

Graphene

a new electronic material

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Carbon is one of the most interesting elements and plays a unique role in nature. It exists in many allotropes, some known from ancient times (diamonds) and some which were discovered in the last decades (fullerenes, nanotubes). The two-dimensional form of carbon, called Graphene, is the most recently discovered modification. This first two-dimensional material has very peculiar electronic properties, that make it interesting both for fundamental research and possible applications.

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1 Introduction

Carbon exists in many modifications: three-dimensional crystals (diamond, graphite), one-dimensional nanotubes and zero-dimensional fullerenes. The two-dimensional graphene was thought not to exist¹, because thermal fluctuations should destroy any long-range correlation in one or two dimensions. Because of its simplicity Graphene has been a perfect subject for theoretical studies. Planar, hexagonal arrangements of carbon atoms - graphene - is the starting point in all calculations on carbon nanotubes, fullerenes and graphite. In 2004 a group of physicists from Manchester University, led by Andre Geim and Kostya Novoselov found a way to extract a single layer of atoms from graphite². Graphene attracted the interest of many more scientists instantly, so that many of the predicted electronic properties were verified in experiments.

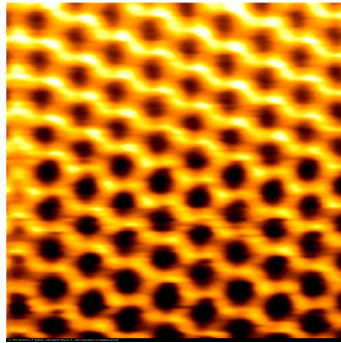


Figure 1: atomic force microscope (AFM) image of graphite surface, 2x2 nm (Exp. Phys. VI, Uni Augsburg)

2 Preparation of Graphene

2.1 top-down-approach

There are two fundamentally different approaches to prepare nanostructures, like one single layer of atoms. In the top-down-approach you start with macroscopic structures and break them down into smaller ones. Novoselov and his colleagues developed a technique they called "micromechanical cleavage" to extract single sheets of atoms from three dimensional crystals. Graphite is a crystal made of layers of graphene that are weakly coupled together by van-der-Waals forces, which is exactly the property used in this technique.

The Manchester group started with an 1mm thick highly-oriented pyrolytic graphite crystal, etched it down to a thickness of 5 μm and baked this crystal to a glass surface. Then they peeled off the top layers using simple scotch tape, released the flakes left on the glass in acetone and washed them on a silicon wafer. After ultrasound cleaning in propanol only the thinnest flakes stick to the SiO_2 .

¹Landau & Lifshitz, Vol. 5

²after Novoselov et al., Science 306, 666 (2004)

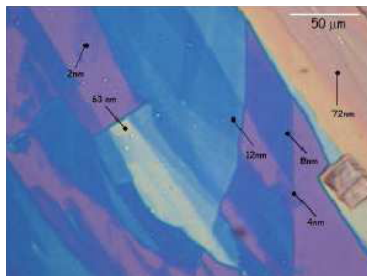


Figure 2: Wafer with graphene flakes, optical microscope (Novoselov et al., Science 306, 666 (2004))

Unfortunately the final step is the lengthy process of finding a suitable flake of graphene. This is done with a combination of optical microscopes, scanning electron micrographs (SEM) and atomic force microscopes (AFM). While this technique is very cheap and very simple, the results cannot be predicted. It perfectly suits the needs of laboratories, since it produces high quality graphene flakes in the size of micrometers, but cannot be used when it comes to applications and real electronic devices.

2.2 bottom-up-approach

It is obvious that the straight forward top-down-approach cannot produce large graphene layers (in the size of mm) that would be needed for chips or other devices. The so called bottom-up-approach is much more interesting for technological applications. The idea is to grow single layers of graphene from carbon atoms. The top-down approach avoided all issues with the stability of small crystallites, that occur when graphene is grown from scratch. A better solution is to grow on a bulk crystal of silicon-carbide (SiC).

