

Graphene: The Magic of Flat Carbon

by Konstantin S. Novoselov

Graphene is the first example of a truly two-dimensional atomic crystal. This opens many interesting directions of research concerning the thermodynamics, lattice dynamics, and structural properties of such systems. Being a zero-overlap semimetal 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 such as carbon transistors. Recent developments in production of large quantities of graphene, as well as the possibility of its chemical modification make such developments very realistic.

Electronic Properties

Graphene is the thinnest material known to us. It is a monoatomically thin 2D film of carbon atoms arranged laterally in a honeycomb benzene ring-like structure. It was previously considered to be thermodynamically unstable form of carbon until it was shown to exist in the free state.^{1,2} Graphene is a zero-overlap semimetal, where the charge carriers have a linear dispersion relation near the Dirac point.³ The ambipolar electric field effect in graphene makes it possible to control the charge carriers with concentrations of up to 10^{13} cm⁻² and room temperature carrier mobilities of $\sim 20,000$ cm²/Vs are routinely observed. These mobilities were found to be weakly temperature dependent, which means that if impurity scattering was reduced, $\sim 200,000$ cm²/Vs mobilities could be achieved.^{4,5} Transport in this system is ballistic and carriers can travel submicrometer distances (~ 300 nm) without scattering. In addition, the charge carriers in graphene were found to behave like a 2D gas of massless Dirac fermions,^{6,7} and the quantum Hall effect was observed at room temperature.⁸ Collectively these factors not only make graphene a novel material for electronics but also spintronics and valleytronics research. The opportunity to control the charge carriers in graphene along with their spin by an applied gate voltage adds to its advantages for applications in spintronics.

From the point of view of its electronic properties, graphene is a two-dimensional zero-overlap semimetal and its low-energy quasiparticles can be 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. Neglecting many-body effects, this description is accurate theoretically and has also been proven experimentally by measuring the energy-dependent cyclotron mass in graphene⁶ (which yields its linear energy spectrum) and, most clearly, by the observation of a relativistic analogue of the integer QHE.^{6,7}

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 symmetric and antisymmetric configurations of 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, that is formally a projection of pseudospin on the direction of motion, which is positive and negative for electrons and holes, respectively.

Applications and Mass Production

Exceptional electronic properties of graphene and its formidable potential in various applications have ensured a rapid growth of interest in this new material. One of the most discussed and tantalizing directions in research on graphene is its use as the base material for an electronic circuitry that is envisaged to consist of nanometer-sized ribbons or quantum dots.⁹⁻¹¹ Such applications, however, would rely heavily on the availability of high-quality large (wafer-size) graphene crystals. Methods for epitaxial growth of graphene are being actively developed at the moment.

Still, there are a number of applications which do not require high quality graphene. Graphene is only one atom thick, optically transparent, chemically inert and an excellent conductor. These properties seem to make this material an excellent candidate for applications in various photonic devices that require conducting but transparent thin films. It has been shown that a monolayer of graphene absorbs only 2.3% of light,¹² which makes it a very attractive material for transparent electrodes in liquid crystal displays¹³ and solar cells.¹⁴

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Such devices can in principle utilize graphene films which consist of a number of overlapping graphene flakes. Such films could be produced by reducing graphene oxide^{14,15} or by direct chemical exfoliation of graphite. The latter involves making a graphene suspension by direct chemical exfoliation of graphite (rather than graphite oxide), which is subsequently used to obtain transparent conductive films on top of glass by spin- or spray-coating.

Crystals of natural graphite (Nacional de Grafite¹⁶) were exfoliated by sonication in dimethylformamide (DMF) for over 3 hours. DMF “dissolves” graphite surprisingly well, and the procedure resulted in a suspension of thin graphitic platelets with large proportion of monolayer graphene flakes, DMF also wets the flakes preventing them from conglomerating. The suspension was then centrifuged at 13,000 rpm for 10 minutes to remove thick flakes. The remaining suspension consists mostly of graphene and few-layer graphite flakes of sub-micrometer size. The thickness of the exfoliated flakes has been verified by atomic force microscopy and transmission electron microscopy. Both techniques indicate high proportion of monolayer flakes (up to 50%).

The suspension was spray-deposited onto a preheated glass slide which yielded thin (~1.5 nm) films over centimeter sized areas, which consisted of overlapping individual graphene and few-layers graphene flakes. These films were then annealed for 2 hours in argon(90%)/hydrogen(10%) atmosphere at 250 °C. The transparency of such graphitic layers was approximately 90%, which is expected for 4-5 layers of graphene coverage, and is still well within the margins of being relevant for industrial applications.

In order to measure resistivity of our films, a mesa structure in the shape of the Hall bar with typical dimensions of 1 mm was prepared, and the four-probe resistance was measured as a function of temperature. The high temperature region (above 10K) is well described by $\exp(T_0^{1/3}/T^{1/3})$ dependence, characteristic for variable range hopping in two dimensions. The room temperature sheet resistance is of the order of 5 k Ω , which, together with the high transparency of 90%, is already acceptable for some applications, and can be decreased further by increasing the film thickness. Resistance at low temperatures deviates from the variable-range-hopping dependence but can be described by the simple activation dependence $\exp(-\Delta/T)$. This low-temperature behavior can be attributed to weak tunneling-like coupling between overlapping flakes, possibly due to contamination with organic (DMF) residues. The procedure that was used also can modify the chemical termination of the dangling bonds of our graphene crystallites, which might affect the transport properties of the films obtained (although on a lesser level than the contamination between the overlapping flakes). This indicates some potential for improvements as better cleaning and annealing procedures can potentially improve coupling between graphene crystallites and decrease the film resistance further.

Conclusions

Graphene is the first example of a truly two-dimensional atomic 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. Bilayer graphene has a very unusual gapless, parabolic spectrum, giving a system with an electron wave equation that is different from both Dirac and Schrödinger systems. These peculiarities are important for developing new electronic devices such as carbon transistors. Furthermore, high optical transparency, low resistivity and high chemical stability of graphene makes it an excellent choice for transparent electrodes in various optoelectronic

devices. There are already several technologies that potentially allow mass production of thin graphene-based transparent conductors. These techniques are capable of producing continuous graphene films of thickness below 5 monolayers, which is required for realistic applications.

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