Graphene

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(Dated: October 2, 2013)

Graphene has become a popular subject in the scientific and layman community due to its amazing physical properties and to the great expectations for applications. In this work we approach the subject from the point of view of how it unifies disperse branches of physics. We combine the historical developments that led to the success of graphene with a more technical description of its beauties in various physical aspects.

I. INTRODUCTION

It is lighter than a feather, stronger than steel, yet incredibly flexible and more conductive than copper. It has been hailed as the miracle material, its possible uses apparently almost endless. This is the head of an article named "Graphene: A new miracle in the material world" that appeared in a UK news paper August 2013^1 . It is only an example of the myriads of similar claims that can be seen in the written and virtual press since the Nobel Prize for physics in 2010 was awarded for the synthesis of graphene. In this article we will examine some of these miracles under a different point of view: How the material establishes a grand unification in the physics world.

All theories in physics are effective in the sense that they describe phenomena within a given range of energies (often translated into masses, sizes or velocities). As such, we have classical mechanics explaining the motion of macroscopic bodies (sizes much bigger than their Compton wavelengths, a condition encoded in the limit $\hbar \rightarrow 0$), moving at low speeds ($v \ll c$). Quantum mechanics (small objects – \hbar sizeable – with low speeds), relativistic mechanics (large bodies with big velocities) or quantum field theory (QFT) (\hbar sizeable and $v \sim c$). Systems with a large number of particles can be described with statistical mechanics (classical or quantum but usually non relativistic) or many body physics (condensed matter), a discipline that combines quantum mechanics with solid state and statistical concepts in the non-relativistic limit. Systems of hot, relativistic, and many particles were located in the so-called plasma physics and similarly complex phenomena occur in a traditionally difficult discipline: hydrodynamics.

The standard classification of branches in physics has been challenged in later times due to a conjunction of fortunate circumstances: Important players are the extraordinary accuracy reached in experimentally driven areas such as condensed matter physics where temperatures of nano-Kelvin $(10^{-9}K)$ are now routinely achieved, and the increasing complexity involved in high energy physics experiments as the heavy ions collisions in the Large Hadron Collider (LHC). Simultaneously the reductionist approach that lead the scientific method in the past century has been

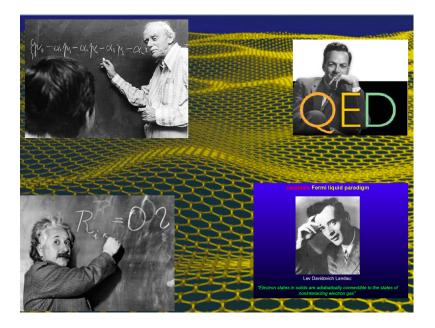


FIG. 1: (Color online) The graphene fusion.

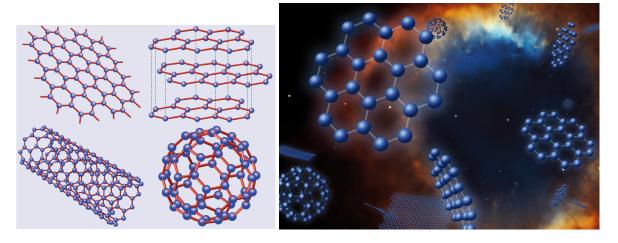


FIG. 2: Left: The graphene allotropes: Graphene, graphite, carbon nanotubes and fullerene C_{60} . Right: Artists impression of the graphenes (C24) and fullerenes found in a Planetary Nebula. (Image courtesy of the National Optical Astronomy Observatory, Tucson, USA.)

replaced by ideas of emergent degrees of freedom 2,3 .

Graphene is perhaps the material system where these changes are better exemplified. It is a monoatomic crystal of carbon atoms sitting at the nodes of a Honeycomb lattice (see Fig. 5). As such, its properties should be found within the solid state discipline. Yet, because of the combination of its two dimensional nature and the special geometry of the lattice, its elementary excitations obey the Dirac equation. This is an intrinsically relativistic description belonging to the world of elementary particles. Moreover the interacting system realizes a particular quantum field theory model similar but not equal to quantum electrodynamics (QED). These special electronic properties are at the origin of many proposed applications. Soon it was realized that its mechanical characteristics are even more exciting: The graphene crystal is one of the hardest existing materials yet it presents corrugations and supports elastic deformations typical of soft membranes. These properties are described with models coming from elasticity and even cosmology (more later). Last but not least, graphene can be reasonably argued to be the simplest example of a topologically non-trivial material precursor of the so-called topological insulators, Weyl semimetals and similar systems whose physical responses involve concepts of algebraic topology, such as Chern numbers.

We will try to combine the historical developments that led to the success of graphene with a more technical description of its beauties as relating different branches of physics and the interesting mathematical aspects involved. We will also give some trustable references for the reader interested in applications and production. Although the description and choice of topics presented in this article is a matter of personal taste, the bibliography will provide the reader with a broader view on the subject. There are all kinds of reviews on graphene. Among the most popular and informative from the early stages of the field are 4–7. The classical specialized early review is 8 and there is also now a very good book⁹. For an updated account including applications see 10.

