Localized states, spin-polarisation and transport in graphene grain boundaries

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INTRODUCTION

Grain boundaries (GBs) are abundant in graphene grown by CVD [1]. One may, as a start, consider GBs as bi-crystal interfaces, with a mis-orientation (twist-angle), θ. The GBs display a remarkable complexity of reconstructions with varying degrees of order along the GB, and it can host localized states [2]–[4]. GBs may display a transport gap up to $\sim$ 1eV around the Dirac point due to momentum mismatch along the GB ($k_\perp$), tied to θ [5], [6]. However, the role of the GB structure as a scatterer on the transport is less understood [7], together with the experimental evidence for f.ex. the quasi-localized and magnetic states [8], and their relation to buckling, gating, and finite bias effects. Here we present a work-flow for DFT-NEGF enabling screening of the transport properties and electronic structure of many GBs.

I. METHOD

The generation of GB geometries and setup of DFT-NEGF [9] is non-trivial for the mis-oriented crystals acting as electrodes, cf. Fig. 1. We have devised a work-flow starting from (i) randomly matched geometries, (ii) two relaxation steps, (iii) electronic structure and transport characterization with DFT-NEGF [9], see Fig. 2. We generated ca. 150 GBs, and have studied the effect of carriers doping (gating), and finite bias.

II. RESULTS

In Fig. 3 and Fig. 4 we present an example of $k_\perp$-resolved device DOS and transmission functions. While these are dominated by the overlapping electrode Dirac-cones, we find that intricate structure show up both inside the gapped *and* conductive regions. This is related to 1D/quasi-1D electronic states localized at the GB, resulting in 1D bands, which may be dispersionless. We calculate the wave-functions of these bound states at the peaks in the DOS (at energy ϵ and $k_\perp$) by solving the "quasi-particle"-type equation involving the device Hamiltonian (H_d) and electrode self-energies (Σ),

$$[H_d + \frac{1}{2}(\Sigma(\epsilon) + \Sigma^\dagger(\epsilon))]\psi^{QP} = \epsilon\psi^{QP} \qquad (1)$$

Roughly, four types of GBs appear from the dataset when considering their conductive properties: Transparent, opaque, insulating and spin-filtering GBs. Availability of transmission channels in conjunction with the local electronic structure and out-of-plane buckling produce these different classes. Opaque GBs often display the bound states cutting into the 2D-continuum, which show interference effects in the transmission function. We find that these bound states are sensitive to gating, giving a gate-dependent transmission (Fig. 4). We also find that the bound states can be affected by applying even a small bias (Fig. 3) Finally, a high spin-filtering has been found for GBs with large buckling (Fig. 5).

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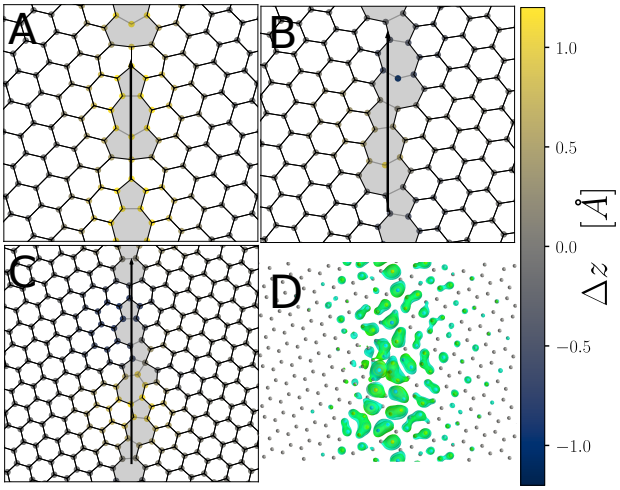

Fig. 1. Examples of bi-crystal grain boundaries with different twist-angle, θ. Transport direction is left-right. A) $\theta = 32.20°$. B) $\theta = 42.10°$. C) $\theta = 26.01°$. D) Quasi-particle state (cf. Eq. (1)) of GB in panel C with $E = +0.23$eV at $k_\perp = 0$.

