# A new 2D world for physicists?

Recent successes in producing for the first time crystal structures made of an isolated single atomic layer (i.e. the atoms are located in a periodic lattice that is contained in a plane, a 2D space) are expected to open up a new world of scientific wonders (even if 2D world does not mean Disney World 2) and maybe practical applications and generated a lot of excitement both in the so-called "Surface Science" and nanotechnology communities. Surface scientists, i.e. mad scientists that like to study the surface of materials (that devilish region of the materials according to ….) have been dealing with 2D systems for many years trying to better understand the new properties that arise when the 3D periodicity of bulk materials is missing at the border between two different worlds which can be either the interface between two different materials or between a material and the vacuum. In the last forty years a lot has been learned about these systems which are extremely relevant to many aspects of everyday life, concerning the properties of the interfaces (structural and electronic) and the processes that occur in this region of reduced symmetry (chemical reactions, catalysis, adhesion and friction, electrical contact, etc.) but all these systems were connected in some way to a 3D substrate that was giving them stability. Surface scientists' most authentic 2D toys were maybe thin or very thin films deposited on surfaces. New deposition methods like Molecular Beam Epitaxy allowed them to control the deposited material at the level of less than a single atomic or molecular layer. These films, on the other hand, always interact with the substrate and in fact when the interaction with the substrate is too weak the deposited material inevitably tends to roll up or aggregate in mesoscopic clumps (clusters) to reduce the expose surface. In fact to produce a surface costs energy and if atoms are mobile enough they behave like Hg mercury droplets on a surface.

This tendency in fact makes scientists wonder if a really bi-dimensional crystal was even theoretically possible with no 3D support and actually calculations predicted that it would be impossible. Carbon has come to the aid of scientists once more: the most stable form of carbon is

graphite the material of which pencils (as the Greek root of the word suggests) are made (the most stable crystalline form means that diamonds which are another crystalline form of carbon are just "metastable" and eventually will go back to graphite, an unpleasant destiny for an expensive engagement ring). In graphite the carbon atoms are arranged in a peculiar way, they form a so-called honeycomb structure in a plane and the atoms in the plane are very strongly bound one to the other, they are held together by very strong covalent bonds (where electrons, once more our old friends, are shared between different atoms), while the interaction between different planes is rather weak (no much sharing of electrons). The crystal planes are therefore very easily separated or cleaved and based on this property is the use of graphite for writing (when you write with a pencil you leave carbon crystal planes on the paper), and also as a dry lubricant.
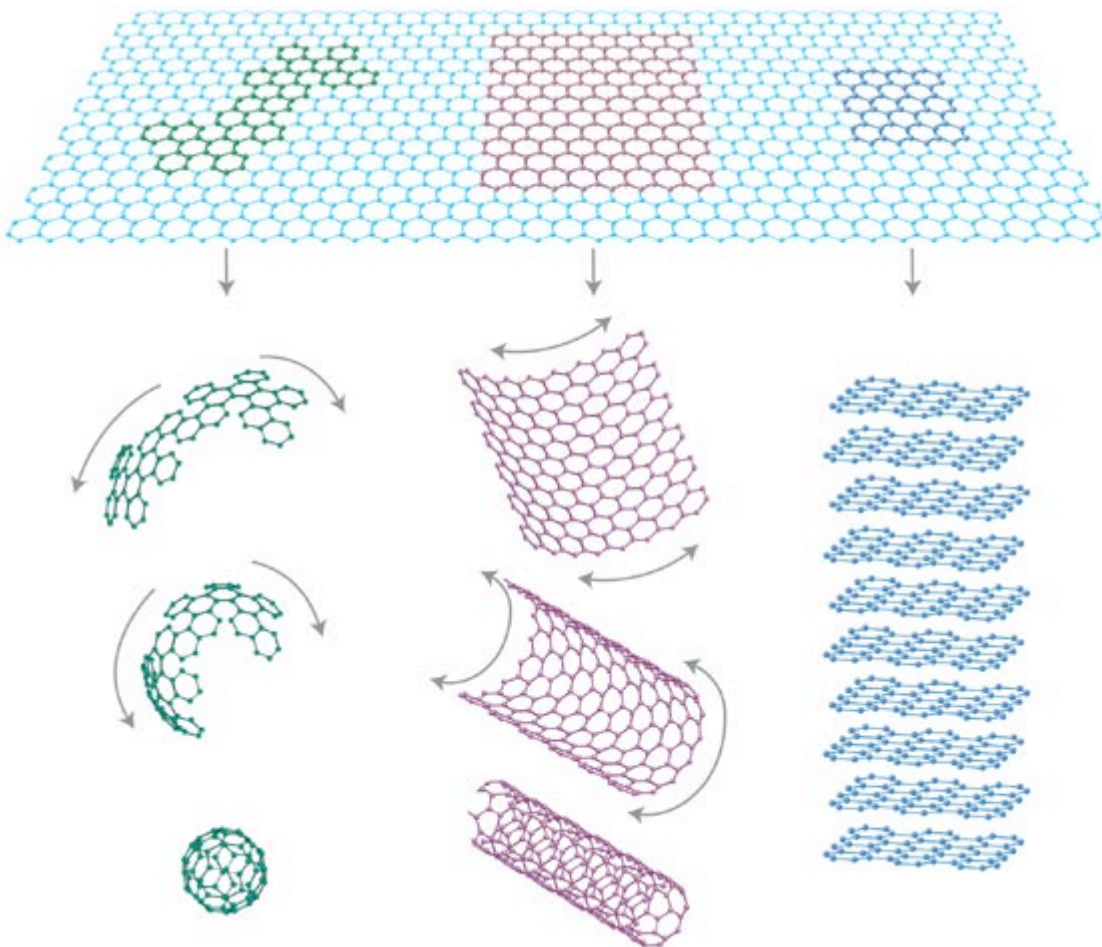
The fact that a single plane is weakly bound to the nearest ones makes graphite a good candidate for a real 2D system if you manage to separate them so precisely to reach the absolute minimum thickness of a single atomic layer. The material eventually obtained in this way is called graphene. We have encountered this word before since both 0-D objects like the fullerene and 1-D objects like carbon nanotubes can be ideally obtained by either wrapping or rolling a graphene sheet or a piece of graphene sheet. (see figure).

