A cosmological model for corrugated graphene sheets.

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Abstract. Defects play a key role in the electronic structure of graphene layers flat or curved. Topological defects in which an hexagon is replaced by an n-sided polygon generate long range interactions that make them different from vacancies or other potential defects. In this work we review previous models for topological defects in graphene. A formalism is proposed to study the electronic and transport properties of graphene sheets with corrugations as the one recently synthesized. The formalism is based on coupling the Dirac equation that models the low energy electronic excitations of clean flat graphene samples to a curved space. A cosmic string analogy allows to treat an arbitrary number of topological defects located at arbitrary positions on the graphene plane. The usual defects that will always be present in any graphene sample as pentagon-heptagon pairs and Stone-Wales defects are studied as an example. The local density of states around the defects acquires characteristic modulations that could be observed in scanning tunnel and transmission electron microscopy.

1 Introduction.

The recent synthesis of single layers of graphite -graphene - \cite{1,2}, has opened the way to study a new really two-dimensional system that constitutes an excellent laboratory to test some of the most fruitful ideas of recent condensed matter: localization, existence-or not- of Fermi liquids in two dimensions, or the nature of the metallic state in two dimensions. Moreover the experiments have been able to verify the beautiful theoretical model predicted years ago for the low energy excitations described by the massless Dirac equation \cite{3} in two dimensions \cite{4,5,6} and permit to envisage graphene as a laboratory to test field theory or cosmological ideas \cite{7}.

Most of the experimental samples studied in recent times show mesoscopic corrugations \cite{8} which are produced in the process of cleavage and are observed by atomic force microscopy. The height of the observed ripples go up to several Amstrongs and the lateral size is typically a few tens of nanometers. They have been invoked to explain the reported absence of weak (anti)-localization observed in graphene \cite{9,10} and to strengthen the effects of the spin orbit coupling \cite{11}. The presence of this curved regions in graphene can have strong effects on the physical properties and has not yet been fully explored.

A systematic study of the electronic properties of slightly curved graphene sheets has been started in \cite{12,13} where it is suggested that the observed ripples are due to the presence of heptagon-pentagon pairs or Stone-Wales defects in the graphene sheet. This type of defects have been observed in the previously existing forms of graphene (nanotubes and fullerenes) and should be very natural in the flat samples. In this work we explain the derivation of a model based on a cosmological analogy that can describe an average flat graphene sheet with regions

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Fig. 1. Formation of a Stone Wales defect in the honeycomb lattice.

of non zero curvature induced by an arbitrary number of heptagons and pentagons. We also present some results on the charge inhomogeneities to be expected in samples with this type of disorder.

2 Disorder in graphene. Experimental observation of topological disorder in graphene and related compounds.

Disorder has a very strong influence on the electronic properties of low dimensional systems. During the "first revolution" of graphene after the synthesis of fullerenes and nanotubes, there appeared many works treating vacancies, adatoms, edges, and what we call topological disorder produced by substitution of a hexagonal ring in the honeycomb of graphene by an n-sided polygon. Observations of all these types of disorder were reported in [14]. Topological disorder was responsible for the formation of fullerenes and had also a strong influence on the electronic properties of nanotubes. One of the most popular types of defects in nanotubes were the Stone-Wales defects made by a $\pi/2$ rotation of a graphene bond giving rise to the formation of two pentagons and to heptagons. Among the topological defects these have minimal activation energy and their presence allows to design nanotubes which are metallic at one end and semiconducting at the other. Pentagon-heptagon pairs were also used to join nanotubes of different chiralities or diameters [15]. A very important property of the topological defects that will be discussed in this work is that they generate a long range potential. This makes a big difference with vacancies or impurities modelled by local potentials.