The possibility to grow graphene layers on SiC was discovered when experimentalists tried to put contacts on SiC crystals. The contacts were not very good, but their quality improved when the setup was heated. Quizzingly looking under the contacts the physicists discovered graphite. They found out, that under certain conditions the silicon atoms evaporate from heated SiC crystals and that the remaining carbon atoms reconstruct to form a graphene/graphite lattice. De Heer and his colleagues from the Georgia Institute of Technology grew graphene layers on SiC and verified their 2D-electron gas behavior³

The advantage of this method, is that one obtains large "graphene"-layers on a substrate, which can be further processed with standard methods like lithography, without labor-intensive harvesting of suitable flakes. The disadvantages are that the monolayer crystal flakes are most vulnerable to damage while being cooked up in the ovens ($T \approx 900\text{K}$) and that their quality is not comparable to graphene layers peeled off from graphite. The electron mobility, which is mainly limited by defects, of grown graphene reaches $10.000 \text{ cm}^2/\text{Vs}$, while peeled layers have shown mobilities up to $50.000 \text{ cm}^2/\text{Vs}$. But still this approach could be a route toward graphene-based nanoelectronics.

³C. Berger et al., J. Phys. Chem. B **108**, 19912(2004)

3 Atomic and Electronic Structure

3.1 atomic structure of graphene

As already mentioned graphene is a planar, hexagonal crystal of carbon atoms. The next-neighbor distance is $a = 2.45\text{\AA}$. The unit cell holds two carbon atoms, which belong to two different sublattices A and B. The A atoms are connected only to B atoms and vice versa, this is called a bipartite lattice.

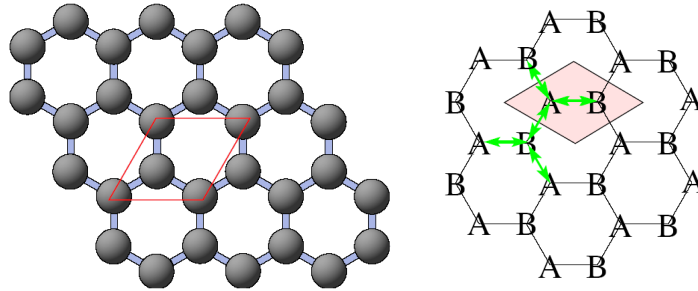


Figure 3: atomic structure of graphene, bipartite lattice

3.2 electronic band structure of graphene

The Brillouin zone of graphene is also a honeycomb lattice and also has the bipartite symmetry. In the momentum space we see what is really behind this symmetry: If we change the role of K and K' lattice points we actually reverse our time (flipping a K vector gives a K' vector). The time reversal is also connected to the chirality of particles: reversing time changes the roles of particles and antiparticles (electron and holes in our case). So the K and K' states are not equivalent (e.g. an electronic state in K forces the K' state to be positronic). This correlation will get more important in the discussion of the anomalous quantum Hall effect.

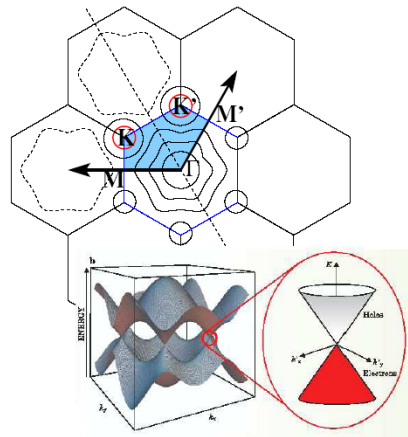


Figure 4: Brillouin zone with conic point

The electronic band structure of graphene shows a very interesting conic point at the K and K' points in the Brillouin zone. The linear bands cross exactly at the Fermi energy, so that there is only one state, which can be treated as a hole or as an electron. Since there are no conducting states at the Fermi level, graphene behaves like a gapless semiconductor (also called semi-metal).