II. SOME HISTORY

Carbon is the most interesting and versatile element in the periodic table and a fundamental constituent of life. As it is known, the atom has six electrons, two internal ones tied to the nucleus, and four of them able to make links to form structures. We learned in school that carbon appears in nature in two allotropes: diamond, the beautiful crystal that uses all four valences to become a brilliant, hard insulator, and graphite that uses three valences to make planar structures weakly attached to each other via Van der Waals forces. These two minerals were both very useful in industry but, for some reason, they were seen as the beauty and the beast. Moreover it was thought that *Diamonds are forever*. All this has changed now. First, more allotropes appeared in the nineties, the fullerenes: Carbon cages with the structure of graphene with some hexagons (exactly 12 because of Euler's theorem: Think why) replaced by pentagons. These new structures were recognized with the Nobel Prize in Chemistry 1996. Interestingly, the fullerenes were first identified in spectral lines in interstellar matter and they have been seen recently in astronomic observations (See Fig. 2). With the same building blocks of graphene there appeared together with the fullerenes, carbon nanotubes, cylindrical sheets of graphene of nanometer sizes that put the basis of the actual nanotechnology. Finally, looking at the phase diagram of carbon as a function of pressure and temperature (see Fig. 3), it can be seen that diamond is metastable and eventually can decay into graphite (do not panic: The so–called activation energy

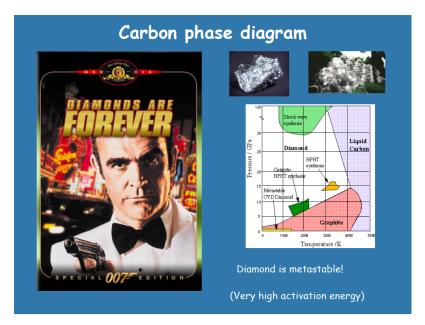


FIG. 3: The phase diagram of natural carbon. One GPa (GigaPascal) is approximately 10.000 atm (the athmospheric pressure is 1 atm) and room temperature ~ 20 C is 293K (Kelvin). Graphite is the most stable form at room temperature and pressure.

which rules the transition is very high so the probability for the occurrence is very small). So, two dimensional carbon based on a Honeycomb lattice was there in the mid nineties but the natural, planar structure was missing until 2003. Why? Let first notice that, although fullerenes and nanotubes models can be constructed by cutting and gluing graphene pieces, this is not the way they are synthesized. They form by evaporating graphite in certain special conditions: The carbon "gas" recombines into the new structures. Once they form they remain stable. This means that the new allotropes are not "natural" but they exist as synthetic materials.

The way graphene was synthesized is different. It was obtained by successive exfoliation of graphite in a context that it is worthwhile to know. At the time (beginning of 2000 decade) there was an urgent demand for increasing miniaturization of electronic devices. In parallel there was the issue of "how thin a material can be", more a scientific curiosity. It was the even more academic question of the impossibility for a two dimensional crystal to exist at all due to some theorems (Mermin-Wagner-Hohenberg-Coleman: No long-range order in two dimensions¹¹⁻¹³). Finally it was the empirical evidence that, when trying to build two dimensional crystals either by adding atoms in hydrocarbon molecules, or by using thin films, there was a critical number of atoms or layers below which the system collapses and recombines into a three dimensional mess. In words of A. Geim, nature hates two dimensions. All this was a real challenge for a curious scientist. Since the issue did not seem very promising as getting immediate or practical results, Andre Geim decided to make it a "Friday evening experiment" for his Ph. D. student Kostya Novoselov. The idea of these Friday evening experiments was: Here we are with this very expensive equipment and the impossibility to "play" with it because the necessity to produce results to justify the budget necessarily involves more or less conservative experiments with predictable outcomes. On Friday evenings, tired, having done all the week's work, they close the lab and probe interesting new ideas with uncertain results. It is paradoxical to note that A. Geim was already famous by his Friday evenings experiments with the levitating frog that won him the Ig-Nobel price in 1990 shared with the mathematical physicist M. Berry who worked out the theory of the levitron and, similarly, to the levitating frog¹⁴. As a last sociological remark lets mention that the final success to get a few layers graphite was accomplished by Kostya by "searching into the garbage". Metal surfaces are routinely cleaned (cleaved) by the simple procedure of sticking a cello tape (scotch in the USA) into the surface and stripe it off. The tape is thrown to the garbage. Saving the pieces adhered to the tape and repeating the procedure ended up with tiny portions of monolayers, bilayers etc. This is one of the reasons why graphene was thought to be poor people's subject: Any humble lab can get it this way. Of course this is quite misleading. One thing is to have it – anybody writing with a pencil or burning paper has probably produced some graphene – and an another matter is to be able to identify the micrometric sample, extract it, deposit in an appropriate substrate, and make the contacts to measure its properties. All this requires a sophisticated lab and a great deal of expertise. One of the reasons why the subject became so popular lies on the generous behavior of the Manchester team who was willing to explain the procedure and give samples to their colleagues. The 2010 Nobel prize for physics awarded to Geim and Novoselov for the synthesis of graphene has been received with great satisfaction by almost all the scientific community around it.

