Complex evolution of the electronic structure from polycrystalline to monocrystalline graphene: generation of a new Dirac point

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First calculations, employed to address the properties of polycrystalline graphene, indicate that the electronic structure of tilt grain boundaries in this system display a rather complex evolution towards graphene bulk, as the tilt angle decreases, with the generation of a new Dirac point at the Fermi level, and an anisotropic Dirac cone of low energy excitations. Moreover, the usual Dirac point at the K point falls below the Fermi level, and rises towards it as the tilt angle decreases. Further, our calculations indicate that the grain-boundary formation energy behaves non-monotonically with the tilt angle, due to a change in the the spatial distribution and relative contributions of the bond-stretching and bond-bending deformations associated with the formation of the defect.

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Graphene - an isolated layer of $sp^2$-bonded carbon atoms arranged in a honeycomb structure - was until very recently, a “theoretical” reference system for the study of the properties of the “real” $sp^2$-bonded carbon forms, such as fullerences, nanotubes, and graphite. Since the recent report of the isolation of a stable single-atom-thick carbon layer, by exfoliation of graphite, graphene itself has occupied the center stage of Materials Physics, as a paradigmatic system for “relativistic” condensed-matter phenomena, as well as a promising material for Nanoelectronics, due to its exceptional electronic properties. Graphene is a null-gap semiconductor with a vanishing density of states at the Fermi level, and electronic bands that are linear and isotropic within $\sim 1$ eV from the Fermi level. This linearity and the presence of two sub-lattices imply that charge carriers in graphene effectively behave as massless chiral “relativistic” particles, being described by Dirac’s equation. Due to the chiral nature of the electronic excitations, which leads to the absence of backscattering, graphene holds ballistic charge transport on the microscale, even at room temperature, and with high concentrations of defects and impurities. In the last few years, scientific interest in graphene has rapidly intensified, and the material is expected to play a major role in Nanoelectronics in the future.

Presently, common synthesis routes for graphene are the original exfoliation method, that produces monocrystalline graphene samples, and epitaxy, mostly on SiC and metallic substrates. Recent works on epitaxially-grown graphene report the occurrence of superstructures interpreted as Moiré patterns based on STM, AFM, and STS measurements. Moiré patterns and superstructures, associated with layer stacking, as well as the occurrence of bulk and surface grain boundaries, are topics of prominence in the physics of highly-oriented pyrolytic graphite (HOPG) itself. Grain boundaries (GB) are among the most commonly occurring extended defects in HOPG, because of its polycrystalline character. For large scale graphene production and application, it is expected that synthesis methods will be epitaxy based, being quite conceivable that polycrystalline samples will be produced. Indeed, the occurrence of GBs on the graphene layer has been recently reported, speculated as a probable source of long-range electronic perturbations in graphene on SiO$_2$, and further, the lower carrier mobility of epitaxial graphene (when compared with exfoliated samples), in a macroscopic-size graphene field-effect transistor, has been tentatively assigned to the electronic perturbations associated with GBs.

Previous works have addressed the electronic properties of disordered graphene, but these have focused on the effects of point defects, corrugation, and extended edge states in graphene ribbons, drawing only speculative conclusions in what regards the electronic states of GBs. In this scenario, addressing properties of GBs in graphene is of primary relevance. In the present work, we employ first principles calculations to examine the energetics and electronic properties of GBs in graphene. We
focus on the structural GB model proposed by Simonis et al. [11] who observed a large-angle tilt boundary on the surface of HOPG, on STM experiments. These authors proposed that, in the absence of stress, the observed GB consists of a periodic structure that can be described as a regular succession of pentagon-heptagon pairs, as shown in Fig. 1. Based on this model, we investigate three GBs of different periodicities along the boundary, hence with different relative orientation between the grains.

We find that, while large-angle tilt GBs do not introduce localized states at the Fermi level in graphene, various resonance peaks appear in the density of states of the material, over a broad energy range, starting at an energy of ~0.3 eV from the Fermi level, in agreement with recent experimental work. [15] More importantly, the changes in electronic structure with the GB tilt angle indicate a non-trivial evolution towards graphene bulk, as the GB angle decreases: we observe the generation of a new Dirac point at the Fermi level, which lies on a line that evolves towards the \( \Gamma - M \) direction of the graphene Brillouin zone (BZ), with the usual Dirac point at the \( K \) point falling below the Fermi level, and rising towards it as the tilt angle decreases. The Dirac cone of low-energy excitations around this new Dirac point is non-isotropic, with the effective “speed-of-light” depending on the direction in the BZ away from the Dirac point. Furthermore, our calculations indicate that, within the structural model we consider, the GB formation energy does not behave monotonically with the period of the GB (or, equivalently, with the tilt angle). A Keating analysis of the elastic energy, associated with the formation of the defect, indicates that a change in the distribution and relative contributions of the stretching and bending deformations leads to the non-monotonicity indicated by our results.

