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Harmonic model of graphene based on a tight binding interatomic potential

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ABSTRACT

Like in many other materials, the presence of topological defects in graphene has been demonstrated to modify its behavior, thus enhancing features aimed at several technological applications, more specifically, its electronic and transport properties. In particular, pristine defect-free graphene has been shown to be of limited use for semiconductor-based electronics, whereas the presence of individual or cluster defect rings along grain boundaries hinders electron transport and introduce a transport gap, unveiling the possibility of novel electronic device applications based on the structural engineering of graphene-based materials. In this work, we present an atomic bondwise force-constant model from the tight binding potential by Xu et al. (1992), that accounts for the electron-mechanical coupling effects in graphene. First we verify that this computational scheme is capable of accurately predicting the defect energies and core structures of dislocation dipoles based on the theory of discrete dislocations of Ariza and Ortiz (2005). In order to demonstrate our ability to characterize the effect of patterned distributions of structural defects on the electronic structure of graphene, we present the electronic band structures and density of states curves of several defective graphene sheets.

1. Introduction

Ever since its rapid rise to prominence in 2004, and mostly due to its large surface area and rich and transport properties, graphene has been touted as a promising material for a variety of applications. Indeed, compared to silicon, graphene has superior mobility, thermal conductivity, and current-carrying and transport capabilities.

One of the most crucial issues in Material Science is to understand the existence, behavior and evolution of defects which are always present in crystalline materials associated with growth processes or manufacturing post-processes. The presence of defects usually has a strong influence on electronic, optical, thermal, mechanical and magnetic properties of materials. On one side, these defects might considerably deteriorate the aforementioned properties (Han et al., 2014; Xiao and Staniszewski, 2010; Grantab et al., 2010), but on the other side, defects can also provide intriguing properties, e.g., trapping impurities such as metal atoms (Cretu et al., 2010) and opening electronic band gaps (Yazyev and Louie, 2010a). Additionally, defects can be introduced voluntarily into the lattice by means of electron or ion irradiation (Meyer et al., 2009; Hashimoto et al., 2004), chemical treatments (Bagri et al., 2010) and during the manufacturing process. Therefore, engineering defects

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in crystalline lattices would open a novel and innovative via to use graphene for a variety of applications, with functionalities beyond what pristine graphene would offer.

Structural defects such as dislocations, mono-vacancies, multi-vacancies, adatoms and grain boundaries are always present in graphene, and have been analyzed by a variety of techniques that mostly rely on first-principles calculation methods or on semi-empirical interatomic potentials. Using first-principles-based simulations, Jeong et al. (2008) have studied the stability of dislocation dipoles with 5–7 core structures, and Yazyev and Louie (2010b) have investigated the thermodynamic and electronic properties of dislocations and grain boundaries. Additionally, interatomic potentials have been widely used for modeling carbon-based materials, and particularly graphene. For instance, Liu et al. (2011) have studied the structures and energies of symmetric tilt grain boundaries using the empirical AIREBO potential (Stuart et al., 2000), whereas Ariza et al. (2010, 2012), based also on the AIREBO (Stuart et al., 2000) and ReaxFF potentials (van Duin et al., 2001), have studied the thermal stability of dipole and quadrupole dislocations in graphene, and investigated glide and shuffle generalized stacking faults (GSF) and the existence of metastable partial dislocations for the glide GSF, respectively.