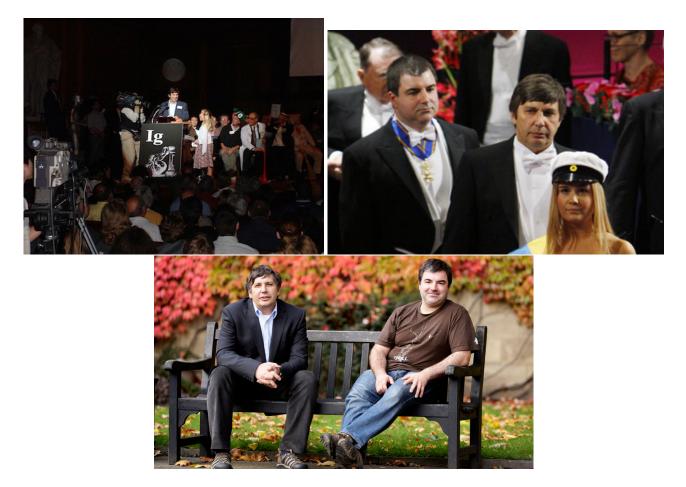


FIG. 4: Upper left: A. Geim receiving the Ignobel prize in Physics 1990. Upper right: A. Geim and K. Novoselov receiving the Nobel prize in 2010. Down: Their more natural appearance.

III. SPECIAL FEATURES AS A CONDENSED MATTER SYSTEM

The construction of the free action in condensed matter physics proceeds in a very similar way as in QFT. The non interacting hamiltonian is determined by the discrete (crystal) and internal symmetries of the system. The "band theory" provides the dispersion relation of the material and the electronic properties for a given electron occupancy. The low energy expansion of the dispersion relation arising in most of the usual crystal lattices in two and three dimensions is of the type $\varepsilon(k) = k^2/2m$. This quadratic dispersion implies a finite density of states at the Fermi surface that screens the Coulomb interactions and provides a very simple model of Fermi liquids, the Landau Fermi liquid (LFL) theory¹⁵. This standard model of metals is rooted on the existence of a finite, extended, Fermi surface (line in 2D, point in 1D). The effective description is that of a free Fermi gas with an effective mass that absorbs all the effects of interactions. The effective mass (directly related to the finite density of states at the Fermi level) is the main parameter of the theory that enters in all the physical observables¹⁶.

In what follows we will see that the special geometry of the Honeycomb lattice leads to a very different situation where the Fermi surface is reduced to two points in k space and the quasiparticles obey a massless Dirac equation in two space dimensions. Besides having a zero effective mass, the density of states at the Fermi level also vanishes, a feature responsible for most of the novel electronic behavior of the material.

The carbon atom has four external $2s^2$, $2p^2$ orbitals able to form molecular bonds. The crystal structure of graphene consists of a planar honeycomb lattice of carbon atoms shown at the left hand side of Fig. 5. In the graphene structure the in-plane σ bonds are formed from 2s, $2p_x$ and $2p_y$ orbitals hybridized in a sp^2 configuration, while the $2p_z$ orbital, perpendicular to the layer remains decoupled. The σ bonds give rigidity to the structure and the π bonds give rise to the valence and conduction bands. The exotic electronic properties of graphene are based on the construction of a model for the π electrons sitting at the positions of the Honeycomb lattice drawn by the σ bonds. Alternatively, the mechanical properties involve the σ bonds with characteristic energies of the order of 7-10 eV. The low energy excitations around the Fermi energy will have characteristic energies ranging from a few meV up to 1 eV.

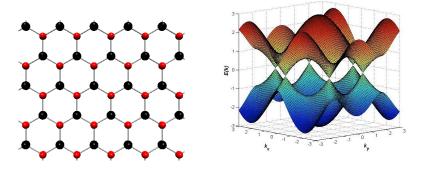


FIG. 5: Left: The graphene lattice. All circles represent carbon atoms. The different colors represent geometrically non-equivalent sites in the Honeycomb lattice (see text). Right: The dispersion relation.

Most of the crystal lattices discussed in text books are Bravais lattices. In two dimensions they can be generated by moving an arbitrary lattice point along two defined vector lattices. This happens in the generalized square and triangular lattices. It is easy to see that this is not the case of the hexagonal lattice. This lattice is very special: It has the lowest coordination in two dimensions (three) and it has two atoms per unit cell. As it can be seen in the left hand side of Fig. 5, the hexagonal lattice can be generated by moving two neighboring atoms along the two vectors defining a triangular sublattice. This is the first distinctive characteristic responsible for the exotic properties of the material.

The dispersion relation of the Honeycomb lattice based on a simple tight binding calculation is known from the early works in the literature¹⁷. We will not repeat here the derivation which is very clearly written in any graphene review but will instead highlight the main properties. The first is that two atoms per unit cell implies a two dimensional wave function to describe the electronic properties of the system. The entries of the wave function are attached to the probability amplitude for the electron to be in sublattice A or B.

