventional Si-based electronics.

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