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Electronic properties of graphene

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Graphene is the first example of truly two-dimensional crystals – it's just one layer of carbon atoms. It turns out that graphene is a gapless semiconductor with unique electronic properties resulting from the fact that charge carriers in graphene obey linear dispersion relation, thus mimicking massless relativistic particles. This results in the observation of a number of very peculiar electronic properties – from an anomalous quantum Hall effect to the absence of localization. It also provides a bridge between condensed matter physics and quantum electrodynamics and opens new perspectives for carbon-based electronics.

1 Historical overview

Carbon demonstrates unusually complicated behavior, forming a number of very different structures. As well as diamond and graphite, which have been known since ancient times, recently discovered fullerenes [1–3] and nanotubes [4] are currently a focus of attention for many physicists and chemists. Thus, only 3-dimensional (diamond, graphite), 1-dimensional (nanotubes), and 0-dimensional (fullerenes) allotropes of carbon were known. The *two-dimensional* form was conspicuously missing, resisting any attempt at experimental observation – until recently.

The elusive two-dimensional form of carbon is named graphene, and, ironically, it is probably the best-studied carbon allotrope theoretically. Graphene – planar, hexagonal arrangements of carbon atoms – is the starting point for all calculations on graphite, carbon nanotubes, and fullerenes. At the same time, numerous attempts to synthesize these two-dimensional atomic crystals have usually failed, producing instead nanometer-size crystallites [5]. These difficulties are not surprising in light of the common belief that truly two-dimensional crystals cannot exist [6–10] (in contrast to the numerous known *quasi*-two-dimensional systems). Moreover, during synthesis, any graphene nucleation sites will have very large perimeter-to-surface ratios, thus promoting collapse into other carbon allotropes.

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In 2004, a very different and, at first glance, even naive approach to obtain graphene lead to a revolution in the field [11–13]. A single sheet (a monolayer of atoms) was extracted from 3-dimensional graphite using a technique called micromechanical cleavage. Graphite is a layered material and can be viewed as a number of two-dimensional graphene crystals weakly coupled together. By using this top-down approach and starting with large, three-dimensional crystals, the researchers avoided all the issues with the stability of small crystallites. Furthermore, the same technique has been used to obtain two-dimensional crystals of other materials [11], such as boron-nitride, some dichalcogenides and high-temperature superconductor Bi–Sr–Ca–Cu–O. This astonishing finding sends an important message: two-dimensional crystals do exist and they are stable at ambient conditions.

Amazingly, this humble approach allows easy production of large (up to 100 μm in size), high-quality graphene crystallites, and immediately triggered enormous experimental activity [14, 15]. Moreover, the quality of the samples produced are so good that ballistic transport [12] and a quantum Hall effect (QHE) [14, 15] can be observed easily. The former makes this new material a promising candidate for future electronic applications, such as ballistic field-effect transistors (FETs). However, while this approach suits all research needs [16], other techniques that provide a high yield of graphene are required for industrial production. Among the promising candidate, one should mention exfoliation of intercalated graphitic compounds [17–21] and Si sublimation from SiC substrates [22, 23].

2 Linear spectra

From the point of view of its electronic properties, graphene is a two-dimensional zero-gap semiconductor and its low-energy quasiparticles formally described by the Dirac-like Hamiltonian $H = -i\hbar v_F \sigma \nabla$, where $v_F \approx 10^6$ m/s is the Fermi velocity, and $\sigma = (\sigma_x, \sigma_y)$ are the Pauli matrices [24–27]. Neglecting many-body effects, this description is accurate theoretically and has also been proven experimentally by measuring the energy-dependent cyclotron mass in graphene (which yields its linear energy spectrum) and, most clearly, by the observation of a relativistic analogue of the integer QHE which will be discussed below.