The nearest-neighbor tight binding approach reduces the problem to the diagonalization of the one-electron hamiltonian

$$\mathcal{H} = -t \sum_{\langle i,j \rangle} a_i^+ a_j \tag{1}$$

where the sum is over pairs of nearest neighbors atoms i, j on the lattice and a_i, a_j^+ are the usual creation and annihilation operators. The Bloch trial wave function has to be built as a superposition of the atomic orbitals from the two atoms forming the primitive cell:

$$\Psi_{\mathbf{k}}(\mathbf{r}) = C_A \phi_A + C_B \phi_B. \tag{2}$$

The eigenfunctions and eigenvalues of the hamiltonian are obtained from the equation

$$\begin{pmatrix} \epsilon & -t\sum_{j} e^{ia\mathbf{k}\mathbf{v}_{j}} \\ -t\sum_{j} e^{ia\mathbf{k}\mathbf{v}_{j}} & \epsilon \end{pmatrix} \begin{pmatrix} C_{A} \\ C_{B} \end{pmatrix} = E(\mathbf{k}) \begin{pmatrix} C_{A} \\ C_{B} \end{pmatrix} , \qquad (3)$$

where \mathbf{u}_j is a triad of vectors connecting an A atom with its B nearest neighbors, and \mathbf{v}_j the triad of their respective opposites, a is the distance between carbon atoms and ϵ is the $2p_z$ energy level, taken as the origin of the energy. The tight binding parameter t estimated to be of the order of 3eV in graphene sets the bandwidth (6eV) and is a measure of the kinetic energy of the electrons. The eigenfunctions are determined by the the coefficients C_A and C_B solutions of equation (3). The eigenvalues of the equation give the energy levels whose dispersion relation is

$$E(\mathbf{k}) = \pm t \sqrt{1 + 4\cos^2\frac{\sqrt{3}}{2}ak_x + 4\cos\frac{\sqrt{3}}{2}ak_x\cos\frac{3}{2}ak_y} .$$
(4)

A plot of the dispersion relation can be seen at the right hand side of Fig. 5. The neutral system with one electron per lattice site is at half filling. The Fermi surface consists of six Fermi points as can be seen in Fig. 5 (only two are independent). This is the most important aspect of the system concerning its unusual properties. The existence of a finite Fermi surface (a Fermi line in two dimensions) in metals is the heart of the Landau Fermi liquid standard

model. It implies a finite density of states and the screening of the Coulomb interaction. Moreover it allows the construction of the Landau kinematics leading to the possibility of superconductivity and other collective excitations in the otherwise free electron system¹⁸. Having the Fermi surface reduced to two points invalidates in principle the LFL construction and is at the basis of the anomalous behavior of the system to be discussed later.

A continuum model can be defined for the low energy excitations around any of the Fermi points, say K_1 , by expanding the dispersion relation around it. Writing $\mathbf{k} = K_1 + \delta \mathbf{k}$ in (3) gives the low energy effective hamiltonian

$$\mathcal{H} \sim -\frac{3}{2} ta \left(\begin{array}{cc} 0 & \delta k_x + i \delta k_y \\ \delta k_x - i \delta k_y & 0 \end{array} \right).$$
(5)

The limit $\lim_{a\to 0} \mathcal{H}/a$ defines the continuum hamiltonian

$$H = v_F \vec{\sigma}.\vec{k},\tag{6}$$

where σ are the Pauli matrices and the parameter v_F is the Fermi velocity of the electrons estimated to be $v_F \sim 3ta/2 \sim c/300$. Hence the low energy excitations of the system are massless, charged spinors in two spatial dimensions moving at a speed v_F . We must notice that the physical spin of the electrons have been neglected in the analysis, the spinorial nature of the wave function has its origin in the sublattice degrees of freedom and is called pseudospin in the graphene literature. The same expansion around the other Fermi point gives rise to a time reversed hamiltonian: $\mathcal{H}_2 = v_F(-\sigma_x k_x + \sigma_y k_y)$. The degeneracy associated to the Fermi points (valleys in the semiconductor's language) is taken as a flavor. Together with the real spin the total degeneracy of the system is 4.

There are several experimental evidences of the Dirac physics in graphene. The first and most compelling appeared in the two main works where graphene was introduced to the community^{19,20} and refer to the observation of an anomalous pattern in the quantum Hall conductivity. The quantum Hall effect occurs when a homogeneous magnetic field is applied perpendicular to a two dimensional electron gas. The response of the system to an external in-plane electric field is a voltage difference in the direction perpendicular to the applied field. This transverse Hall current is quantized in integer units of e^2/h :

$$J_{i} = \sigma_{ij}^{H} E_{j} , \ \sigma_{ij}^{H} = \nu \frac{e^{2}}{h} , \ \nu = 1, ..N.$$
(7)

In a regular two dimensional electron gas the energy levels of the system in a magnetic field (Landau levels) are equally spaced and grow linearly with the field strength B: $E_n = \hbar \frac{eB}{m}(n+1/2)$. Solving the Dirac equation in a perpendicular magnetic field is an easy exercise that gives the energy spectrum $E_n = v_F \sqrt{2e\hbar B|n|}$. This is what was observed in the original references.

One of the most important aspects of graphene is the direct observation of quantum mechanical effects at room temperature. Normally, the observation of quantum mechanical phenomena requires temperatures of a few degrees above absolute zero. High $-T_c$ superconductors with quantum transition at around 150K are perhaps the main exception. The quantum Hall effect is observed at room temperature in the clean, suspended graphene samples mostly due to the perfection of the lattice and the high mobility of the electrons as it will be commented later.

