One-dimensional structural irregularities in graphene: chiral edges and grain boundaries

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Abstract. Many properties of graphene strongly depend on the presence of disorder and confinement effects. Using computational approaches based on model Hamiltonians and first-principles formalisms, we investigate the structure and electronic properties of chiral edges and grain boundaries in graphene. We show that magnetic edge states are inherent to low-symmetry graphene edges and exhibit a number of systematic structure-property relations. Certain grain boundary structures are shown to dramatically affect electronic transport in polycrystalline graphene by reflecting charge carriers in considerable energy ranges.

1. Introduction
Graphene has attracted considerable interest due to its extraordinary physical properties. One striking feature of this two-dimensional material is a sensitive dependence of its properties on the presence of disorder and confinement [1]. For instance, one-dimensional nanostructures made of graphene, the so-called graphene nanoribbons, exhibit dramatic dependence of their electronic structure on the crystallographic orientation of the edges [2,3]. While graphene nanoribbons with the edges cut along the armchair high-symmetry direction are semiconductors with band gap depending on the width and terminating structure, nanoribbons having zigzag high-symmetry edges would have flat band of zero-energy localized electronic edge states in an independent-particle picture neglecting many-electron effects. Electron-electron interactions are expected to remove the divergent density of state and the electronic instability associated with these zero-energy states resulting in a novel type of magnetic ordering [3-5]. The edge-state magnetism in graphene has been a matter of intense investigations in the last several years. A recent experimental study of graphene nanoribbons with ultrasmooth low-symmetry (chiral) edges revealed both the presence of edge states and a clear indication of magnetic ordering [6].

It has been realized recently that large-scale samples of graphene tend to be polycrystalline. In the case of graphene produced by means of micromechanical cleavage of graphite, the size of single-crystalline samples of graphene is limited by the size of graphite crystallites. Similarly, substrate imperfections and multiple nucleation centers limit the size of crystalline domains in graphene produced by epitaxial growth techniques. Indeed, recent experimental studies have revealed the polycrystalline nature of epitaxial graphene samples showing the presence of one-dimensional grain-boundary defects [7,8]. Issues of interest include: What determines the structure of defects in...
polycrystalline graphene? And how do these defects affect the charge transport properties of graphene?

In this article, we briefly describe our recent theoretical studies directed towards understanding the two above-mentioned types of one-dimensional structural irregularities in graphene – chiral edges and grain boundaries. We show that although these defects can affect the properties of graphene in undesirable ways, they can also be used for purposeful engineering graphene nanostructures and materials with novel functionalities.

2. Chiral graphene edges and nanoribbons
We investigate the electronic structure of graphene nanoribbons using a mean-field approximation to the Hubbard model Hamiltonian

\[
H = -t \sum_{\langle i,j \rangle, \sigma} [c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}] + U \sum_i (n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\uparrow} \rangle n_{i\downarrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle),
\]

in which the strength of electron-electron interactions responsible for the onset of magnetic ordering is controlled by the magnitude of the on-site Coulomb repulsion \( U \) relative to the hopping integral \( t \). In graphene, the magnitude of \( U \) is expected to be comparable to or less than that of \( t \). Moreover, we point out that this effective parameter \( U \) should also incorporate environmental factors such as the enhancement of screening due to the proximity of dielectric or metallic substrate [6].

\[\text{Figure 1.} \ (a) \text{ Chiral graphene nanoribbon with edge defined by} \ (3,1) \ \text{vector} \ (\theta = 13.9^\circ). \ \text{Circle areas correspond to the local magnetic moments from the mean-field Hubbard model solution obtained at} \ U/t = 1 \ (\text{closed circles – spin-up; open circles – spin-down}). \ (b) \text{ Band structure and} \ (c) \text{ density-of-states plot for the nanoribbon shown in panel (a) obtained at} \ U/t = 0 \ (\text{dashed line}) \ \text{and} \ U/t = 1 \ (\text{solid line}). \]
Figure 1(a) shows a representative example of chiral graphene nanoribbon with the edge oriented along the translational vector (3,1) of the graphene lattice. This edge orientation characterized by chirality angle $\theta = 13.9^\circ$ is situated roughly in the middle between the high-symmetry zigzag ($\theta = 0^\circ$) and armchair ($\theta = 30^\circ$) directions. In the absence of electron-electron interactions ($U/t = 0$) the band structure features a zero-energy flat band of edge states (Fig. 1(b)). At $U/t = 1$, the ground state solution for this system is a semiconducting magnetic state. The density-of-states plot shown in Figure 1(c) has one peak at $E = 0$ in the absence of electron-electron interactions which splits into four peaks characterized by the energy splittings $\Delta^0$ and $\Delta^1$ once the Hubbard term is introduced into the model Hamiltonian in Eq. (1). This scenario is qualitatively very similar to the case of zigzag graphene nanoribbons. However, the magnetic moment per edge unit length $M$ is about twice smaller for this chiral graphene nanoribbon than that in the zigzag case. The energy splittings, in particular $\Delta^1$, are reduced in comparison with the corresponding splittings in the case of zigzag graphene nanoribbon of equivalent width.

**Figure 2.** Dependence of (a) magnetic moment per edge unit length $M$ and (b) energy splittings $\Delta^0$ and $\Delta^1$ on chirality angle $\theta$ for 5-nm-wide nanoribbons obtained from the mean-field Hubbard model ($U/t = 1$) calculations. The dotted line shows magnetic moments in the limit of infinite width (cf. Eq. (2)).

