Electronic transport across realistic grain-boundaries in Graphene

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Abstract

We perform a MonteCarlo simulation in order to study the connection between the morphology and the transport properties of grain boundaries (GBs) in graphene. We explore the configurational space of GBs to generate ensembles of realistic models of disordered interfaces between graphene misoriented domains. Among other observables, transmission across GBs has been probed all along the simulation, thus making us able to establish a connection between averaged transmission and the topological invariant of GBs, the misorientation angle. We extend to disordered GBs the remarkable result that the low angle regime is characterized by a decrease of the individual GB conductance upon a reduction of the angle, as first found for periodic GBs[1]. However, we explored a comprehensive range of misorientation angles such that our results should serve as a starting data set to study the effect of polycrystallicity on transport in large samples.

Introduction

Graphene is the first genuine two-dimensional material ever unearthed, being a one-atom thick sheet of graphite[2][3]. As a consequence, its novelty, soon supported by the fascinat-
ing physical properties which it has been showing\textsuperscript{4}, has rapidly appealed many researchers. After almost a decade of intensive studies one can hardly find a field of condensed matter Physics which has not been touched with reference to graphene. The effect of polycrystallicity on graphene physical properties doesn’t make exception. Indeed, it is now established that grain-boundaries - the topological defects characteristic of polycrystalline materials - are ubiquitous in extended graphene samples grown, for example, by chemical vapor deposition\textsuperscript{5–9}. Their strong impact over electronic, thermal and mechanical properties is nowadays out of debate\textsuperscript{10–12}. However, for electronic transport in polycrystalline graphene is far from being achieved and, in particular, theoretical estimates of the intrinsic electronic performances of realistic polycrystalline samples are lacking\textsuperscript{13–17}. This is surprising since the technological applications for which graphene is expected to be a promising candidate (electronics, clean energy and related domains) require large scale industrial processes - e.g. chemical vapor deposition technique - which mostly end up with the realization of polycrystalline graphene samples, as confirmed by numerous recent experiments\textsuperscript{18,19}.

The first theoretical studies on polycrystalline graphene have regarded grain boundaries as arrays of dislocations, that is, adopting the theory of Read and Shockley\textsuperscript{6,20}. Both dislocations and grain-boundaries, differently from point defects, are topological meaning that no local modification of the atoms network can eliminate them. This distinctive nature of these defects, combined with the characteristics of pristine graphene, is at the origin of rich as well as non trivial transport features. A work focusing on periodic structures have unveiled the existence of a class of grain-boundaries for which a full suppression of the low-energy conductance occurs, consequence of momentum conservation\textsuperscript{21}.

A recent study has explored the more general situation of those periodic grain-boundaries in which no symmetry-related selection applies, also addressing the effect of perturbations to the periodic order\textsuperscript{1}. This has provided a general picture of transport in low angle grain-boundaries, that is, the ones which allow the fewest arrangements of the defective rings and, consequently, do not bear a high degree of disorder\textsuperscript{5,6}. On the other hand, large angles grain-
boundaries are often highly disordered, that is, many defects arrangements are compatible with a given misorientation angle\cite{8,9,19}. This poses a serious obstacle to an understanding of the effect of a single grain-boundary on charge transport based on simple and general arguments.

In this work, we address the problem of estimating the conductance of disordered grain-boundaries numerically, this approach being the only possible. Having a collection of realistic grain-boundaries for a given misorientation angle is propaedeutic to the calculation of any physical observable. We have chosen to employ a MonteCarlo simulation in order to explore the configuration space of the interface between two misaligned domains. This has provided bunches of defective structures not selected randomly but weighted by their formation energy with respect to the corresponding ordered low-energy configuration . Thereafter, we have sampled several observables to have a complete picture of both the morphology (number of atoms of the rings, atomic connectivity, formation energy), and the spectral and transport properties (DOS, Transmission, Conductance). The statistical analysis of the data has put the connection of the average conductance of a single grain-boundary and its misorientation angle on a quantitative basis.