The fact that charge carriers in graphene are described by the Dirac-like equation rather than the usual Schrödinger equation can be seen as a consequence of graphene's crystal structure, which consists of two equivalent carbon sublattices A and B. Quantum mechanical hopping between the sublattices leads to the formation of two energy bands, and their intersection near the edges of the Brillouin zone yields the conical energy spectrum near the "Dirac" points K and K′. As a result, quasiparticles in graphene exhibit the linear dispersion relation $E = \hbar k v_F$ as if they were massless relativistic particles, with the role of the speed of light played by the Fermi velocity $v_F \approx c/300$. Due to the linear spectrum, one can expect that graphene's quasiparticles behave differently from those in conventional metals and semiconductors where the energy spectrum can be approximated by a parabolic (free-electron-like) dispersion relation.

Although the linear spectrum is important, it is not the only essential feature that underpins the description of quantum transport in graphene by the Dirac equation. Above zero energy, the current carrying states in graphene are, as usual, electron-like and negatively charged. At negative energies, if the valence band is not completely filled, its unoccupied electronic states behave as positively charged quasiparticles (holes), which are often viewed as a condensed-matter equivalent of positrons. Note however that electrons and holes in condensed matter physics are normally described by separate Schrödinger equations, which are not in any way connected (as a consequence of the Seitz sum rule, the equations should also involve different effective masses). In contrast, electron and hole states in graphene are interconnected, exhibiting properties analogous to the charge-conjugation symmetry in QED. For the case of graphene, the latter symmetry is a consequence of its crystal symmetry because graphene's quasiparticles have to be described by two-component wavefunctions, which is needed to define relative contributions of sublattices A and B in the quasiparticles' make-up. The two-component description for graphene is very similar to the one by spinor wavefunctions in QED but the "spin" index for graphene indicates sublattices rather than the real spin of electrons and is usually referred to as pseudospin σ.

There are further analogies with QED. The conical spectrum of graphene is the result of intersection of the energy bands originating from sublattices A and B and, accordingly, an electron with energy E

propagating in the positive direction originates from the same branch of the electronic spectrum as the hole with energy $-E$ propagating in the opposite direction. This yields that electrons and holes belonging to the same branch have pseudospin σ pointing in the same direction, which is parallel to the momentum for electrons and antiparallel for holes. This allows one to introduce chirality [27], that is formally a projection of pseudospin on the direction of motion, which is positive and negative for electrons and holes, respectively.

An alternative view on the origin of the chirality in graphene is based on the concept of "Berry phase". Since the electron wave function is a two-component spinor, it has to change sign when the electron moves along the closed contour. Thus the wave function gains an additional phase π.

3 Electric field effect

In the absence of quality graphene wafers, most experimental groups are currently using samples obtained by the original technique of micromechanical cleavage [11, 12], which provides high-quality crystallites up to 1000 μm^2 in size, which are sufficient for most research purposes and to prove concepts. Superficially, the technique resembles nothing more sophisticated than drawing with a pencil [12] or repeated peeling of graphite by adhesive tape [11] until the thinnest flakes are found. The critical ingredient that made those efforts successful was that graphene becomes visible in an optical microscope if placed on top of a Si wafer with a carefully chosen thickness of SiO_2, owing to a very feeble interference-like contrast with respect to an empty wafer [28]. If not for this simple yet effective way to scan substrates in search of individual graphene crystallites, they would most probably remain undiscovered today. Even if one would search for graphene ignoring its theoretical impossibility, more sophisticated techniques usually employed for investigating atomically thin and small objects (such as scanning-probe microscopy) have too low throughput to allow for finding of rare and isolated graphene crystals, whereas scanning electron microscopy is also unsuitable because of the absence of clear signatures for the number of atomic layers. Note however that graphene was recently found to have a clear signature in Raman microscopy [29, 30], which is likely to make this technique widely used for thickness inspection, although potential crystals would still have to be identified optically first.

SiO_2 also serves as an insulating layer, so a back-gate voltage can be applied to vary carrier concentration. Graphene is found to exhibit a pronounced ambipolar electric field effect (Fig. 1) such that charge carriers can be tuned continuously between electrons to holes in concentrations n as high as 10^{13} cm^{-2} and their mobilities can exceed 10000 cm^2/Vs and is practically temperature independent [12]. This translates into ballistic transport on submicron scales. The room-temperature mobility is limited by impurities or corrugations of the graphene surface, which means that it can still be improved significantly, perhaps up to 100.00 cm^2/Vs.