All calculations are performed using Kohn-Sham density functional theory [17], the generalized-gradient approximation (GGA) [18] for the exchange-correlation term, and norm-conserving Troullier-Martins pseudopotentials [19] to describe the electron-ion interaction. We use the LCAO method implemented in the SIESTA code [20], with a double-zeta pseudo-atomic basis set plus polarization orbitals, with an energy cutoff of 0.01 Ry. Structural optimization is performed until the total force on each atom is less than 0.02 eV/Å. In order to simulate an isolated honeycomb sheet, we use supercells that are periodic along the graphene plane, and are surrounded by a 33 Å vacuum region, such that the interactions between each layer and its periodic images are negligible.

Periodicity along the graphene plane requires the supercell to contain two GBs of opposite tilt angles (a GB and the corresponding “anti-GB”), as shown in Fig. 1 for the GB1 geometry. The experimental value in Ref. [11] for the relative orientation between grains is 21\( ^\circ \), defined here by the angle \( \alpha \) between vectors \( \vec{M}_L \) and \( \vec{M}_R \), drawn respectively on the left and right grains adjacent to the GB, as shown in Fig. 1. This model can be extended to GBs with smaller tilt angles, by adding lines of hexagons, such that the period \( L \) of the pentagon-heptagon pattern along the GB increases. In the \( L \rightarrow \infty \) (\( \alpha \rightarrow 0 \)) limit, we recover the perfect single-crystal graphene lattice. We study three different GB geometries, with the theoretical values for \( L \) and \( \alpha \) indicated in Table I. GB1 is the model proposed in Ref. [11], with \( \alpha = 21.8^\circ \) and \( L = 6.6 \) Å; GB2 has \( \alpha = 13.3^\circ \) and \( L = 10.9 \) Å; and for GB3 \( \alpha = 9.6^\circ \) and \( L = 15.2 \) Å. In order to ensure that we simulate the properties of an isolated GB, we consider supercells with increasing distances \( d \) between the GBs and their periodic images. Formation energy results are converged for \( d = 14.9 \) Å. The geometric parameters \( \alpha, d, \) and \( L \) are shown in Fig. 1 with values for \( \alpha \) and \( L \) given in Table I.

The band-structure of the GB1 (\( \alpha = 21.8^\circ \)), is shown in Fig. 2(a). The Brillouin zone for this GB supercell is shown in Fig. 3(b). The \( \Gamma - Y \) direction is along the GB, and the \( \Gamma - X \) direction is perpendicular to it. In Fig. 3(b), we also indicate lines we denoted as \( \Gamma - M \) and \( \Gamma - K \), which correspond to these high-symmetry directions in a single-crystal graphene sheet with the orienta-

| \( N_a \) | \( \alpha \) | \( L \) | \( \bar{E}_f \) | \( \bar{E}_{el} \) | \( \bar{E}_{el}^{\text{str}} \) | \( \bar{E}_{el}^{\text{bend}} \) |
|--------|--------|--------|--------|--------|--------|--------|
| GB1    | 72     | 21.8\(^\circ\) | 6.6    | 0.33   | 0.42   | 0.10   |
| GB2    | 120    | 13.3\(^\circ\) | 10.9   | 0.42   | 0.47   | 0.15   |
| GB3    | 168    | 9.6\(^\circ\) | 15.2   | 0.40   | 0.41   | 0.15   |

FIG. 2: Band structure and density of states for (a) GB1, (b) GB2, and (c) GB3 geometries. The Fermi level is indicated by the dashed line. Brillouin-zone lines are shown in Fig. 3.
The nature of the electronic dispersion in the region around the $X$ and $K$ points, also indicated in Fig. 3(b), are shown in Fig. 3(e) and (f), for the GB1 and GB3, respectively. For the GB3, there is very little dispersion around the $X-K$ direction, resulting in a straight wedge cutting through this line, while in the GB1, the shape of the energy dispersion is also wedge-like, but a “flowery” shape develops at higher energies. Furthermore, the band crossings at the $X$ and $K$ points move up towards the Fermi level, as $\alpha$ decreases, which is consistent with the $\alpha \rightarrow 0$ limit, where the Fermi level occurs at the $K$ point. The energy difference between the Dirac point at $D$ and the $K$ point is 1.00 eV for the GB1, 0.73 eV for the GB2, and 0.64 eV for the GB3.