As an important ingredient to the transport theory, it has been recently showed that the presence of multiple grain-boundaries, which is expected in polycristals, leads to a simple law of direct proportionality between the conductance of the sample and the average linear size of the single grain\cite{22}. This can be easily interpreted as the emergence of ohmic behavior induced by the presence of multiple grain-boundaries. At this point, our quantitative estimates for the conductance across a single grain-boundary combined with the knowledge of the transport regime let us glimpse the opportunity for a multiscale determination of the intrinsic transport performances in large area polycrystalline samples. A very minimal, although meaningful, illustrative example is given at the end of this work.
Description of the work

In order to perform a MonteCarlo simulation two ingredients are necessary: the basic move and the acceptance criteria. We have chosen the Wooten-Winer-Waeire move consisting in the rotation of two bound atoms by 90° as illustrated in Fig. 1b. The system is therefore relaxed by minimizing a classical potential suited for carbon. Within a pristine area of graphene this move results in the creation of the so-called Stone-Wales defect (see Fig. 1b), characterized by a high formation energy of about 5 eV. When the rotation is done in the vicinity of a dislocation (i.e. a pentagon-heptagon pair) it often represents an energetically low-cost move allowing for the evolution of the defect (see Fig. 1c). In the proximity of a grain-boundary - we remark that a GB can be thought as an array of dislocations - the move can even lead to a structure with a lower energy, thus disclosing the exploration of the configuration space. Therefore, our final choice is to rotate bonds which connect at least one atoms owning to the GB. We adopt the Metropolis scheme as the acceptance criteria. It is important to say that, for our purpose, the MC simulation is not intended as a tool to obtain a thermodynamic ensemble of configurations. Indeed, the growth of the grains in a chemical vapor depositions, leading to the formation of boundaries, happens in conditions which are out of thermodynamic equilibrium. In our case, the simulation rather consists in a tool to collect grain-boundary configurations.... In this spirit, it must not confuse that the main temperature chosen for the simulation \( T = 5000 K \) is close to the melting temperature for graphene. In fact, our simulation involves only few degrees of freedom in the boundary region and the energy corresponding to the temperature \((= 0.43 eV)\) divided by the average distance between two carbon atoms \((1.42 \text{ Å})\) is comparable to the typical formation energy of a GB \((0.2 – 0.8 \text{ eV/Å})\). In other words, we have chosen a temperature such that the system has a significant probability to assume distinct configurations along the simulation. After each move, the system is relaxed by mean of a classical force field. The minimized energy is then employed in the Metropolis scheme. The coherent conductance across the GB is numerically assessed by mean of the Landauer-Büttiker theory, in which the conductance
$G(E)$ at a given energy $E$ is proportional to the transmission $T(E)$ as $G(E) = G_0 T(E)$, with $G_0 = 2e^2/h$ being the conductance quantum. We use a two-terminal device configuration in which contacts are represented by semi-infinite ideal graphene leads. More details can be found in the Methods section.

Figure 1: Sketch of the simulation setup and MC move outcomes. Panel (a) presents the initial configuration of a two-domains system with a misorientation angle $\theta = \theta_L + \theta_R = 21.2^\circ$. Both the directions parallel and orthogonal to the GB are periodic. The atoms in the green regions are kept fixed along the simulation. Panel (c) shows the effect of a bond rotation in a pristine graphene area which results in the formation of a Stone-Wales defect. Panel (d) illustrates three relevant outcomes of the bond rotation around a 5-7 pair: pair creation (1), glide (2), a higher energy formation including an eight member ring (3).
Results and discussion

We have performed simulations for starting from 8 symmetric grain-boundaries covering a range of misorientation angle $\theta \in [7.3^\circ, 51.5^\circ]$ and 1 asymmetric with $\theta = 30^\circ$. Data collected along a typical simulation are presented in Fig. 2. The starting configuration is the left one sketched in panel b. It consists in a $\theta = 21.2^\circ$ GB made of 8 pentagon-heptagon pairs.

Figure 2: Observables sampled during the simulation of the $\theta = 21.2^\circ$ GB. (a) Evolution of the formation energy and the conductance integrated between $-0.5 \text{ eV}$ and $0.5 \text{ eV}$. (b) Ground state and three low-energy configurations extracted from the simulation. The corresponding energies are highlighted in the upper plot by red circles. (c) The main frame contains a scatter plot of conductance vs. formation energy. All conductances are normalized by the value pertaining to a pristine graphene sheet of the same size of the polycrystalline sample.