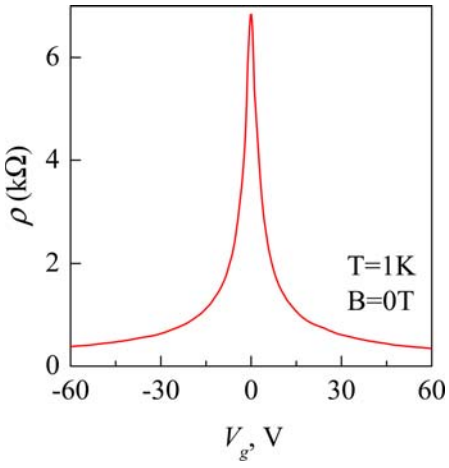

Fig. 1 (online colour at: www.pss-b.com) Ambipolar electric field effect in single-layer graphene. Positive (negative) V_g induce electrons (holes) in concentrations $n = \alpha V_g$ where the coefficient $\alpha \approx 7.2 \times 10^{10}$ cm^{-2}/V for our field-effect devices with a 300 nm SiO_2 layer used as a dielectric. The rapid decrease in resistivity with adding charge carriers indicates their high mobility (in this case, $\mu \approx 5000$ cm^2/Vs and does not practically change with temperature up to 300 K).

Another important observation is that graphene's zero-field conductivity σ does not disappear in the limit of vanishing n but instead exhibits values close to the conductivity quantum e^2/h per carrier type [14]. We emphasize that it is the resistivity (conductivity) rather than the resistance (conductance) that is quantized, in contrast to all other known quantum transport phenomena. Minimum quantum conductivity has been predicted for Dirac fermions by a number of theories [31–37]. Some of them rely on a vanishing density of states for the linear 2D spectrum. However, comparison between the behaviour of massless and massive Dirac fermions in graphene and its bilayer allows one to distinguish between chirality- and masslessness-related effects. To this end, bilayer graphene also exhibits a minimum conductivity of the order of e^2/h per carrier type which indicates that it is chirality, rather than the linear spectrum, that is more important [38]. Moreover, most theories suggest $\rho_{max} = \pi h/4e^2$, which is π times larger than the typical value observed experimentally. This disagreement has become known as "the mystery of a missing pie", and it remains unclear whether it is due to approximations used by theory or because the experiment probed only a limited range of possible sample parameters. In particular, experiments indicate that, at low concentrations ($n < 10^{11}$ cm^{-2}), graphene conducts as a random network of electron and hole puddles. Such microscopic inhomogeneity is inherent to the neutrality point but has so far not been taken into account by theory. Furthermore, macroscopic inhomogeneity (on the scale larger than the mean free path l) may also play an important role. Experiments show that, improving sample homogeneity by thermal annealing or using smaller samples, changes ρ_{max} so that it gets closer to $h/4e^2$.

4 Quantum Hall effect

At this early stage, main experimental efforts have been focused on electronic properties in graphene, trying to understand the consequences of its QED-like spectrum. Among the most spectacular phenomena found in graphene so far are two new ("chiral") quantum Hall effects.

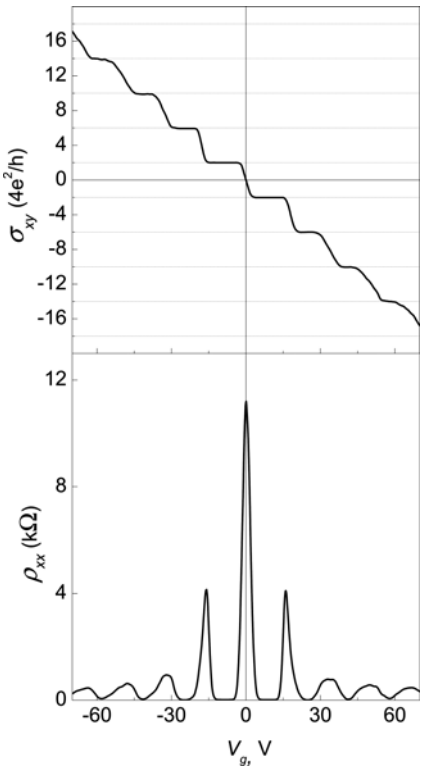

Fig. 2 Hallmark of the QHE for massless Dirac fermions is plateaux in σ_{xy} (top panel) at half integers of $4e^2/h$ whereas ρ_{xx} (bottom panel) vanishes for the same carrier concentrations n. $T = 4$ K; $B = 14$ T.