Most computational simulations to date have relied on Molecular Dynamics (MD) as their chief representational and computational paradigm. One of the main reasons for that has to do with the vast number of available empirical interatomic potentials, thereby allowing to simulate many different systems. Particularly, there is a long list of empirical potentials for C-based materials, such as AIREBO (Stuart et al., 2000), REBO (Brenner, 1990) and ReaxFF (van Duin et al., 2001) reactive potentials, the force-constant model developed by Aizawa et al. (1990) and the MEAM-type potential by Xiao et al. (2009), among others. However, the aforementioned potentials suffer a lack of electronic information, and therefore turn to be inappropriate when studying systems in which their electronic structure constitute an essential information to investigate their current and future technological applications. This drawback is generally overcome by recourse to ab initio-based models, which are extremely accurate and provide the sought electronic structure information, although their broad application is limited by their high computational cost. In addition to these approaches, the tight binding (TB) formalism represents a compromise between both previous outlined methodologies. Interatomic potentials based on the TB formalism are typically two to three orders of magnitude faster than ab initio-based models, they are more accurate than empirical potentials and also capable of characterizing the electronic properties of materials, e.g., band energies and density of states.

Tight binding potentials can be classified into orthogonal (Goodwin, 1991; Saito et al., 1998; Xu et al., 1992; Tang et al., 1996) and non-orthogonal models (Amara et al., 2009; Porezag et al., 1995; Menon et al., 1996), depending on whether they are defined by an orthogonal or non-orthogonal orbital basis set, respectively. Moreover, depending on the range of these basis functions, they can be classified into first-nearest neighbor interactions (Goodwin, 1991; Saito et al., 1998; Xu et al., 1992; Tang et al., 1996) or further-nearest neighbor interactions (Reich et al., 2002; Correa et al., 2010) potentials. Most TB potentials adopt an orthogonal basis set, along with the two center approximation, i.e., the hopping and repulsive functions only depend on the interatomic distance and thus do not account for the environment-dependent interactions. Additionally, they also neglect the self-consistency condition, i.e., the Hamiltonian matrix does not depend upon the distribution of electrons. The simplest TB interatomic potential is the one in which the hopping and repulsive functions do not depend on interatomic distances and, thus, take constant values (Saito et al., 1998).

For C-based materials, Xu et al. (1992) proposed a model which uses an orthogonal basis set and the two center approximation (Slater and Koster, 1954) for the hopping and repulsive parameters which are scaled by a scaling function that depends on interatomic distances. Later on, Tang et al. (1996) extended this model taking into account multicenter interactions. The TB model described by Xu et al. (1992) has been successfully used for modeling different carbon-based systems in general (Esfarjani et al., 1998; Ozaki et al., 2000; Farajian and Mikami, 2001) and graphene in particular (Gorjizadeh et al., 2011; Smith et al., 2013; Souma et al., 2013). For instance, Gorjizadeh et al. (2011) studied the effect of defects, such as vacancies and adatom-vacancies, on the conductance of graphene nanoribbons through the equilibrium Green's function technique and the tight binding framework; Souma et al. (2013) evaluated the effect of various types of in-plain strain on the electronic transport property in the single layer graphene connected to two metallic electrodes; and, Smith et al. (2013) proposed a novel pressure sensor based on a suspended graphene membrane.

In this work, we present an application of the theory of discrete dislocations (DD) presented by Ariza and Ortiz (2005), Ramasubramaniam et al. (2007), and extended to graphene later on Ariza and Ortiz (2010), to the analysis of patterned distributions of structural defects in graphene, while accounting for the electronic coupled effects. This theory combines lattice harmonics, the theory of eigendeformations presented by Mura (1987), and the Discrete Fourier Transform (DFT) in order to derive expressions of the displacement field and the stored energy of graphene sheets containing an arbitrary periodic distribution of defects, particularly dislocations. Previously, using this framework, these authors have investigated the existence and stability of dislocation dipoles and quadrupoles in graphene (Ariza et al., 2010, 2011, 2012) based on two different empirical interatomic potentials: the harmonic potential by Aizawa et al. (1990) and the reactive potential AIREBO (Stuart et al., 2000). In this work, we present a different approach, we will extend the DD theory to include a force-constant model derived from a tight binding interatomic potential. Thus, we will be able to predict the electronic properties of defective graphene, whereas being able to simulate large atomic systems.

2. The discrete dislocation theory

A general theory of discrete dislocation in crystal lattice has been developed by Ariza and Ortiz (2005), but will stand a