Topological defects can be seen as disclinations of the lattice which acquires locally a finite curvature. The accumulations of various defects may lead to closed shapes. Rings with $n < 6$ sides give rise to positively curved structures, the most popular being the $C_{60}$ molecule that has twelve pentagons. Polygons with $n > 6$ sides lead to negative curvature as occur at the joining part of carbon nanotubes of different radius and in the Schwarzite [16], a structure appearing in many forms of carbon nanofoam [17]. This type of defects have been observed in experiments with carbon nanoparticles [14,18,19,20] and other layered materials [21]. Conical defects with an arbitrary opening angle can be produced by accumulation of pentagons in the cone tip and have been observed in [22,23]. Inclusion of an equal number of pentagons and heptagonal rings in a graphene sheet would keep the flatness of the sheet at large scales and produce a flat structure with curved portions that would be structurally stable and have distinct electronic properties.
As it is well known, the low-energy excitations with momenta in the vicinity of any of the Fermi points $K_+$ and $K_-$ of graphene have a linear dispersion and can be described by a continuous model which reduces to the Dirac equation in two dimensions [3]. In the absence of interactions or disorder mixing the two Fermi points, the electronic properties of the system around the Fermi point $i$ are well described by the effective low-energy Hamiltonian density:

$$H_{0i} = \hbar v_F \bar{\Psi}_i(r)(\sigma_x \partial_x + \sigma_y \partial_y)\Psi_i(r),$$

(1)

where $\sigma_{x,y}$ are the Pauli matrices, $v_F = (3ta)/2$, and $a = 1.4\AA$ is the distance between nearest carbon atoms. The components of the two-dimensional wavefunction:

$$\Psi_i(r) = \begin{pmatrix} \varphi_A(r) \\ \varphi_B(r) \end{pmatrix},$$

(2)

correspond to the amplitude of the wave function in each of the two sublattices (A and B) which build up the honeycomb structure.

Substitution of an hexagon by an n-sided polygon in the graphene lattice can be described by a cut-and-paste procedure as the one shown in Fig. 2 for the particular case of a pentagon. A $\pi/3$ sector of the lattice is removed and the edges are glued. In this case the planar lattice acquires the form of a cone with the pentagon in its apex. Such a disclination has two distinct effects on the graphene sheet. It induces locally positive (negative) curvature for $n < 6$ ($n > 6$) and, in the paste procedure, it can break the bipartite nature of the lattice if $n$ is odd while preserving the symmetry if $n$ is even. This makes a difference with the case of the formation of nanotubes where the bipartite nature of the lattice always remains intact. There are then two distinct effects to take into account: the curvature that we will treat later, and the non-trivial boundary condition that the frustration induces on the spinor field. Both effects are well known in other branches of physics, the second is related to the holonomy or Berry phase.

In relativistic quantum field theory where there is a very tight connection between the spin and the statistics, a spin 1/2 particle is described by a field that belongs to the so-called spinor representation of the Lorentz group. A distinct characteristic of spinor representations is that when they move around a closed path they pick up a minus sign (upon a $2\pi$ rotation they acquire a phase of $\pi$). A spinor going around a closed path encircling the pentagon in Fig. 1 will acquire a phase proportional to one half the total angle of the path ($2\pi - \pi/3 = 2\pi(1-1/6)$). When solving the Shrodinger equation $H\Psi = E\Psi$ with the Hamiltonian this condition has to be imposed on the wave function as a boundary condition which often are hard to deal with.
A way to incorporate the constraint attached to the boundary condition to the hamiltonian is to remember the Bohm-Aharonov (BA) effect and substitute the pentagon by a fictitious magnetic field located at the same point. The flux of the field can be adjusted so that the phase acquired by the spinor when going around the vector potential is the same as the one induced by going around the pentagon. This procedure has the advantage to be easily generalized to defects of arbitrary opening angle. In the BA effect the phase is proportional to the circulation of the vector potential along the closed path:

\[ \oint \mathbf{A} \cdot d\mathbf{r} = 2\pi(1 - \pi/3). \] (3)