Various microscopic methods have been tried to separate a single atomic layer but only recently methods have been found at Manchester University and at Columbia able to produce consistently and reproducibly a reasonable number of samples the lateral dimensions (of the order of a micron or more) of which are large enough for use in experiments.

In the end the most efficient method found till now is one that makes use of an apparently not very high-tech instrument like a piece of commercial Scotch tape to remove progressively thinner and thinner layers of graphite down to the single atomic layer (sometimes low tech comes to the rescue of high-tech). By this mechanical cleavage method a lot of flakes of various thicknesses are produced but we want to be able to easily collect the very thin ones. Again low tech helps in this case. Highly sophisticated microscopic techniques are able to observe and measure down to the single atom (like scanning probe microscopies that we have discussed above) but are very slow and therefore very inefficient in selecting the right flakes. Instead a fortunate coincidence makes, in this particular case, optical microscopy (an old fashioned technique) an efficient method to distinguish thickness down to the single layer when these flakes are deposited on a particular substrate formed by a well-defined thickness (300 nm) of silicon oxide on pure silicon. In fact a clear contrast can be observed with a normal optical microscope between the light reflected by even a single layer of graphene and the light reflected by the bare substrate, a rather surprising effect since the wavelength of visible light is much larger (1000 times) than the thickness of the graphene film.
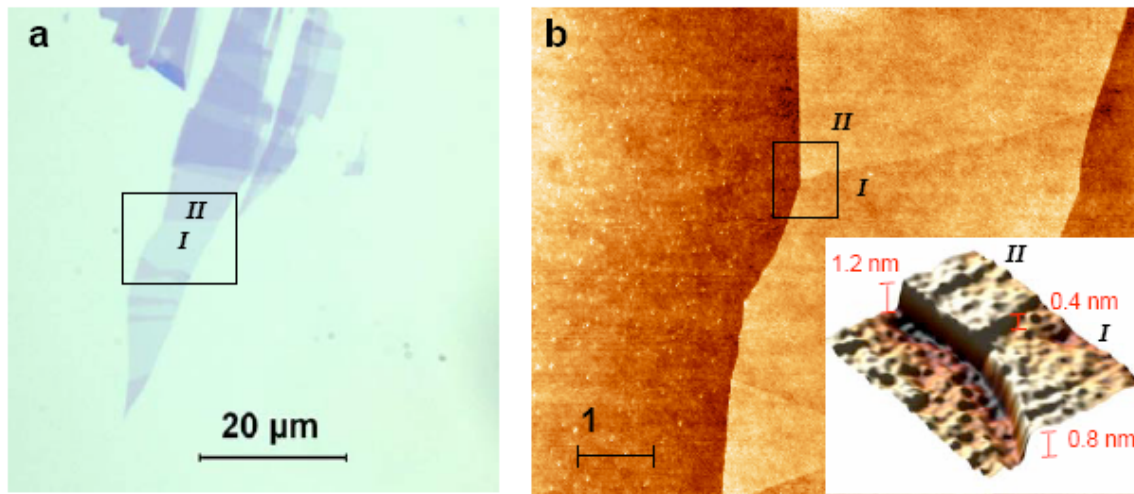
Small flakes of graphene observed on the right by optical microscope and on the left by an atomic force microscope: regions I and II correspond respectively to single and double layer graphene.

