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An open-source code to generate carbon nanotube/graphene junctions

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ABSTRACT

Carbon nanotube (CNT)/graphene nanostructure has the potential to extend the superior mechanical, thermal, and electrical properties of graphene from two dimensions to three. While the theoretical investigation of CNT/graphene nanostructure based on atomistic modeling is garnering great attention, an open-source numerical tool to generate covalently bonded CNT/graphene junctions is still in lack for material scientists. In this work, a pathfinding algorithm is used to exhaust all possible configurations on graphene to seamlessly connect to a given CNT. The least squares approach method follows to sort out the configuration with minimum energy. The combined methods are able to generate CNT/graphene junction for any CNT type (m, n). Molecular dynamics simulation further reveals that the formed junctions are thermodynamically stable, and thus ready to serve as basic block for a CNT/graphene network. By providing an easy-to-use numerical tool in the form of MATLAB code, the intention is to free material scientists from the tedious preparation of atomic configuration.

1. Introduction

Graphene has attracted great attention due to its superior thermal conductivity [1–3] and mechanical properties [4–6], and unique optical and electrical properties [4,7–9]. It is known that strong covalent bonds are along the carbon plane and weak van der Waals interactions in the transverse directions [10]. The structure causes anisotropy in electrical, mechanical and thermal properties, which significantly limits its three-dimensional applications. One strategy to mitigate the problem is to fuse graphene layers using carbon nanotube (CNT). The covalent bonded CNT/graphene junction can serve as high-efficiency mechanical/thermal/electrical transferring channel. It has been demonstrated that a CNT/graphene network connected by covalent bonds exhibits superior mechanical properties, thermal and electrical properties [11–17].

Attempts to experimentally fabricate high-quality covalently-bonded CNT/graphene junctions have never ceased. Post-organization methods such as self-assembling [18,19] and liquid phase reaction [20,21] suffer from poor connection, which is mostly dominated by physical bonding instead of covalent bonding. Direct chemical vapor deposition is the means to produce stable covalently bonded CNT/graphene junctions [22,23]. Lee et al. [24] applied plasma-enhanced chemical vapor deposition (PE-CVD) to grow vertical carbon nanotubes on the graphene oxide platelets with pre-deposited nanopatterned iron catalyst particles. It was found that the prepared carbon hybrid films showed high mechanical stretchability and low electrical resistance along all three dimensions. Paul et al. used CVD method to grow carbon nanotube on graphene. Through high-resolution transmission electron microscopy (HRTEM), seamless crystalline interface with clear lattice fringe between CNT and graphene was observed. Zhao et al. [25] investigated the defects in the graphene/single-walled carbon nanotube hybrids fabricated by catalytic CVD. Through Raman spectra, the I_D/I_G ratio was measured as 0.28, which was larger than that of single-walled carbon nanotubes (0.12). The increased ID/IG ratio indicated the rupture of sp^2 bonds and there could have defects at the fabricated CNT/graphene junction.

Numerically, atomistic models have been widely used to study the mechanical, thermal and electrical properties of CNT/graphene hybrid materials. The modelling requires an initial hybrid configuration with controlled structure. Melchor et al. developed a software called “CoNTub” to fuse CNTs by controlling connecting angles and the positions of defects [26,27]. However, a software tool to generate CNT/graphene junction is still unavailable. The first effort towards generating atomic CNT/graphene junction was made by Baowan et al. based on energy minimization [28]. The constructed junctions have been used by Novaes et al. to study the electronic transport between graphene sheets covalently linked by nanotubes [15]. It is also noticed that there are also efforts to apply variational calculus to formulate continuous models for the fusion of CNT and graphene [29,30]. Instead of directly minimizing the discrete atomic bonding energy as in [28], the

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alternative variational approach is to minimize the continuous elastic energy by assuming that carbon nanotubes deform as in perfect elasticity. Due to its continuum nature this approach has the advantage of releasing the residual stress at a relatively large scale, but does not ensure a realistic atomic structure because of the lack of atomic details. Hence, the method developed in [28] is more practical in facilitating atomistic modeling. It is noted that, however, a group of possible graphene configurations have to be manually selected in the seminal method developed in [28]. The manual selection step significantly limits the application of the approach. For a given CNT with a random type (m, n), one has to repeat the manual selection process. Especially, when the size of CNT becomes large, manual selection becomes impossible. It is also noticed that in the energy minimization process, the nanotube is only allowed to rotate along one axis. As a result, the residual strain caused by non-hexagons cannot be fully released.

In this work, we use a pathfinding algorithm to generate all possible configurations that can seamlessly fuse a given CNT (m, n) to graphene. With the new added module, the tool is capable of joining any type CNT to graphene with optimized covalent bonding. After identifying all possible configurations, the least squares approach is applied to find the structure with minimum bonding energy. In the formulation of bonding energy, we also introduce full rotational freedoms to nanotube, therefore enabling a better accommodation of residual strain induced by non-hexagons in the formed junction. Molecular dynamics simulation is also integrated in the screening process to ensure the thermal and dynamic stabilities of the generated structure. The work leads to an open-source code (createCNT2D.m in supplementary materials) to automatically produce any CNT/graphene junction, which can be used as basic block for a CNT/graphene network.