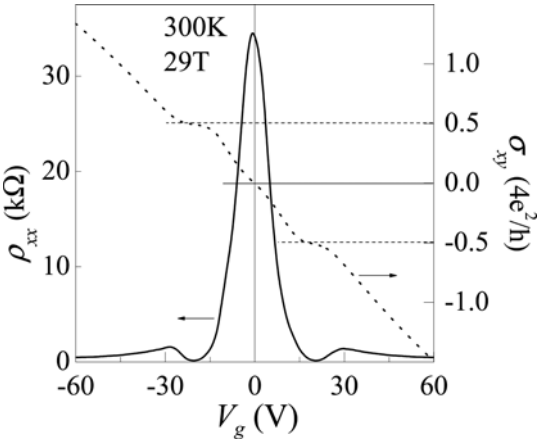

Fig. 3 Room-temperature quantum Hall effect. Because quasiparticles in graphene behave as massless Dirac fermions and exhibit little scattering even under ambient conditions, the QHE survives up to room *T*. The dotted curve is the Hall conductivity σ_{xy} that exhibits clear plateaux at $2e^2/h$ for both electrons and holes. The longitudinal conductivity ρ_{xx} (solid curve) reaches zero at the same gate voltages.

Figure 2 shows the QHE behaviour observed in graphene. QHE in single layer graphene shows up as an uninterrupted ladder of equidistant steps in Hall conductivity σ_{xy} which persists through the neutrality (Dirac) point, where charge carriers change from electrons to holes (Fig. 2). The sequence is shifted with respect to the "standard" QHE sequence by 1/2, so that $\sigma_{xy} = \pm 4e^2/h(N + 1/2)$ where N is the Landau level (LL) index and factor 4 appears due to double valley and double spin degeneracy. The QHE has been dubbed "half-integer" to reflect both the shift and the fact that, although it is not a fractional QHE, it is not the integer QHE either. The unusual sequence is now well understood as arising due to the QED-like quantization of graphene's electronic spectrum in magnetic field B, which is described by $E_N = \pm v_F\sqrt{2e\hbar BN}$ where sign ± refers to electrons and holes [26, 27, 39–41]. The existence of a quantized level at zero E, which is shared by electrons and holes, is essentially everything one needs to know to explain the anomalous QHE sequence [38, 40, 41]. An alternative explanation for the half-integer QHE is to invoke the coupling between pseudospin and orbital motion, which gives rise to a Berry phase of π accumulated along cyclotron trajectories [14, 15]. The additional phase leads to a half-period shift in the phase of quantum oscillations and, in the QHE limit, to a half-step shift [14, 15].

Graphene linear spectra and the large value of the Fermi velocity ensures huge orbital splitting. The energy gap between $N = 0$ and $N = \pm 1$ Landau levels is given by $\Delta E \approx 400\ (\mathrm{K})\sqrt{B}$, where B is magnetic field in Tesla. This implies that at $B = 30$ T the splitting is of the order of 2200 K, almost an order of magnitude higher than the room temperature. Moreover, temperature independent high mobility ensures that the high field limit $\mu \cdot B \gg 1$ is satisfied in a modest field of a few Tesla. These led to observation of QHE at room temperatures [42] (Fig. 3), which is very promising for metrology applications.

5 Conclusions

Graphene is the first example of a truly two-dimensional crystal. This opens many interesting questions concerning the thermodynamics, lattice dynamics, and structural properties of such systems. Being a gapless semiconductor with a linear energy spectrum, single-layer graphene realizes a two-dimensional, massless Dirac fermion system that is of crucial importance for understanding unusual electronic properties, such as an anomalous QHE, absence of the Anderson localization, etc. These peculiarities are important for developing new electronic devices.

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