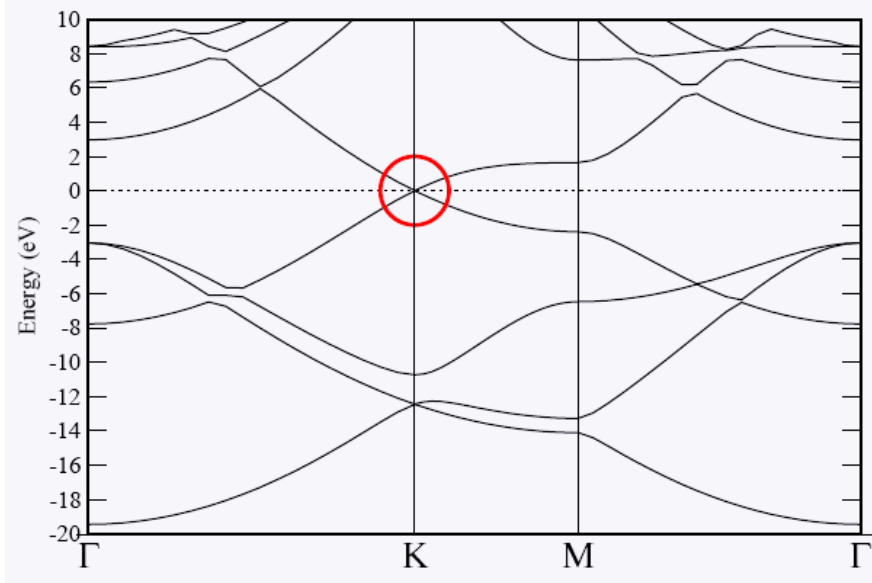


Figure 5: electronic band structure of graphene

4 Description as Dirac Fermions

Around the K (K') point the interpretation in terms of "effective" mass is impossible and requires a different approach. As mentioned before, the electronic energy spectrum around the K and K' points is linear, just like a light cone. The dispersion relation can be approximated with the following formula (where $v_F \approx 10^6$ m/s):

$$E(k) = v_F |k - K| \quad (1)$$

The Hamiltonian near K (K') can be approximated with (where $q = k - K$)

$$H_K = \begin{pmatrix} 0 & v_F(q_x - iq_y) \\ v_F(q_x + iq_y) & 0 \end{pmatrix} \quad (2)$$

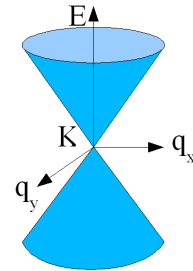


Figure 6: "light cone"

This Dirac Hamiltonian usually describes massless relativistic Fermions (e.g. neutrinos). The 2x2 structure comes from the 2 atoms in the unit cell. Just like in the free Dirac equation there is a new degree of freedom: spin. In our case this is some sort of pseudo spin, which is not related to the real physical spin. The Hamiltonian can be rewritten, so that it is a projection of momentum (always measured from the K point) on spin operators:

$$H_K = \begin{pmatrix} 0 & v_F(q_x - iq_y) \\ v_F(q_x + iq_y) & 0 \end{pmatrix} = v_F \begin{pmatrix} \sigma_x & \sigma_y \end{pmatrix} \begin{pmatrix} q_x \\ q_y \end{pmatrix} \quad (3)$$

Pseudo spin can be either parallel or anti parallel to the momentum (relative to K). Furthermore pseudo spin is coupled to the chirality, parallel orientation means it is an electronic state and anti parallel means it is a positronic state (hole). We also see, that the Pauli matrices (pseudo spin operators) commute with the Hamiltonian, which means pseudo spin is conserved (since there are no potentials that operate on spin).

5 Anomalous Quantum Hall Effect

The anomalous and the normal quantum Hall Effect (QHE) is the quantization of conductivity of a thin (or even two-dimensional) conductor in magnetic field. Quantum Hall effects are usually observed at low temperatures, but with graphene they can be studied at room temperatures. The setup is the following:

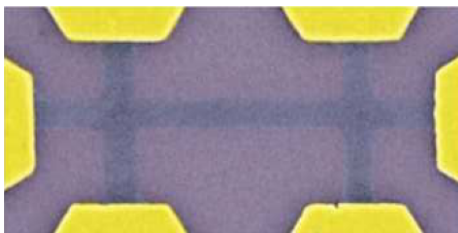


Figure 7: SEM picture (false colors) of the device used, $L = 200\text{nm}$ (Novoselov et al., Nature 2005)

When the two-dimensional conductor is exposed to a magnetic field perpendicular to the conductor, the continuous energy bands split into discrete energy levels, the so called Landau levels.