2. Methodology

To seamlessly join CNT with graphene, it requires to connect the dangling bonds of a CNT to the dangling bonds of a graphene sheet. A three-step method is developed to generate stable structures for CNT/graphene junctions. Given a CNT, the configuration and number of dangling bonds is known. The first step is thus to delete atoms on a perfect graphene sheet to obtain the equal number of dangling bonds as that of the given CNT. A number of configurations can be generated on graphene in the first step. However, many of these configurations cannot form stable sp^2 networks. The second step is to select and optimize configurations that are able to minimize the bonding energy. Following that, the third step is to further testify the dynamic and thermodynamic stabilities of the produced configurations using the large-scale atomic/molecular massively parallel simulator (LAMMPS), an open-source molecular dynamics simulation package [31].

2.1. Step I: Generating dangling bonds on graphene through pathfinding algorithm

Given a CNT, Step I is to delete atoms on graphene sheet to generate equal number of dangling bonds. A CNT can be described by a chiral vector (n, m), in which n and m determine the configuration of CNT. Particularly, (n, 0) is zigzag CNT and (n, n) is armchair type. For a CNT with arbitrary n and m values, there are n + m dangling bonds at its end. The graphene sheet can be viewed as a graph with carbon atoms as nodes. The edges, however, are not limited to C—C bonds. All C—C pairs with a distance smaller or equal to $2 * a$ (a is the distance for a sp^2 bond) are viewed as edges. Therefore, there will be three types of edges as shown in Fig. 1. That is to say, for any atom on the graphene, its neighbor atoms are allocated to three groups according to the distances between them. Type 1

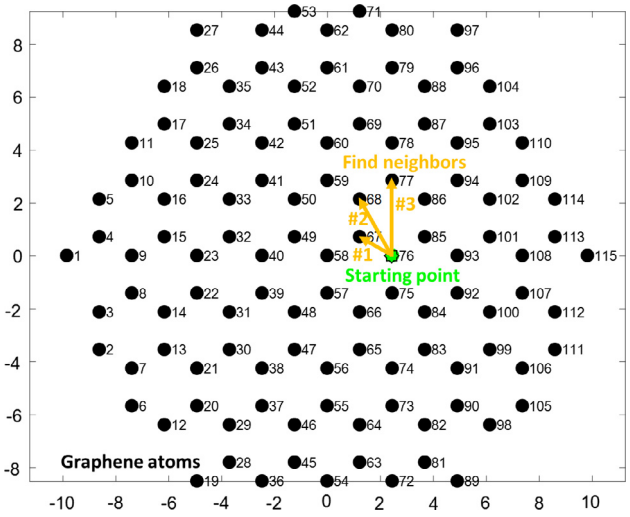

Fig. 1. Schematic of the pathfinding algorithm to find next node with three possible paths.

neighbor atoms will form carbon-carbon bonds; Type 2 neighbor and type 3 neighbor are the second nearest neighbor and the farthest neighbor, respectively. The essence of Step I is thus to find all possible closed paths (circuits) with equal number of dangling bonds as that of the given CNT (n, m). A data structure is designed to store the information of graphene as a graph, and node number is used to label carbon atoms (black dots in Fig. 1). A distance matrix D is established to store the distance between graphene atoms. In D, D_{ij} represents the distance between the graphene atoms #i and #j. Here, graphene atoms are marked with different numbers as shown in Fig. 1. Then, comparing the D matrix with the distances of three types of neighbors, convert the D matrix to neighboring type matrix with 1, 2 and 3. When the distance between two atoms is larger than the type #3 neighbor, the neighboring type is set as 0. As shown in Table 1, in the neighboring type matrix T, T_{ij} takes 0, 1, 2, or 3. To start the path searching, we randomly select a node as a starting point (marked as green star). Considering the geometrical symmetry of the graph, three edges (within 60°) in the anti-clockwise direction marked as yellow arrows in Fig. 1 are selected as the next possible paths to find the next node. The same selecting procedure is applied on the following node through a recursive algorithm. The terminating criterion is that the number of nodes reaches n + m. If the path searching returns to the starting point after termination, a qualified path is thus found. Because it is a recursive algorithm, all possible paths will be exhausted eventually. A qualified configuration is a polygon with n + m edges and the atoms inside the polygon are removed. Note that, after finding all possible configurations, there will be many identical to each other due to rotational symmetry. A sorting procedure based on neighboring type is applied to detect these rotational symmetrical structures.

In order to reduce the searching time, three practical rules can be applied. Firstly, because the qualified configuration is a closed loop, the angle between two adjacent path vectors (one is from the currently selected atom to the next selected atom, another is from the previously selected atom to the currently selected atom) is confined between 0 and 150°. Secondly, the last-selected atom should be able return to the starting-point atom within double bond length, and the distance between the atom selected at the (n + m) step and the starting-point atom should be less than ((n + m) * 3/4) * a. The last selected atoms is not allowed to exceed the Y coordinate of the starting-point atom to avoid overlap in the loop. Thirdly, a sp^2 bonding network requires that each