IV. CONNECTION WITH HIGH ENERGY PHYSICS

A. Relativistic quantum mechanics

Quantum field theory (QFT) combines quantum relativistic phenomena in a fully consistent way, its main characteristic is the ability to create particles from the vacuum. Previous attempts to introduce relativity in the quantum mechanics formalism where the number of particles remains constant, the relativistic quantum mechanics, were plugged with some inconsistencies or paradoxes. One of the classical examples is the Klein paradox²¹ according to which a relativistic quantum particle described by the Dirac equation can penetrate through a sufficiently high potential barrier without exponential damping.

The chiral structure of the spectrum described above and the quantum mechanical nature of the condensed matter system (as opposite to QFT), allows to test several predictions of the old relativistic quantum mechanics. In particular electrons in the graphene system will tunnel with transmission probability one through a step barrier hit at normal incidence. This realization of the Klein paradox^{21,22} has been experimentally confirmed^{23,24}. A similar phenomenon is the so–called Zitterbewegung or fast trembling motion of the electrons in external fields^{25,26} whose experimental signature has been proposed in²⁷. A particularly interesting phenomenon is the supercritical atomic collapse^{28,29}

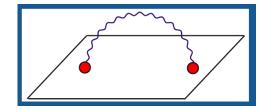


FIG. 6: Brane reduced QED: Only the charges are confined in the plane. Photons are exchanged in all three dimensions.

in graphene, a consequence of the large value of the "graphene fine structure constant" (see later). Another very interesting phenomenon is the possible realization of the Schwinger mechanism³⁰, i. e. the production of charged particle–antiparticle pairs driven by an external constant electric field^{31,32}.

The former phenomena are not only curious realizations of relativistic quantum mechanics, they have profound consequences on the experimental aspects of the material system most of them not observed before in condensed matter. In particular the Klein paradox implies that impurities and other most common sources of disorder will not scatter the electrons in graphene. The graphene system also evades the Anderson localization³³, a very important result establishing that any amount of disorder in free electron systems in two space dimensions will localize the electrons turning the system to an insulator. This gives rise to the high mobility at room temperature and the excellent metallicity of the system. Zitterbewegung was suggested in²⁵ as an explanation for the observed minimal conductivity of the samples⁷, one of the most interesting aspects of graphene whose origin remains uncertain.

B. Brane reduced QED

One of the big successes of theoretical physics in the 20th century was the construction of quantum field theory, the ability to make sense of the (diverging) perturbative series and the perturbative calculation of parameters such as the fine structure constant, α_{QED} with incredible accuracy. Quantum electrodynamics (QED), the theory of the electromagnetic interaction is its biggest exponent. The prize to pay for making sense of perturbative QFT is that the physical parameters as the electron mass or charge are not constant but depend on the energy of the experiment where they are probed. In particular the fine structure constant of QED, α_{QED} measured to be 1/137 in experiments done at energies of the order of the electron mass (about 0.5 MeV), is found to increase to 1/128 in experiments in the Large Electron-Positron collider (LEP) that ran at CERN at energies of about 90 GeV (90 × 10³ MeV). The "running" of the coupling constants is a purely QFT phenomenon tightly linked to the bad definition of QFT and with the infinities arising when computing physical quantities in perturbation theory.

We sure do not need QED at the table top as much as we appreciate low energy analogs of black holes or other inaccessible objects³ since QED is experimentally accessible. Nevertheless it is amazing that a solid state crystal whose natural description belongs to many body quantum mechanics, obeys the rules of QFT up to its more intrinsic aspects: renormalizability.

The Coulomb interactions between quasiparticles in graphene were analyzed in the early nineties³⁴ when it was not expected that the material would ever exist. This was the type of purely theoretical analysis, almost academic, done for a completely different motivation: to find a so-called "non Fermi liquid behavior" in (2+1) dimensions, something interesting at the time in relation with the physics of high temperature superconductors. These works had always the sentence assume that we have a single layer of graphite.

Once we realize that the free system is described by the massless Dirac equation in two space dimensions and that the Coulomb interaction is not screened it is tempting to think that the behavior of the interacting system is that of planar QED(2+1). However there is an important difference: In QED(2+1) all the fields, including the electromagnetic potential A_{μ} are defined in two space dimensions and vector fields in QFT have a $1/k^2$ propagator in any number of dimensions. In the case of graphene, only the charges are confined into the plane, the photons propagate in (3+1) dimensions with the standard propagator (Fig. 6). Integrating over the dimension perpendicular to the plane one gets an effective gauge propagator behaving as 1/k what changes drastically the structure of the interacting theory. The graphene Lagrangian is

$$\mathcal{L} = \int d^2 x \, dt \, \left[\overline{\Psi} \gamma^\mu \partial_\mu \Psi + e j^\mu A_\mu \right] \,, \tag{8}$$

where A_{μ} is the gauge potential $\mu = 0, 1, 2$ with the effective 1/k propagator, and the electronic current in our case

FIG. 7: Left: Graphene is the strongest material ever measured (artistic). Right: A graphene balloom from Ref. 38.

is defined as

$$j^{\mu} = (\overline{\Psi}\gamma^{0}\Psi, \frac{v_{F}}{c} \ \overline{\Psi}\gamma^{i}\Psi) , \qquad (9)$$

where v_F is the Fermi velocity, an important parameter that can be extracted from the experiments and that should be the speed of light, c, if the system were Lorentz invariant.