The discovery of this method allowed the research groups cited above to obtain consistent amounts of samples which could be used to probe the wonderful properties of this new material. You would not think that on the tip of your pencil you have such a gold (diamond rather?) mine of scientific wonders but now I will try to illustrate a few of them. First of all the theoretical controversy about the mechanical stability of a piece of material made of a single atomic layer could be solved in a pragmatic way. In fact the single layer flakes could be isolated and shown to remain stable when just gently leaning on supports providing very little interaction, but an even more striking demonstration has been obtained: the same groups in fact have been able also to produce self-sustained flakes suspended on nanoscopic contacts.

The properties that make graphene so extraordinary are related to the characteristics of the quantum states in which our old friends the electrons are located in this material. The particular geometrical characteristics of the periodic lattice (the so-called honeycomb lattice) of the graphene film cause these electrons to behave in an extraordinary way.

The quantum properties of electrons in a periodic environment like a crystal (as you may remember from above, most of the solid material is in crystalline form even if to our limited human eyesight it does not look like that, so when we consider crystals we are not talking about materials and properties relevant only to scientists or jewellers) is dictated by the so called band structure, one of the most important theoretical and experimental discoveries of solid state physics. The band structure determines the mechanical properties of the electrons of the solids. The most interesting electrons are those with the highest energy but that are still confined inside the material (i.e. the electrons that are less tightly bound to the single atoms of the lattice and that are, in the QM slang, "delocalised" in the entire solid). These electrons are responsible for example of the electrical properties and the heat transfer in the solids. More precisely the band structure provides the relation between the energy and the reciprocal of the wavelength (so called wavevector k) of the electron. I already mentioned that quantum mechanics assigns to particles also wavelike properties and for massive particles the wavelength is related to a quantity called momentum that is usually the product of velocity times mass and indicated with the symbol **p**. The wavelength is inversely proportional to this quantity, it means that the higher the velocity or the mass the shorter the wavelength. Another quantity that we have to consider for our tour of the graphene electrons properties is the energy of a particle. There are various forms of energy but the one that is most relevant to our discussion is the so-called Kinetic energy, i.e. the energy related to the motion of the particle. This energy, for normal massive particles (but also for you or a car or a train), is proportional to the square of the velocity, i.e. if your speed doubles your energy becomes four times larger. Now from this you could deduce that if you quadruple your kinetic energy, you double your speed and you reduce your wavelength of a factor 2 and I mean really you, if you walk twice as fast. There are, on the other hand, physical entities like the photon which have a different relation between energy and wavelength. The photon, introduced by Einstein to explain the photoelectric effect that we will discuss soon, is the quantum of the electromagnetic energy and from the point of view of quantum mechanics is a particle with no mass and that therefore is condemned to travel