The simplest vector potential having the property (3) is a vortex:

\[ \mathbf{A}(x, y) = \left( \frac{-y}{x^2 + y^2}, \frac{x}{x^2 + y^2} \right) = -\nabla \theta(r), \]

which in polar coordinates reduces to the gradient of the polar angle \( \theta \). The presence of a pentagon in the lattice has an additional consequence which was discussed at length in [6]: by going along a closed path encircling the pentagon the two Fermi points are also exchanged. This new condition can be fulfilled by attaching a quantum number (flavor) to the Fermi points, and considering the two bispinors \( \psi_i(r), i = 1, 2 \) of eq. (2) as the two components of an SU(2) flavor doublet. The vector field will now be a non-abelian gauge field able to rotate the spinors in this flavor space. The full boundary condition to impose on the spinor when circling a pentagon (or any conical singularity of arbitrary defect angle \( \varphi \)) is

\[ \Psi(\theta = 0) = T_C \Psi(\theta = 2\pi) \Leftrightarrow \Psi(\theta = 0) = \exp\left( \oint_C \mathbf{A}_a T^a d\mathbf{r} \right) \Psi(\theta = 2\pi), \] (4)

where \( \mathbf{A}_a \) are a set of gauge fields and \( T^a \) a set of matrices related to the flavor SU(2) degree of freedom of the system. The situation becomes more complicated when there are various conical defects in the sample. The problem of the holonomy, i.e. of the transformation properties of the spinor upon parallel transport around closed paths can be generalized as described in [24,25], the effect of the curvature is much harder to treat.

In [5] the gauge model was used to compute the electronic spectrum of the \( C_{60} \) and other spherical fullerenes. To account for curvature effects, we solved the Dirac equation on the surface of a sphere -thereby smoothing the curvature singularities-. The effect of the fictitious magnetic field was in turn smoothed over the sphere by considering an abelian monopole sitting at its center with the total magnetic charge appropriate to account for the 12 pentagons needed to close the structure. The simplified model for the icosahedral \( C_{60} \) with an abelian monopole of charge 3/2 reproduced the observed low-energy spectrum and the comparison with more detailed calculations was quite reasonable.

4 A cosmological model.

The approach described in the previous section allows to account for both the curvature and the holonomy induced by topological defects when the graphene sheet is wrapped on a surface with an explicit parametrization. It has been applied to the case of the ellipsoid or the hiperboloid in [26]. The system that we try to describe, namely, an asymptotically flat graphene sheet with some portions curved, can be modelled by the presence of an equal number of pentagons and heptagons in the lattice. Modelling the heptagons is a problem and so it is to include the curvature. Conical singularities have been studied in cosmology as they are produced by cosmic strings, a type of topological defect that arises when a U(1) gauge symmetry is spontaneously broken [27]. The authors of ref. [28] study the Green’s function of different fields in a cosmological
scenario with an arbitrary number of cosmic strings. The metric of a two dimensional space in presence of a single cosmic string in polar coordinates is:

\[ ds^2 = -dt^2 + dr^2 + c^2 r^2 d\theta^2, \]

(5)

where the parameter \( c \) is a constant related to the deficit angle \( b \) (=2\( \pi /6 \) in the case of a pentagon) by \( c = 1 - b \). The case of a single cosmic string which represents a deficit angle in the space can be generalized to describe seven membered rings representing an angle surplus by considering a value for \( c \) larger than 1. This situation is non-physical from a general relativity viewpoint as it would correspond to a string with negative mass density but it makes perfect sense in our case. The scenario can also be generalized to describe an arbitrary number of pentagons and heptagons by using the following metric:

\[ ds^2 = -dt^2 + e^{-2A(x,y)}(dx^2 + dy^2), \]

(6)

where

\[ A(r) = \sum_{i=1}^{N} 4\mu_i \log (r_i) \]

and

\[ r_i = [(x - a_i)^2 + (y - b_i)^2]^{1/2}. \]

This metric describes the space-time around \( N \) parallel cosmic strings, located at the points \((a_i, b_i)\). The parameters \( \mu_i \) are related to the angle defect or surplus by the relationship \( c_i = 1 - 4\mu_i \) in such manner that if \( c_i < 1(>1) \) then \( \mu_i > 0(<0) \).