A standard QFT renormalization group analysis of the model was done in Ref. 34 and predicted that the Fermi velocity would "run" to higher values when the energy decreases while the electron charge e (which is renormalized in QED) remains constant. As a result, α_G decreases at low energies making perturbation theory more reliable just as happens in QED. The theory is infrared stable. Amazingly the exotic prediction of v_F growing at lower energies has been experimentally confirmed first in Ref. 35 and later in several experimental reports. A comparison of the experimental situation of graphene versus QED can be found in Ref. 36.

The dimensionless coupling constant equivalent to the fine structure constant of QED is $\alpha_G = e^2/4\pi v_F$. Since the measured value of v_F is approximately $v_F \sim c/300$, the graphene fine structure constant is 300 bigger than α_{QED} so $\alpha_G \sim 2$. The perturbative analysis of this interaction done in Ref. 34 and in many following works (for a review see Ref. 37) is not justified a priori given the large value of the coupling but it works beautifully and its predictions have been experimentally confirmed. As discussed in Sec. VI, this is, in my point of view, one of the fundamental questions that remain open in graphene.

V. MORPHOLOGICAL ASPECTS

Among the "graphene superlatives"⁷ the morphological aspects occupy a place as important –if not more – than the electronics: It is the thinnest material in the universe and the strongest ever measured. In its perfect crystalline form it is so strong that "it would take an elephant, balanced on a pencil, to break through a sheet of graphene"³⁹. Yet, it supports elastic deformations of up to 10 percent (see Fig. 7). It is impermeable even to Helium and transparent to light. These properties and the connection between lattice structure and electronic properties will be at the basis of future applications. From the point of view of this article this relation provides two wonderful connections: Gauge fields from elastic deformations, and cosmological models for curved graphene sheets.

A. Gauge fields from elastic deformations

One of the most interesting aspects of graphene is the tight relation between its structural and electronic properties reviewed in Ref. 40. The observation of ripples in the graphene samples both free standing and on a substrate⁴¹ has given rise to a very active investigation around the membrane-like properties of graphene and the origin of the ripples remains as one of the most interesting open problems in the system. The modeling of curvature by gauge fields in graphene was suggested in the early publications associated to topological defects needed to form the fullerene

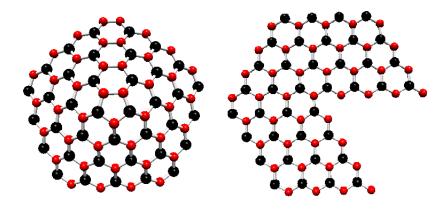


FIG. 8: Cut-and-paste procedure to form the pentagonal defect. The points at the edges are connected by a link what induces a frustration of the bipartite character of the lattice at the seam.

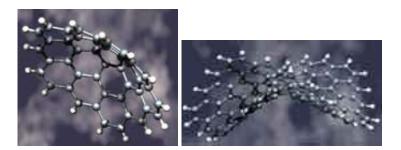


FIG. 9: A pentagon (heptagon) induces positive (negative) curvature in the hexagonal lattice.

structures⁴². The main idea was that the phase acquired by an electron circling a pentagonal defect is the same as that arising when circling a solenoid with the appropriate magnetic flux in analogy with the Aharonov–Bohm effect. The fictitious magnetic fields were also found by applying the tight binding method described in Sec. III to the deformed lattice⁴³. A combination of tight binding and elasticity theory allows to deduce the effective Hamiltonian:

$$H = -i\hbar v_F \vec{\sigma} \left(\vec{\nabla} - i\vec{A}\right),\tag{10}$$

where the vector potential associated to a given lattice deformation is written in terms of the strain tensor as 43 :

$$A_x = \frac{\beta t}{a} \left(u_{xx} - u_{yy} \right), A_y = -\frac{2\beta t}{a} u_{xy}, \tag{11}$$

where β is a parameter characteristic of the material, t is the tight binding parameter, and a the lattice constant. $u_{ij} = 1/2(\partial_i u_j + \partial_j u_i)$ is the linearized strain tensor as a function of the atomic displacement u_i .

This simple description has been very popular in the field and gave rise to the so-called "strain engineering", proposals to designing the appropriate strain to improve the performance of the samples. Again, graphene has been kind enough to show the predicted behavior in an experiment: In Refs. 44,45 it was proposed that a trigonal deformation of the sample along the three natural lattice vectors would give rise to a uniform elastic magnetic field in the central region and Landau levels could form. The observation of the predicted Landau levels was reported in Ref. 46 using Scanning Tunneling Spectroscopy (STM).

B. Relation with cosmology: QFT in curved space

One of the most intriguing properties of the suspended graphene samples is the observation of mesoscopic corrugations in both suspended⁴¹ and deposited on a substrate. Since the low energy excitations of graphene are well described by the massless Dirac equation, a natural way to incorporate the effect of the observed corrugations at low energies is to couple the Dirac equation to the given curved background. The main assumption of this approach is that the elastic properties of the samples –determined by the sigma bonds – are decoupled from the (pi) electron dynamics. The ripples can then be modeled by a fixed metric space defined phenomenologically from the observed corrugations and the electronic properties of the system will be found from the computation the Green's function in the curved space following the standard formalism set in gravitational physics⁴⁷. This approach was used in Ref. 48 to study the influence of the presence of defective rings – often called topological defects – on the electronic density of states and is described in detail in the review article Ref. 40.