The evolution of the formation energy, plotted in 2a shows that there are several low-energy configuration occurring frequently. Three of these disordered GBs are sketched in 2b,1-3. From a comparison with the initial ordered configuration (2b,0) it can be seen that each of them results from a combination of glides, creations or annihilations of pentagon-heptagon pairs. These transformations have been recognized as the ones responsible for the life cycle of dislocations and for the evolution of grain-boundaries. An histogram
showing the distribution of the rings is contained in figure S2. The absence of members with less than 5 members and the rare occurrence of 8-membered rings has to be put in connection with the high energy cost of those defects (Refs.??). As a general fact, in all our simulations, the GBs lying in the low energy region, are formed by an equal number of 5 membered and 7-membered rings. All along the evolution of the GBs the coordination number of the atoms is identically equal to 3 excluding few very high-energy (and rare) configurations in which four-coordinated or two-coordinated carbon atoms may appear. A mismatch between the number of pentagons and heptagons of a GB also implies a higher formation energy. However, even in the high energy region, the typical shape of a grain boundary tends to be meandering but still continuous. This is in accordance with what was found in experimental atomic resolution imaging of GBs??

Together with the energy, 2a shows the evolution of the conductance in an energy window 1 eV wide centered around the Fermi level of pristine graphene. For sake of clearness the conductance $G$ has been normalized by the conductance $G_P$ of a pristine graphene sample of the same size of the sample employed in the simulation. 2c contains a statistical analysis of the data. A broad distribution characterized the histogram of the conductance, although it still shows the persistence of high transmitting configurations. The main panel clearly indicates the existence of some inverse correlation between the conductance and the energy, meaning that, on average, a higher energy corresponds to a lower conductance. This can be explained by appreciating the fact that configurations with high energy correspond to more disordered GBs constituted by a larger number of non six-membered rings, that is, by a larger number of scatterers for the charge carriers.

Fig.3 reports the distribution of the integrated conductance for the different GBs. Going through increasing misorientation angles, one sees that the distributions evolve almost continuously with a sudden change registered between 21.8° and 30°, giving an indication for an abrupt mutation of the conductance trend. This strong suppression of the conductance cannot be attributed to the asymmetry of the $\theta = 30°$ GB. In fact, the GB with the next
larger angle $\theta = 32.2^\circ$ has a similar distribution, though being symmetric i.e. presenting a radically different arrangement of the defects. This has to be considered an indication for the misorientation angle $\theta$ to be the main variable which determines the transport across the GB.

When conductance is evaluated at energies close to the Fermi level ($E = 0.02\,\text{eV}$) the distributions are broader, although the average conductance is slightly higher. This instability at the Fermi level is reduced when the conductance is integrated over an energy interval. The existence of correlations between formation energy and conductance is also more evident after the integration.

Figure 3: Distributions of the conductance for different systems characterized by the misorientation angle $\theta$, as reported in the panels. The unit adopted for the conductance is the same as Fig. 2.

A more detailed picture of the effect of the presence of disorder is obtained by looking at transmission and density of states (DOS) as a function of energy, reported in Fig. 4. Independently of the energy, the average transmission is significantly reduced with respect to that of the ground (ordered) state, that is, the effect of disorder in GBs is to add further charge carrier backscattering with respect to the ordered case. This feature is common to the majority of the systems, the only exception being the case in which the ordered configuration
has already a low conductance compared to pristine graphene. In such a situation the average conductance doesn’t differ significantly (see S3).

Figure 4: Average transmission (upper panels) and density of states (lower panels) as a function of Energy for two representative systems characterized by $\theta = 21.8^\circ$ and $\theta = 46.8^\circ$. The dashed lines represent the calculated values for a pristine graphene sheet of the same size, the red curves are the simulation averages of the observables and the black solid lines represent the calculated values for the structural ground state configuration.

The effect of a finite simulation temperature on the averaged DOS can be summarized in two aspects. First, characteristic peaks of the ground state configuration get smeared out. Secondly, there is an increase of the spectral weight around $E = 0$.