always at the same speed, the speed of light i.e. 300.000 km/s. For this particle the energy does not depend from speed (always the same) or mass (no mass) but is inversely proportional to the wavelength, so if you take a photon with half wavelength it will have double energy while you would have quadruple energy. "Normal" particles i.e. particles that have a mass like you if they have very high velocities and therefore high energies, also follow the same behaviour as photons. To have a high velocity means tomove very near the speed of light that according to the special relativity theory is a limit velocity (nothing can travel faster) for any object. The mechanical properties of these high energy particles, called relativistic particles, are rather different to those of usual or "classical" ones (called "classical" since follow the classical mechanics) and also the QM of these high energy particles (relativistic quantum mechanics) is different. In particular strange tunnelling properties have been predicted for high energy particles, even stranger than those of normal particles (that could have given young Toerless a headache), so strange to deserve the name of Klein paradox.

After this long digression you could ask yourself where I have taken you and why I'm making you waste your time with these complicated explanations and moreover what this has to do with graphene, why are we talking of particles travelling at the speed of light that are more probably bound to the interstellar space or the gigantic accelerators like CERN or Fermilab rather than to very tiny pieces of pencil. The point is that if you manage to produce very thin layers of graphite, composed of just 1 or 2 atomic planes, the properties of the electrons in the film are defined by a "band structure" that corresponds to the an energy-wavelength dependence similar to the one followed by photons or high energy particles. To be precise, the band structure of a normal particle shows a quadratic dependence of E from K (like you when you walk) while in the case of graphene electrons, as a result of the honeycomb like potential produced by the nuclei of the graphene and of being confined in a 2D structure, E is just proportional to K more like photons or relativistic particles. This fantastic property allows us to carry out "on the tip of a pencil" experiments that

otherwise would need apparatuses that are extremely expensive or even unconceivable at the moment. Effects that could occur in black holes or far away stars could be mimic in graphene. The wonders of graphene don't end here: the electrons in graphene present also another property that makes this material very promising for future applications and studies of fundamental processes of solid state physics: the electrons can travel very long distances without being scattered by defects. In normal materials electrons are easily scattered by defects or vibrations of the lattice called "phonons" (again the Greek root of the word should help you) and can travel unperturbed only very short distances: the results of this scattering is for example a non zero electrical resistance of even the best conductors that unfortunately convert part of electric energy into heat. (only certain materials at very low temperature can end up in a special state called superconductive state which is able to sustain electrical currents with no energy loss). The possibility of electrons to travel in graphene for long distances without scattering (ballistic transport) has already raised the interest of the electronics industry: it is conceivable to use graphene to build devices on the nanoscale where electrons just travel along the entire device with no scattering making the device faster and less energy demanding: in this way also the apparently insurmountable problems of heat removal that rise as the electronic devices shrink in dimension and increase in density should become less severe. Theoretically devices based on the control of a single electron have already been proposed.

Related to electrical resistance and the transport of charge in metallic and semiconductor materials is an effect called the Hall effect. Charge particles are deviated from a rectilinear trajectory by a magnetic field (for example produced by a permanent natural magnet or an electromagnet) and so also electric currents that are due to the movement of charges in materials. If a piece of material where an electric current is flowing is placed in a magnetic field, due to the curved trajectory of the electrons charges accumulate on the sides of the conductor producing an electric field perpendicular to the current flow. This field and the corresponding voltage can be measured with simple instruments and can provide information about the properties of the electrons in the materials (for

