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Emergent magnetism in irradiated graphene nanostructures

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ABSTRACT

We model the atomistic restructuring of different types of carbon nanoribbons as they are irradiated and subjected to uniaxial stress. Time scales relevant to realistic experimental conditions are achieved with an original Monte-Carlo algorithm that enacts rare events in a stochastic manner using the structure adjacency information. We use a Hubbard model Hamiltonian to analyze the appearance of magnetic domains emerging from the concerted rearrangement of armchair edged sections into zigzag configurations. The self-consistent Hamiltonian is also used to compute electronic transport properties to establish the presence of spin-polarized current flowing across the initially non-magnetic nanoribbons.

1. Introduction

Carbon nanostructures, and two dimensional graphene in particular, have garnered much attention in the search for magnetic structures entirely composed of organic or light elements [1,2]. Finding such materials is of great interest due to the many possible applications they could enable, including data storage [3], spintronics, and quantum computing [4]. Pristine graphene is nonmagnetic, but exotic magnetic behaviors may emerge when dopants and/or structural defects are present [5]. When 2D graphene is transformed into a quasi-1D structure, which is best described as a finite width strip of graphene, the resulting graphene nanoribbon (GNR) can display electronic and magnetic properties which depend critically on the GNR's width and the atomic configuration of its edges. This is the case when the edges assume a zigzag-like patterning, resulting in a high electronic density along the edges if the GNR is in a nonmagnetic configuration. The instability due to the high charge density is resolved via spin polarization. While the spin alignment is ferromagnetic along each edge of the ribbon, these zigzag GNRs (ZGNRs) have been predicted to exhibit anti-ferromagnetic (AFM) and metastable ferromagnetic (FM) edge-to-edge spin alignment configurations which are close in energy and are distinguished by whether the relative alignment is anti-parallel or parallel respectively [6–8]. These particular electronic and magnetic properties of ZGNRs result in unusual behaviors, such as half-metalicity [9]. In contrast, ribbons with edge atoms that assume an armchair-like configuration, classified as armchair GNRs (AGNRs), exhibit only a nonmagnetic state in their pristine form, and show an electronic band-gap which decays with increasing width through three distinct families of behaviors, according to the number of $C-C$ dimer lines along the GNR's non-periodic direction [8,6].

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Owing to their unique properties, pristine GNRs have been studied extensively using density functional theory and other theoretical methods based on semi-empirical formalism, that are augmented to include spin–spin interactions within the mean-field framework of the Hubbard Hamiltonian [1]. In an effort to tune the electronic properties of GNRs, extensive research has turned towards examining defective and modified structures [10,11]. Theoretical studies involving these modified GNR systems have revealed emergent properties such as nonzero spin conductance [12] and large magnetoresistance [13].

The primary goal of this work is to examine the theoretical time evolution of GNRs as they are simultaneously exposed to electronic irradiation and uniaxial mechanical stress. The use of irradiation has been experimentally demonstrated to yield precisely designed carbon nanoassemblies [14,15] with emergent properties such as transistor-like behavior [16]. It seems that in most cases, an additional stimulus is necessary to steer restructuring in a desired direction. In that respect, experimental works have repeatedly shown that the combination of irradiation and other physical stimuli, such as an increased temperature [17], or Joule heating [18], can yield specific carbon nanostructures that have forms vastly differing from their original ones. Here we will focus on uniaxial mechanical stress and strain as the additional driving force for structural mutations under irradiation. By stretching the GNR, we promote mass flow and the possibility of creating new structural phases. To achieve our goal, we have devised an original simulation scheme to study the structural evolution of a given structure into another. The morphing methodology is based on a Metropolis Monte-Carlo algorithm that allows much larger time scales to be simulated compared to traditional molecular dynamics (MD) approaches. In order to enable fast prototyping, and to monitor the physical properties of the resulting system at each step of the evolution algorithm, we complement our simulation with an efficient set of algorithms [19,20] to compute electronic transport properties [21], based on spin-dependent, semi-empirical methods [22,1] combined with the Landauer formalism [23].

2. Methods

The core method we use for simulating structural evolution is known as the Accelerated Topological Annealing of Carbon (ATAC). ATAC is a Metropolis Monte-Carlo algorithm we originally devised to study the time evolution of carbon nanostructures under irradiation and annealing [24]. The basic underpinning of ATAC is to simulate the electronic irradiation of the structure through the introduction of random topological mutations, which are accepted or rejected depending on the change in system energy they introduce. The set of topological mutations correspond to the well-known structural modifications of the structure under irradiation, and their individual occurrence is governed by a probability distribution function that can be tweaked to faithfully account for realistic experimental conditions.

Specifically, ATAC first loads the input system provided by the user and records its structure in the form of an undirected graph using the system's adjacency matrix. ATAC then randomly applies mutations to the structure by modifying the system's graph and enforcing the corresponding bond structure modifications via a penalty potential function. The present application of ATAC uses the Stone–Thrower–Wales (STW) bond rotation as the elementary mutation (Fig. 1(a)) [25,26]. This is justified by the lower activation energy for STW defects [27] in pristine graphene compared to that of single atom vacancies and other, more energetic, defects [28]. While the structural configuration of a system, including existing defects, and presence of uniaxial stress both reduce the STW rotation and single vacancy defect energies, we find that in our simulations, which are well below the fracture

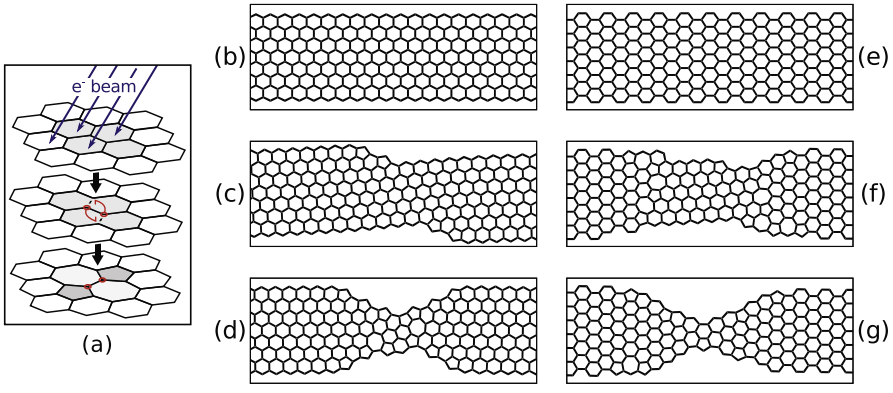

Fig. 1 – (a) The elementary mutation used to simulate the irradiation of the structures, the Stone–Thrower–Wales bond rotation. (b)–(g) Select structural results showing approximately 50 Å sections of the structures with hydrogen atoms not shown. (b) The initial ZGNR structure. (c) A ZGNR structure, after a number of iterations of ATAC, exhibiting deformation along a 30 degree slip plane. (d) A ZGNR exhibiting necking later in the same simulation. (e) The initial AGNR structure. (f) An AGNR simulation in which the structure exhibited a temporary domain shift from armchair oriented edges to zigzag oriented. (g) A separate AGNR simulation which did not exhibit any domain shift, and instead immediately began to show necking. Animations showing the entire evolution of the three aforementioned simulations are provided as supplementary information [46]. (A color version of this figure can be viewed online.)