We stress again that the conductance of disordered GBs has a clear although, not trivial, dependence on the misorientation angle $\theta$. This dependence has been put in evidence in Fig. 5 for two situation. In the left panel the average conductance at low energy ($E = 0.02$ eV) is plotted as a function of the angle $\theta$. In order to make a comparison possible with the case of ordered GBs, we have added an analogous curve for the ground state conductance in the low-angle region. This latter case is characterized by a suppression of the conductance upon a reduction of the misorientation angle $\theta$. This counter intuitive behavior has been explained from the point of view of resonant backscattering induced by quasi-localized states that get closer to the Fermi energy upon a reduction of $\theta$. It becomes immediately evident that this trend is inherited by the average conductance of disordered GBs, showing a maximum at $\theta = 21.8^\circ$. The region $30^\circ < \theta < 60^\circ$, on the other hand exhibits a less clear trend. In any case, conductance is affected by large relative fluctuations of the order of $20 - 50\%$. This
instability at low energy is sensibly improved by integrating the conductance over the usual range \([-0.5 \text{ eV}, 0.5 \text{ eV}]\) (5b). Although after integration the values of average conductance are lower for most of the angles, fluctuations get reduced by approximately a factor 2 allowing to appreciate two well separated trends. Again, starting from the maximum achieved for \(\Theta = 21.8^\circ\) and going toward low angles, the conductance decreases reproducing, initially, the behavior of the ordered GBs. Nevertheless, for a value of \(\theta\) around 10\(^\circ\), the conductance of the ordered GB suddenly rise and is supposed to approach 1 in the limit of \(\theta \to 0\), whereas the averaged conductance follows an almost straight line until \(\theta = 7.54^\circ\). Although computational limitations prevents us from reducing the angle further, we expect the average conductance to approach the conductance of the ordered GBs in the limit of zero angle. In this limit, indeed, the ordered low energy configuration has to be predominant since it is constituted by largely separated pentagon-heptagon pairs and any modification has a high energy cost. As a consequence the average is dominated by the contribution of the low energy configuration.

A different trend characterizes the region 30\(^\circ\) < \(\theta\) < 60\(^\circ\). After a minimum for \(\theta = 30^\circ\), the conductance increases before stabilizing around \(G \simeq 0.45G_p\). ... . Overall, the effect of disordered GBs is to reduce the conductance of pristine graphene to about the 40\% of the conductance of pristine graphene.

![Figure 5: Conductance as a function of the misorientation angle \(\theta\). In panel (a) the conductance is calculated at low energy \(E = 2.7\text{ meV}\), whereas in panel (b) it is integrated between \(-0.5 \text{ eV}\) and \(0.5 \text{ eV}\). The red points are the simulation averages, the width of the gray area corresponds to the standard deviation of the distributions, the black dashed lines represent the conductance for the ground state configurations in the small angle regime.](image-url)
Based on the knowledge of the conductance (or, equivalently, resistance) of a single grain boundary one can address the effect on electronic transport of a distribution of grain boundaries typical of a polycrystalline sample. As showed in ref.\textsuperscript{22}, the effects of many individual grain boundaries add-up incoherently meaning that quantum interference effects are negligible and the resistance due to individual GBs is additive. The resistance of a two-terminal configuration \( R = G^{-1} \) can be viewed as arising from two contributions\textsuperscript{31}:

\[
R = R_P + R_{GB} = G_P^{-1} + G_P^{-1} \left( \frac{G_p - G}{G} \right)
\]  

where \( R_P \) is the resistance due to the semi-infinite graphene contacts (i.e. the resistance of a pristine sample) and \( R_{GB} \) is the resistance of the scattering source - the GB in our case - with the property of being additive. Since the resistance is inversely proportional to the transverse width \( W \), it is convenient to introduce a width-independent grain boundary resistance \( \rho_{GB} = R_{GB} \ast W^{10} \). Our results recast in terms of \( \rho_{GB} \) (see Fig. 6) show an even stronger dependence on the misorientation angle. However, the values of \( \rho_{GB} \) presented in Fig. 6 should be considered as lower boundary estimates since they not account for potential barriers induced by grain-boundaries\textsuperscript{32–35}, incoherent processes triggered by the presence of grain boundaries or ... .

Figure 6: Width independent resistance \( \rho_{GB} \) averaged between \(-0.5\) eV and \(0.5\) eV as a function of the misorientation angle \( \theta \).