What was interesting in the original reference⁴⁸ was the choice of the metric taken from a work on cosmic strings. The dynamics of a massless Dirac spinor in a curved spacetime is governed by the modified Dirac equation:

$$i\gamma^{\mu}(\mathbf{r})\nabla_{\mu}\psi = 0 \tag{12}$$

The curved space γ matrices depend on the point of the space and can be computed from the anticommutation relations $\{\gamma^{\mu}(\mathbf{r}), \gamma^{\nu}(\mathbf{r})\} = 2g^{\mu\nu}(\mathbf{r})$. The covariant derivative operator is defined as $\nabla_{\mu} = \partial_{\mu} - \Omega_{\mu}$, where Ω_{μ} is the spin connection of the spinor field that can be calculated using the tetrad formalism. Once the metric of the curved space is known there is a standard procedure to get the geometric factors that enter into the Dirac equation.

Pentagonal or N-gons with N < 6 (> 6) in graphene induce negative (positive) curvature to the sheet (see Fig. 9). In fact this is the only way to generate curvature in two dimensional lattices. This type of defects is very common in graphite and constitute the building blocks of the fullerenes. They have been observed in defective graphene samples. Since they break badly the lattice structure (see Fig. 8), the standard tight binding–elasticity model is not easy to implement. They are conical defects and the induced curvature is a delta function located at the position of the apex. Conical singularities also exist in the structure of spacetime in the form of cosmic strings whose signature is a doubling of far away objects. In 48 the metric of a set of parallel cosmic strings was taken to model the curvature of the samples with an equal number of heptagons and pentagons located at arbitrary positions and the results obtained for the density of states are compatible with the experimental observations. A very interesting inverse analogue: Instead of using condensed matter systems to model cosmological objects, we use cosmology to model the effect of topological defects in the graphene lattice on the electronic properties.

The curved QFT formalism was also used to model smooth curvature as the one attainable in the elasticity approach and came with the prediction of a space–dependent Fermi velocity that was later obtained in the tight binding formalism⁴⁹.

VI. DISCUSSION AND FUTURE

The field of production and applications is very active these days. I have not much to say about it. Only a warning about the things that can be found in the net which very often contain gross exaggerations that will in the long term be harmful to the field. It is important to distinguish what is unique in graphene (what A. Geim calls "graphene superlatives") and what is shared by other materials. This is explained with detail in A. Geim's talk available in the net: www.tntconf.org/2010/Presentaciones/TNT2010-Geim.pdf?. A good review of applications is Ref. 10 and the web pages of the University of Manchester that are constantly updated. I recommend in the doubt to stick to articles by the scientists originally working in the field.

Topological aspects have been left out of this work. Some of them can be examined in the review $\operatorname{article}^{50}$.

After all that has been said about graphene and looking to the current articles it might seem that the fundamental problems have already been solved and the future will be devoted to technological developments. Although there is some excitement driven by the experimentalists associated with the building of other two-dimensional crystals and of heterostructures combining the best of individual layers, I will restrict myself to the bare single layer graphene.

Here are two of what I consider open fundamental problems in graphene that rise important conceptual questions. (Looking back to the physics of the 20th century perhaps these problems will remain open forever: Think of quark confinement, quantization of gravity, origin of mass).

The first puzzling fact concerns interactions. Many of the experiments performed in the clean, suspended samples can be explained using perturbation theory. Most of them even at the single particle level. Yet the estimated value of the fine structure constant of graphene at the energies probed in the experiments if of order $\alpha \sim 2$. The situation with short range interactions is even worse, the value of the dimensionless Hubbard parameter is $U/t \sim 3-4$. So why is graphene behaving as a weak coupling material?

The second open question is the origin of the ripples observed in all samples. Although more experiments are needed to ascertain the issue, it seems that the ripples are not thermally activated as they would be in a standard membrane.

Under the experimental point of view, almost nothing is known on the thermodynamic properties of the material what, being a two dimensional system, is also a theoretical challenge. We do not know the melting temperature of the

crystal nor the mechanism of melting. Experimental progress has so far been limited by the small sizes of available crystals but we expect this to change soon.

Acknowledgments

This work was supported in part by the Spanish MECD grants FIS2011-23713, PIB2010BZ-00512. I thank all the colleagues and friends that have shared with me the fun of graphene physics.