Here is a common example of the Landau quantization: The Harmonic potential (free electron gas, see Figure 8) has equidistant energy levels:

$$E_n = \pm \hbar \omega_c \left(n + \frac{1}{2} \right) \quad (4)$$

The \pm stands for the electron/hole degree of freedom.

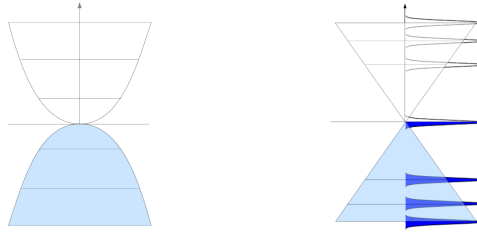


Figure 8: energy dispersion $E(k)$ of free electron gas, and at conic point with Landau quantization

In our case we have a linear dispersion relation, which is described by the relativistic Dirac equation. Landau quantization also happens, but the energy levels are not equidistant:

$$E_n = \pm \sqrt{2|e|B\hbar v_F^2 \left(n + \frac{1}{2} \pm \frac{1}{2} \right)} \quad (5)$$

The first \pm again represents electron-like or hole-like states, while the second \pm represents the pseudo spin. The fundamental difference between the graphene Landau levels and those of the harmonic potential is the zero energy level in graphene. This level is pinned and does not depend on the magnetic field. To see what makes this level so special, we must have a look at degeneracy (we do not consider the real spin). Since we have two cones K and K' , all Landau levels should be realizable two times. It was stated earlier that the pseudo spins of both K and K' cones are correlated, that means there is only one electronic state at the Fermi level. So there is only one possibility to realize the zero energy ($n = 0$ and pseudo spin down). The following plot shows QHE measurement in single layer graphene:

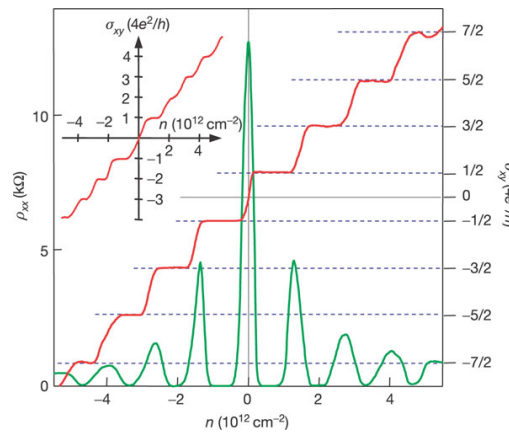


Figure 9: red curve: conductivity in xy direction; green curve: conductivity in xx direction; inset: normal quantum Hall effect (in bi-layer graphene) (Novoselov et al., Nature 2005)

The first step in the anomalous QHE is half-integer sized while all other steps are full-integer steps. This verifies that the spectrum is truly linear, and that the theoretic description with the Dirac equation is appropriate.

6 Tunneling of Chiral Particles

Since graphene is a semi metal, with electronic bands that cross in exactly one point, the conductivity with the Fermi level going through the conic point should drop to zero at low temperatures, where there should be no excited conducting states. But the fact is that conductivity doesn't drop below a minimum which is on the order of the minimal conductivity $\frac{e^2}{h}$.

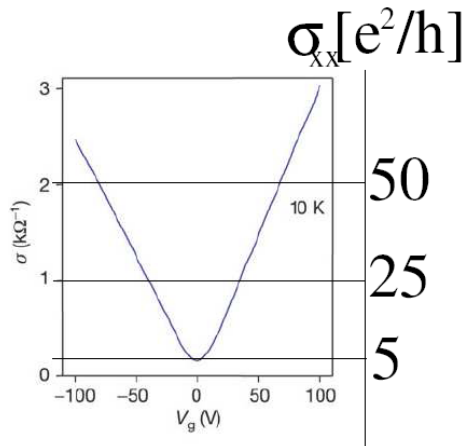


Figure 10: conductivity of graphene at a low temperature (Novoselov et al., Nature 2005)

Usually one and two-dimensional electron systems should crystalize at low temperatures. This effect is called Anderson localization: any wavefunctions in a small random potential in one or two dimensions is exponentially dampened. So when the system is cooled down to that point when the kinetic energy is of the order of the random potential strength, the electrons localize and do not contribute to the conductivity. This seems not to happen in graphene, which means that the random potential barriers somehow do not influence the electrons in graphene.