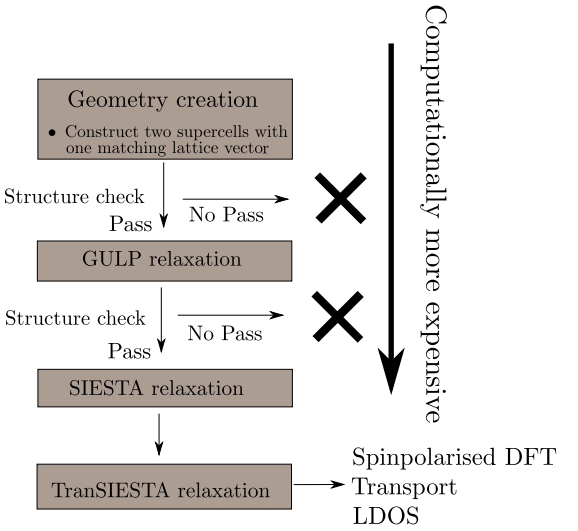

Fig. 2. Flow-chart for GB creation and transport calculation with DFT-NEGF. The method is utilising the Siesta scripting package siesta_python, the Siesta-code and the force-field code GULP [J.D. Gale, A.L. Rohl, *Molecular Simul.* **29** 291 (2003)]. The structure check involves checking if there are more than three angles outside the bound $100° < \theta < 160°$ in the 2D plane of the structure. All atoms within $|x| < 8$Å of the GB can relax freely in three dimensions. In the 3rd step (SIESTA) the left/right groups of atoms with $|x| > 8$Å relax rigidly together.

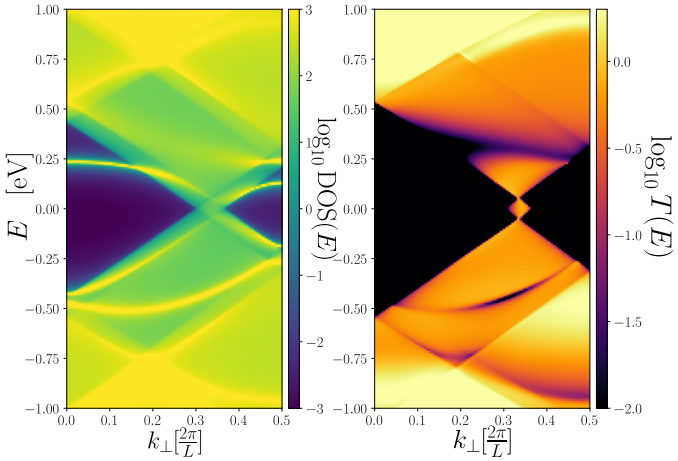

Fig. 3. Out-of-equilibrium $k_\perp$-resolved density-of-states(left) and transmission function (right) of the GB in Fig. 1C. Chemical potentials set to $\mu_L = -\mu_R = 0.1$eV. Presence of Fano-type resonances in the transmission can be seen as black arcs.

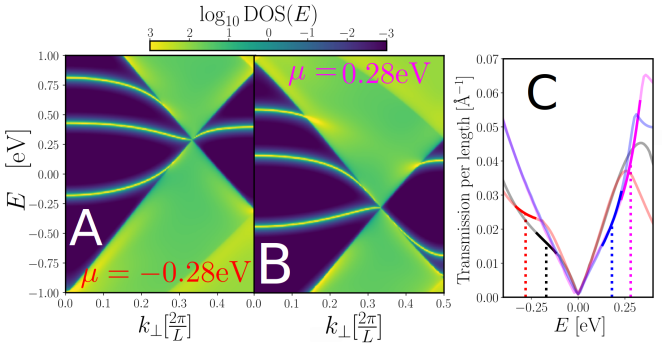

Fig. 4. A-B) $k_\perp$-resolved DOS for p- and n-type doping of GB in Fig. 1A. C) The effect of gating on the Transmission through the GB. As the localised state is pushed into the continuum by gating, more electrons can tunnel through the GB. Red: $\mu = -0.28$eV, black: $\mu = -0.17$eV, blue: $\mu = 0.18$eV, magenta: $\mu = 0.28$eV. μ is measured relative to the Dirac point.

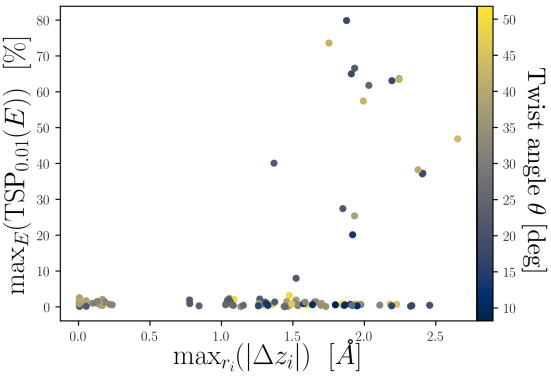

Fig. 5. Spin-polarisation coefficient $\mathrm{TSP}_{0.01}$ where $\mathrm{TSP}_\delta(\epsilon) = |\frac{T_\uparrow(\epsilon)-T_\downarrow(\epsilon)}{T_\uparrow(\epsilon)+T_\downarrow(\epsilon)+\delta}|$, versus maximal out-of-plane buckling relative to average z of each structure. Maximum taken for $-0.5\text{eV} < E < 0.5\text{eV}$. 146 points in plot.