- ¹ The telegraph **18 Aug 2013** (2013).
- ² P. W. Anderson, Science **177**, 393 (1972).
- ³ G. E. Volovik, *The universe in a helium droplet* (Clarendon Press, Oxford, 2003).
- ⁴ A. K. Geim, Nature Mat. **6**, 183 (2007).
- ⁵ A. K. Geim and A. H. MacDonald, Phys. Today **60**, 35 (2007).
- ⁶ M. Katsnelson and K. Novoselov, Solid State Commun. **143**, 3 (2007).
- ⁷ A. K. Geim, Science **234**, 1530 (2009).
- ⁸ A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. 81, 109 (2009).
- ⁹ M. I. Katsnelson, *Graphene. Carbon in Two Dimensions* (Cambridge University Press, 2012).
- ¹⁰ K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, Nature **490**, 192 (2012).
- ¹¹ N. D. Mermin and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966).
- ¹² P. C. Hohenberg, Phys. Rev. **158**, 383 (1967).
- ¹³ S. Coleman, Comm. Math. Phys. **31**, 259 (1966).
- ¹⁴ M. V. Berry and A. K. Geim, Eur. J. Phys. **18**, 307 (1997).
- ¹⁵ L. D. Landau, Soviet Physics JETP **3**, 920 (1957).
- ¹⁶ A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, Methods of quantum field theory in statistical physics (Dover, 1975).
- ¹⁷ P. R. Wallace, Phys. Rev. **71**, 622 (1947).
- ¹⁸ J. Polchinski, Effective Field Theory and the Fermi Surface (World Scientific, Singapore, 1993), proceedings of the 1992 Theoretical Advanced Institute in Elementary Particle Physics, J. Harvey and J. Polchinski eds.
- ¹⁹ K. S. Novoselov, D. Jiang, T. Booth, V. Khotkevich, S. M. Morozov, and A. K. Geim, Proc. Nat. Acad. Sc. **102**, 10451 (2005).
- ²⁰ Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, Nature **438**, 201 (2005).
- ²¹ N. Dombey and A. Calogeracos, Phys. Rep. **315**, 41 (1999).
- ²² M. I. Katsnelson, K. S. Novoselov, and A. K. Geim, Nature Phys. 2, 620 (2006).
- ²³ A. F. Young and P. Kim, Nature Phys. 5, 222 (2009).
- ²⁴ N. Stander, B. Huard, and D. Goldhaber-Gordon, Phys. Rev. Lett. **102**, 026807 (1999).
- ²⁵ M. I. Katsnelson, European Physics Journal B **51**, 1434 (2006).
- ²⁶ R. Winkler, U. Zulicke, and J. Bolte, Phys. Rev. B **75**, 205314 (2007).
- ²⁷ T. M. Rusin and W. Zawadzki, Phys. Rev. B **80**, 045416 (2009).
- ²⁸ A. V. Shytov, M. I. Katsnelson, and L. S. Levitov, Phys. Rev. Lett. **98**, 236801 (2007).
- ²⁹ V. M. Pereira, J. Nilsson, and A. H. C. Neto, Phys. Rev. Lett. **98**, 166802 (2007).
- ³⁰ J. Schwinger, Phys. Rev. **82**, 664 (1951).
- ³¹ D. Allor and T. D. Cohen, Phys. Rev. D 78, 096009 (2008).
- ³² B. Dora and R. Moessner, Phys. Rev. B **81**, 165431 (2010).
- ³³ P. W. Anderson, Phys. Rev. **109**, 1492 (1958).
- ³⁴ J. González, F. Guinea, and M. A. H. Vozmediano, Nucl. Phys. B **424** [FS], 595 (1994).
- ³⁵ D. C. Elias, R. V. Gorbachev, A. S. Mayorov, S. V. Morozov, A. A. Zhukov, P. Blake, L. A. Ponomarenko, I. V. Grigorieva, K. S. Novoselov, F. Guinea, et al., Nature Phys. 7, 701 (2011).
- ³⁶ M. A. H. Vozmediano, Nature Phys. 7, 671 (2011).
- ³⁷ V. N. Kotov, B. Uchoa, V. M. Pereira, A. H. Castro Neto, and F. Guinea, Rev. Mod. Phys. 84, 1067 (2012).
- ³⁸ J. S. Bunch et al., Nano Lett. **8**, 2458 (2008).
- ³⁹ X. Wei, J. W. Kysar, and J. Hone, Science **321**, 385 (2008).
- ⁴⁰ M. A. H. Vozmediano, M. I. Katsnelson, and F. Guinea, Phys. Reports **493**, 109 (2010).
- ⁴¹ J. C. Meyer et al., Nature **446**, 60 (2007).
- ⁴² J. González, F. Guinea, and M. A. H. Vozmediano, Phys. Rev. Lett. **69**, 172 (1992).
- ⁴³ H. Suzuura and T. Ando, Phys. Rev. B **65**, 235412 (2002).
- ⁴⁴ F. Guinea, M. I. Katsnelson, and A. G. Geim, Nature Physics 6, 30 (2010).
- ⁴⁵ F. Guinea, A. G. Geim, M. I. Katsnelson, and K. S. Novoselov, Phys. Rev. B **81**, 035408 (2010).
- ⁴⁶ N. Levy et al., Science **329**, 544 (2010).
- ⁴⁷ N. D. Birrell and P. C. W. Davis, *Quantum fields in curved space* (Cambridge University Press, 1982).
- ⁴⁸ A. Cortijo and M. A. H. Vozmediano, Nucl. Phys. B **763**, 293 (2007).

⁴⁹ F. de Juan, M. Sturla, and M. A. H. Vozmediano, Phys. Rev. Lett. **108**, 227205 (2012).
 ⁵⁰ A. Cortijo, F. Guinea, and M. A. H. Vozmediano, J. Phys. A: Math. Theor. **45**, 383001 (2012).