The dynamics of a massless Dirac spinor in a curved spacetime is governed by the Dirac equation:

\[ i\gamma^\mu \nabla_\mu \psi = 0 \]

(7)

The difference with the flat space lies in the definition of the \( \gamma \) matrices that satisfy generalized anticommutation relations

\[ \{ \gamma^\mu, \gamma^\nu \} = 2g^{\mu\nu}, \]

(8)

and in the covariant derivative operator, defined as

\[ \nabla_\mu = \partial_\mu - \Gamma_\mu, \]

where \( \Gamma_\mu \) is the spin connection of the spinor field that can be calculated using the tetrad formalism[29]. From equation (7) we can write down the Dirac equation for the electron propagator, \( S_F(x, x') \):

\[ i\gamma^\mu(r)(\partial_\mu - \Gamma_\mu)S_F(x, x') = 1\sqrt{-g} \delta^3(x - x'), \]

(9)

where \( x = (t, r) \). The local density of states \( N(\omega, r) \) is obtained from (9) by Fourier transforming the time component and taking the limit \( r \to r' \):

\[ N(\omega, r) = ImTrS_F(\omega, r, r). \]

(10)

We solve eq. (10) considering the curvature induced by the defects as a perturbation of the flat graphene layer.

5 Effect on the density of states.

With the model presented in the previous section we are able to compute the density of states of a system with "ripples". The details of the calculation are given in [13]. The main results are that the local density of states is enhanced around defects with \( n < 6 \) which induce positive curvature in the lattice while the charge is "repelled" from regions with negative curvature \( (n > 6) \). Heptagon-pentagon pairs that keep the graphene sheet flat in the long range behave...
Fig. 3. Correction to the local density of states in a wide region around two pairs of heptagon-pentagon defects located out of the region (see text) for increasing values of the energy.

as dipoles and give rise to characteristic modulations of the DOS that can be observed by Scanning Tunnel Microscopy. The intensity of the oscillations grows with the energy. Fig. 3 shows the relative correction (normalized to the free density of states) to the local density of states in a extended region of the lattice induced by two pairs of heptagon-pentagon defects located out of the region for increasing values of the energy. The color code is indicated in the figure: green stands for the DOS of perfect graphene at the given energy and red (blue) indicates an accumulation (depletion) of the density in the area. The patterns depend also on the relative orientation of the dipoles. The spacial extent of the correction is such that the intensity decays to ten percent in approximately 20 unit cells so they can be observed in scanning tunnel spectroscopy as inhomogeneous regions of a few nanometers.

Another example is depicted in fig. 4 which shows the structure of the local density of states in real space induced in the graphene sheet by the presence of a Stone Wales defect. The left side shows the corrections due to a Stone-Wales defect located in the middle of the area at a fixed intermediate frequency. The modulation of the local density of states around the defects is hardly noticeable due to the strong intensity localized at the defects. The same image is shown in the right hand side of fig. 4 with the Stone-Wales defect located out of plane in the upper right corner. The modulation of the LDOS is clearly visible. The correction obtained is of the order of a few percent.

6 Summary and future.

Topological defects are likely to be present in the recently synthesized graphene samples as they are in nanotubes and other fullerenes. The size and shape observed in [23] coming from a single pentagon is similar to the ripples reported in [9]. This type of disorder generate long range potentials which have a strong influence on the electronic properties. In this work we have presented a model for these defects based on a cosmic string analogy and the results on the inhomogeneities induced by this topological disorder on the density of states. This is yet another example of the fruitful interplay between cosmology and condensed matter[?] but is
has the peculiarity that this time it is cosmology what provides the model to graphene unlike the usual situation in which condensed matter systems are used as laboratories to test high energy models.

The effects of the topological disorder on the transport properties of graphene obtained by averaging over are very interesting and work in this direction will be reported soon[30].

7 Acknowledgments

We thank the organizers of the graphene conference in Dresden for the stimulating atmosphere. We profited there from conversations on transport in long range correlated disorder with B. Altshuler, V. Falko, Igor Gornyi, D. Huertas-Hernando and E. McCann.

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