Theory and hierarchical calculations of the structure and energetics of [0001] tilt grain boundaries in graphene

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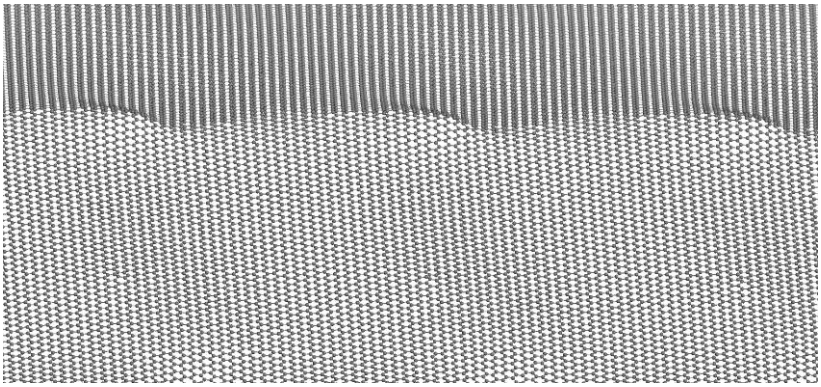
Defect-free graphene has extraordinary properties, but several experiments have revealed the presence of grain boundaries in graphene that may change its electronic and elastic properties[1-3]. Here we present a general theory for the structure of [0001] tilt grain boundaries in graphene based on the Coincidence Site Lattice (CSL) theory. We show that the CSL-theory uniquely classifies the grain boundaries in terms of the misorientation angle θ and periodicity d using two grain boundary indices (m,n), similar to the nanotube indices. The CSL-theory is convenient to derive supercell models for grain boundaries and we have implemented the method into a script in Materials Studio [4]. The script is able to generate grain boundary models for a particular misorientation angle θ with two grain boundaries per supercell.

The structure and formation energy of a large set of grain boundaries generated by the CSL theory for $0° < \theta < 60°$ (up to 15608 atoms) were optimized by force field[4] and bond order potential calculations[5] and validated by density-functional (DFT) calculations[4]. Our calculations show that low energy [0001] tilt grain boundaries in graphene can be identified as dislocation arrays[6]. For small θ do the dislocations form hillocks as can be seen in the Figure below.



These hillocks are in good agreement with the structure of a tilt grain boundary in graphene grown on Ir(111) that has θ=2°, which was observed by Scanning Tunneling Microscopy(STM) [1]. Grain boundaries with larger misorientation angle have an array of dislocation cores with short periodicity in agreement with STM observation of grain boundaries in HOPG[2].

We find that, in contrast to three-dimensional materials, the strain created by the grain boundary can be released via out of plane distortions that lead to an effective attractive interaction between dislocation cores. Therefore, the dependence on θ of the formation energy parallels that of the out-of-plane distortions, with a secondary minimum at θ=32.2° where the grain boundary is made of a flat zigzag array of only 5 and 7 rings. For θ>32.2°, also other non-hexagonal rings are possible in agreement with STM observations of a large angle grain boundary[3].

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