Furthermore it is observed that the graphene samples, which are by far not perfect, are pretty resistant to impurities. Therefore we can assume that potential barriers are somehow transparent to graphene. As it was stated earlier, pseudo spin is conserved, that means that backscattering is forbidden. Flipping of spin cannot happen, because the particle doesn't flip its pseudo spin. Assume an electron hits a potential barrier. Since it's an electron its pseudospin is parallel to its momentum. If this electron was scattered back, the pseudospin would become antiparallel, which means the electron would become a positron (this cannot happen).

The next figure illustrates how an electron in graphene can tunnel through any potential barrier (bands of different color belong to different pseudo-spin σ orientations).

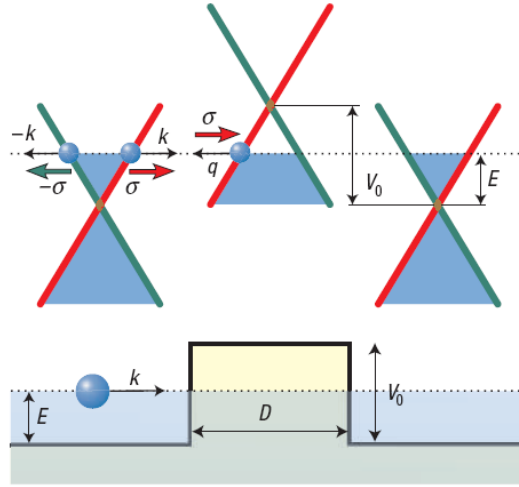


Figure 11: Chiral tunneling in graphene (Novoselov and A. K. Geim, Nature 2006)

In relativistic physics there is the so called Klein Paradox. It states that when a potential barrier exceeds the energy required to create a particle-antiparticle pair it becomes transparent, and is perfectly transparent at infinite size. This is so because a potential that is repulsive for particles is attractive for antiparticles, which means that there are antiparticle states inside the potential barrier. In graphene the gap between electrons and positrons is zero, which means that any potential is transparent for graphene (at least for momenta at the conic points K and K').

This allows ballistic transport, electrons can transport current without being scattered. Up to now ballistic current was measured in graphene over several microns (which is actually the size of the samples), which is actually the holy grail of nanometer-scale electronic engineering.

7 Graphene Devices

A direct application would be a gas sensor, since graphene has an exposed surface. Although it is chemically inert, its conductivity is strongly dependent on the defects. Molecules/atoms from the air can be adsorbed and change the electronic conductivity immediately. With this method even one single molecule can be detected and the surrounding atmosphere can be monitored in real time.

Graphene also has very peculiar electronic properties, e.g. the ballistic transport. This makes the electron mobility in graphene very high which is 20.000 cm^2/Vs to 50.000 cm^2/Vs at 100K. It is only limited by the quality of the samples. The mobility is quite high compared to silicon, which is the base for current chips, 600-1000 cm^2/Vs at room temperatures. Growing graphene on SiC is very promising when it comes to nanometer-scale electronic applications, since the graphene layers comes with its own substrate and can be easily pro-

cessed with lithography.

Another advantage of graphene is its two-dimensional nature. Since the Fermi energy is easily controlled by the gate voltage applied to the substrate, one can build high electron mobility transistors (which use a 2D-electron gas) immediately.

8 Conclusions

Finally one can say that graphene is of interest for both fundamental research and possible applications. Graphene gives an interesting bridge between condensed matter and the quantum field theory, since it allows the study of relativistic effects in a bench-top setup. It shows peculiar electronic effects, like the anomalous QHE, the absence of Anderson localization and allows ballistic transport. There are even more possibilities with bi-layer graphene, which has a harmonic spectrum at K and K' points, but still no energy gap between electrons and positrons. There is still much to study about this high-tech electronic material, that was obtained in the 21st century - using scotch tape.