Figure 2 shows the dependence of magnetic moment per edge length $M$ and energy splittings $\Delta^0$ and $\Delta^1$ on chirality angle $\theta$. Remarkably, the semiconducting magnetic ground-state solutions span almost the whole range of chiralities with exception of a small region close to the armchair direction ($\theta = 30^\circ$). The values of $M$ show monotonic dependence on $\theta$ which reflects a change in the density of edge states as a function of $\theta$ in the limit of infinite width is [9]:

$$\rho(\theta) = \frac{2}{3a_0} \cos \left( \theta + \frac{\pi}{3} \right).$$

(2)

The energy splitting $\Delta^1$ follows a very similar trend (Fig. 2(b)) as $M$, while the band gap $\Delta^0$ shows only weak variations in a broad range of chiralities. Interestingly, the dependence on the nanoribbons width is completely opposite for the two splittings (not shown), owing to the fact that $\Delta^0$ arises from inter-edge interaction whereas $\Delta^1$ arrives from intra-edge interaction. The magnetic moments per edge length $M$ are also mostly independent on width. These revealed structure-property relations thus can serve as unambiguous signatures of edge-state magnetism in graphene [10].

International Symposium "Nanoscience and Quantum Physics 2011" IOP Publishing
Journal of Physics: Conference Series 302 (2011) 012016 doi:10.1088/1742-6596/302/1/012016
3. Grain boundaries and electronic transport in polycrystalline graphene

The properties of polycrystalline materials are determined by the presence of grain boundaries – one-dimensional defects separating single-crystalline domains of different orientations. The structure of these one-dimensional structural irregularities is dictated by the misorientation angle of the two crystallites. In this sense, misorientation angle is a topological invariant which introduces non-local disorder into polycrystalline materials while the local atomic structure of grain boundary defects is determined by thermodynamic arguments at fixed misorientation angle. We found that in graphene for any possible misorientation angle, it is possible to construct a grain boundary structure in which all carbon atoms maintain their three-fold coordination [11]. Such structures have inherently low formation energies. The basic building blocks of grain boundaries in graphene are the dislocations arranged in one-dimensional arrays. The shortest Burgers vector dislocation in graphene represents a pair of edge-sharing five- and seven-membered rings in the honeycomb lattice of graphene. Two examples of large-angle grain boundaries are shown in Figure 3.

![Figure 3. Two examples of grain boundaries in graphene: (a) a low energy symmetric grain boundary characterized by misorientation angle 21.8° and (b) an asymmetric 30° grain boundary that has a significant transport gap.](image)

The grain boundary defects inevitably affect the transport properties of graphene. Remarkably, the periodic grain boundary structures are predicted to show two very different transport behaviors [12]. One way to describe such periodic structures is to refer to the corresponding matching vectors which are translational vectors on the two-dimensional graphene lattice in the corresponding single-crystalline domains, \((n_L, m_L)\) and \((n_R, m_R)\). If \(n_L - m_L = 3p\) and \(n_R - m_R = 3q\), or \(n_L - m_L \neq 3p\) and \(n_R - m_R \neq 3q\) \((p,q \in \mathbb{Z})\), the band structure of graphene dictates that, for any charge carrier with allowed values of momentum and energy in one domain, there exists a conduction channel in the other domain. That is, no transmission channel is blocked by the specific translation symmetry of the grain boundary defect. An example of such structure is shown in Figure 3(a): \((n_L, m_L) = (n_R, m_R) = (2, 1)\). However, selection by symmetry takes place when \(n_L - m_L = 3p\) and \(n_R - m_R \neq 3q\), or \(n_L - m_L \neq 3p\) and \(n_R - m_R = 3q\). In this case, transmission is blocked in the range of energies \(E \in (-E_g/2, E_g/2)\) with transport gap

\[
E_g = \frac{h \nu_f 2\pi}{3d} = \frac{1.38}{d[\text{nm}]} \text{[eV]},
\]

which is dependent only on the periodicity of grain boundary \(d\). An example of such structure is shown in Figure 3(b). The matching vectors defining the structure of this defect are \((5,0)\) and \((3,3)\). Our first-principles non-equilibrium Green’s function calculations for this case predict a large transport gap of 1.1 eV in good agreement with Eq. (3).

The possibility of engineering grain boundaries in graphene characterized by large transport gaps may find important practical applications [12]. Owing to the absence of a band gap and the Klein
tunneling, electrostatic barriers in graphene are ineffective. This is the major obstacle on the way of introducing graphene into digital electronics. Controlling electronic transport by means of engineered grain boundaries relies on the momentum mismatch rather than on tailoring potential barrier profiles. The proposed approach thus may help circumventing the above-mentioned difficulties thus paving a way towards practical graphene electronics.

4. Conclusions
We have shown that one-dimensional structural irregularities in graphene, chiral edges and grain boundaries, exhibit a range of novel structure-property relations. Similarly to zigzag graphene nanoribbons, nanoribbons with chiral edges also host spin-polarized edge states. Moreover, their electronic and magnetic properties can be tuned by changing the edge chirality and the width. Grain boundaries in polycrystalline graphene are shown to affect electronic transport in a dramatic manner. Certain grain boundary structures perfectly reflect charge carriers in large energy ranges. We anticipate that these novel structures can be used for purposeful engineering graphene nanostructures and materials with novel functionalities.

Acknowledgments
We wish to thank C. Tao and M. F. Crommie for discussions. This work was supported by NSF Grant No. DMR10-1006184 (numerical simulations of GNRs) and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering Division, US Department of Energy under Contract No. DE-AC02-05CH11231 (software development of electron correlation effects). O. V. Y. was partially supported by the Swiss National Science Foundation (grant No. PBELP2-123086). R.B.C. acknowledges financial support from Brazilian agencies CNPq, CAPES, FAPERJ and INCT – Nanomateriais de Carbono and the ONR MURI program.

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