example how freely they can move in the material, property that is described by a parameter called mobility). One way to display this behaviour is to report in a graph the so called Hall resistance (the ratio between the transverse voltage V_H and the current flowing). This effect has been clarified in the 19th century by the classical electromagnetic theory and has been used since to determine either the magnitude of unknown magnetic fields using well calibrated materials or the electron mobilities of unknown materials using well defined magnetic fields (mobility is an important parameter to characterize new artificial materials for electronics). In the eighties it was discovered that there is a QM counterpart of this effect called the Quantum Hall effect. To understand this Quantum effect we go back to the dualism particle-wave that we have already encountered in explaining the Quantum size effect. Due to the quantum wave properties of particles an electron confined in a 2D system in a magnetic field cannot make any curved trajectory but only the ones that correspond to circles containing an integer number of electron wavelengths. To this condition correspond quantised energy levels for the electron in the magnetic field called Landau levels. The quantisation of these energetic levels is reflected in the Hall resistivity as a function of the magnetic field which no longer shows a simple proportional dependence as in the classical case but some plateaus separated by steps since it also become quantised and since the steps are multiples of an universal constant they provide a new standard for the resistance measurement. QM effects are difficult to measure directly with simple instruments, they are usually very subtle and easily perturbed and washed out for example by the temperature induced disorder or by defects present in most materials (this does not mean that QM mechanics is irrelevant for everyday life because as already seen it is needed for example to explain most of the chemical phenomena but that is difficult to measure directly the effects of quantization). The Quantum Hall effect was measurable only at very low temperature in well prepared samples with very high magnetic fields i.e. rather extreme conditions, while the fantastic thing of graphene is that it becomes measurable at room temperature and low magnetic fields.
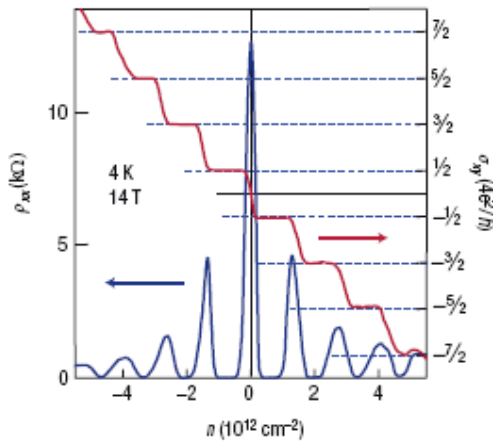
Measurement of Quantum Hall effect in graphene: the quantisation steps are easily detected: the quantised values are defined better than 1 part in 1 billion providing a new practical standard for resistence.

The main feature that characterizes the graphene electrons and that make them behave so strangely is the band structure that shows according to the theoretical predictions a proportionality between p and E. This is the basis of most of the speculations about graphene that we have discussed up to this point but still there is no direct experimental evidence that this theoretical prediction is correct. There is an experimental technique which is able to determine the band structure of materials and that has given a beautiful demonstration of the validity but also discovered some failures of the predictions of quantum solid state physics in this concern and is called Photoemission Spectroscopy. It makes use of the photoelectron effects i.e. the emission of electrons from materials induced by the adsorption of electron magnetic radiation. As already mentioned above this process has been explained by Einstein: the energy that is transported by the electromagnetic waves (radio waves, infrared radiation, visible light, UV, X-ray, γ Ray are all manifestations of the same process, the electromagnetic field and energy that propagate as waves and the only difference among them is the wavelength) is delivered in energy quanta that amount to hc/λ where h is a constant called Planck constant, c is the light velocity and λ is the radiation wavelength. Since every electron in a definite quantum state has a well defined energy and can receive only a well defined energy from an electromagnetic wave with a well defined wavelength i.e. the energy of 1 photon of that wavelength, if we measure the energy and the direction of an electron emitted by a material induced by an electromagnetic wave of well defined wavelength (so called a monochromatic beam of EM

radiation, since different colours correspond to different wavelengths) we can reconstruct the properties of the electron (energy and momentum) inside the material i.e. the band structure. This appears as a simple task but it really requires a complex experimental apparatus. Since the sample to be explored are relatively small (still is difficult to obtain a flake of single layer graphene with shorter dimension much larger of a micron, it would be very important to excite the electron with a bema of photon that is smaller of a micron. Moreover we want to be able to select freely the energy of the photon so to be able to tune the energy of the emitted electrons. In simple words we need a microscope tunable in the Ultraviolet to X-ray range. Where to find such a wonder? Of course in synchrotron radiation source. We plan so to study the band structure of single layer graphene with such a wonderful experimental apparatus and obtain the experimental evidence of the extraordinary bands of graphene.