These results indicate a very complex evolution of the band-structure of polycrystalline graphene with the GB angle. Since fivefold and sevenfold topological defects constitute the core of low-energy dislocations in graphene, they are probably ubiquitous in any realistic model of GBs in this material. Hence, the occurrence of a new Dirac point along the GB direction may prove a robust feature of polycrystalline graphene. We note that previous works have found that, while pentagon-heptagon pairs and the related SW defect introduce no resonant states at the Dirac point in graphene, resonance peaks appear in the density of states starting at a few tenths of an eV from the Fermi level, a result that we have also reproduced with the ab initio method employed here. Our GB electronic structure calculations show, however, that the periodic superstructure formed by these dislocations along the GB line shares with perfect graphene the vanishing gap and the Dirac-like nature of electronic excitations, but in a rather complex structure, with direction-dependent Fermi velocities, the generation of a new Dirac point on the GB direction, and a wedge-like dispersion around the $K$ point that should evolve towards the graphene Dirac cone as $\alpha \rightarrow 0$. We expect charge transport in polycrystalline graphene to reflect the anisotropic structure of the Dirac cones we obtain in our calculations.

|       | $-\hat{y}$ | $\hat{y}$ | $-\hat{x} - \hat{y}$ | $\hat{x} + \hat{y}$ | $-\hat{x}$ | $\hat{x}$ |
|-------|-----------|-----------|---------------------|---------------------|-----------|-----------|
| GB1   | 0.73      | 0.52      | 1.06                | 0.69                | 0.60      | 0.60      |
| GB2   | 0.64      | 0.43      | 0.91                | 0.63                | 0.52      | 0.52      |
| GB3   | 0.55      | 0.45      | 0.53                | 0.55                | 0.57      | 0.57      |

TABLE II: Fermi velocities (in $10^6$ m/s) for the GB Dirac electron cones, along the indicated directions.

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We turn now to the GB energetics. The GB formation energy per unit length is given by $E_f = (E_{GB} - E_{bulk})/2L$, where $E_{GB}$ and $E_{bulk}$ are the calculated total energies of the GB and bulk graphene supercells, respectively. The factor of two on the right-hand side accounts for the presence of two GBs in the cell.

Results in Table 1 show that $E_f$ varies non-monotonically with the GB period. Among the three GBs, GB1 with a tilt angle of $21.8^\circ$ has the smallest formation energy, while GB2 with $\alpha = 13.3^\circ$ has the highest $E_f$ value. We expect that $E_f \to 0$ as $\alpha \to 0$. Our results indicate that $E_f$ initially increases, before reaching this asymptotic limit. Given the absence of broken bonds in the GB geometries, $E_f$ is primarily of elastic nature. In order to understand this non-monotonic behavior, we use a Keating model to analyze the bond-bending $E_{el}^{bend}$, and bond-stretching $E_{el}^{str}$ contributions to the GB elastic energy $E_{el}$. The results are shown in Table 1. For the GB1 we observe that $E_{el}^{bend}$ is a factor of 3.2 larger than $E_{el}^{str}$, while for the GB2 and GB3 structures the $E_{el}^{bend}/E_{el}^{str}$ ratio decreases to 2.1 and 1.8 respectively. These results remain essentially unaltered for different choices of the ratio between the stretching and bending energy parameters of the Keating model. Moreover, the spatial distribution of $E_{el}^{bend}$ and $E_{el}^{str}$ changes as $\alpha$ decreases, as shown in Fig. 4. For the GB1, $E_{el}^{bend}$ is largely concentrated on the atoms at the very core of the boundary, mainly in the pentagon-heptagon pairs, while $E_{el}^{str}$ is a little more spread out towards the interior of the grains. For GB3, we see that both $E_{el}^{bend}$ and $E_{el}^{str}$ have significant contributions from atoms in the interior of the grain, mostly on the hexagon lines that at the pentagon-heptagon at the boundary. Thus, by concentrating the elastic energy on bending distortions at the defect core, the GB1 structure relaxes to a lower energy state than GBs with smaller angles, which leads to the non-monotonic behavior of $E_f$.

To conclude, ab initio calculations indicate that the electronic structure of tilt GBs in graphene display a complex evolution towards graphene bulk, as the GB angle decreases, with the generation of a new Dirac point at the Fermi level, lying on a line that evolves towards the $\Gamma$-$M$ direction of the graphene Brillouin zone, at the vertex of an anisotropic electronic-energy cone. Moreover, the usual Dirac point at the $K$ point falls below the Fermi level, and rises towards it as the tilt angle decreases. Furthermore, our calculations indicate that the GB formation energy behaves non-monotonically with the tilt angle, due to a change in the spatial distribution and relative contributions of the bond-stretching and bond-bending deformations associated with the formation of the defect.

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