Finally, if one accounts for an average value \( \langle \rho_{GB} \rangle \simeq 80k\Omega \ast nm \), a rough estimate for
the intrinsic resistance of a polycrystalline sample of width \( W \) and length \( L \) with a linear density of grain boundaries \( n \) is given by

\[
R = \frac{nL}{W} \langle \rho_{\text{GB}} \rangle
\]

(2)

This formula neglects all details of the angle distribution in realistic GBs, nevertheless, it provides an order of magnitude for the contribution of coherent backscattering due to GBs in polycrystalline graphene. For a square sample with a density \( n = 0.1\, \text{nm}^{-1} \), this contribution amounts to \( \rho_{\text{GB}} \approx 8\, \Omega \).

In conclusion, we have addressed the issue of electronic transport across disordered grain-boundaries combining a MonteCarlo simulation for the grain boundary configurations and transport calculations based on Landauer-Buttiker theory. The disordered averaged conductance exhibits a clear dependence on the misorientation angle which is insensitive to the disorder. The low-angle regime reproduces the reduction of the conductance already seen in periodic GBs\(^{11}\), the minimum of conductance is achieved for \( \theta = 30^\circ \) whereas a saturation characterizes the region \( \theta \in [30^\circ, 60^\circ] \). Based on these results, an estimation of the contribution to total resistance ascribable to the presence of grain boundaries is formulated.

**Methods**

The starting structural models are rectangular with the GB parallel to a side whose length is \( \simeq 6\, \text{nm} \), whereas the perpendicular side measures \( \simeq 10\, \text{nm} \). The total number of atoms lies between 1848 and 2144 atoms (all starting configurations can be found in Fig. S1). Initially, all systems are relaxed in both the atomic and the cell degrees of freedom. After each move the structure is relaxed keeping the cell parameters fixed. Relaxations are achieved by minimizing the structural energy calculated by means of the classical potential LCBOP\(^{24}\), as implemented in the Open Source code LAMMPS\(^{36,37}\). The LCBOP potential has been selected among available alternatives after the comparison of the formation energies.
of several defects (both local and topological) with DFT results. For the description of low energy charge carriers we adopt a next-neighbor Tight-Binding Hamiltonian restricted to $\pi$ orbitals in which the hopping term $t$ is set to 2.7 eV and the energy reference is fixed in such a way that the on-site energy $\varepsilon_0$ vanishes: $H = -t \sum_{\langle i,j \rangle} a_i^\dagger a_j + \text{H.c.}$ where $a_i^\dagger (a_i)$ is the creation (annihilation) operator of an electron at the site $i$. Transmission is evaluated by mean of the Non-Equilibrium Green’s function $G_S$ of the scattering region containing the GB. The transmission is a function of the transverse momentum $k_\parallel$ (defined for the supercell) and the energy $E$: $T(k_\parallel, E) = \text{Tr} \left[ \Gamma_L(k_\parallel, E) G_S^\dagger(k_\parallel, E) \Gamma_R(k_\parallel, E) G_S(k_\parallel, E) \right]$. $G_S$ is defined as $G_S(k_\parallel, E) = \left[ E + i\eta I - H_S - \Sigma_L(k_\parallel, E) - \Sigma_R(k_\parallel, E) \right]^{-1}$, the coupling matrices $\Gamma$ for the left and right lead are given by $\Gamma_{L(R)}(k_\parallel, E) = i \left[ \Sigma_{L(R)}(k_\parallel, E) - \Sigma_{L(R)}^\dagger(k_\parallel, E) \right]$, $H_S$ is the Hamiltonian of the scattering region, $\Sigma_{L(R)}$ are the self-energies coupling the scattering region to the leads and $E^+ = E + i\eta I$ ($\eta \to 0^+$). Conductance $G$ is obtained from transmission as $G = G_0 \int_{V_L}^{V_R} dE \int_{1BZ} T(k_\parallel, E)$. For the integrals, 11 independent $k$-points and 48 energy-points have been used, respectively. DOS has been calculated as $DOS(E) = -\frac{1}{\pi} \int_{1BZ} \text{Im}(G_S(E^+, k_\parallel))$ and the integral has been discretized over a 21 $k$-points grid.

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