Ab initio study of folded armchair graphene nanoribbons

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We present a first principles approach to the characterization of multiply folded armchair graphene nanoribbons using the Vienna Ab-initio Simulation Package, along with built-in ultrasoft pseudopotentials and the Local Density Approximation for the exchange-correlation functional. These tools were used to determine the energy required to produce a number of different folded structures from unfolded armchair nanoribbons as well as to determine the energy as a function of folded width in single fold structures.

I. INTRODUCTION

Recently graphene has become a subject of intense study due to its interesting electronic and mechanical properties. Sheets of graphene can form single- and multi-wall nanotubes, nanoscrolls, cones, buckyballs, and ribbons. Depending on its size and geometric properties it can be a metal, insulator or anything in between. In this study we explore the energetic properties of Armchair-Edge Graphene NanoRibbons (AGNR) that have been folded along their long axis.

It has recently been computationally predicted that radial deformation can alter the band gap of carbon nanotubes, sometimes even causing a transition from semiconductor to metal (Shitogun and Woods, 2009a) and (Shitogun and Woods, 2009b). Others have observed graphene folding freely under mechanical stimulation, (Zhang et al., 2010).

Experiment has shown that folded graphene has the lowest energy when it was folded along the armchair or zigzag directions resulting from the energetically preferable stacking of the lattices on in the flat sections of the structure when these folding angles were used. As a result, approximately 30% of the graphenes were folded in a manner that corresponds to a fold along the long direction of an armchair GNR, another 30% corresponded to a zig-zag nanoribbon and the rest were randomly distributed with folding angles between 0º and 30º. (Zhang et al., 2010) Zig-zag nanoribbons have been shown to be magnetic, making them somewhat more difficult to study.

A number of studies have investigated the properties of so-called carbon nanoscrolls (rolled up sheets of graphene). Like folded graphene, the energies of these structures depend on the competition between the Van der Waals forces between the sheets of graphene and the stress caused by bending the graphene (Grunderman, 2003). One of the most interesting features of the nanoscrolls is that first principles simulation has indicated that some nanoscrolls would be at a lower energy than the corresponding unrolled graphene sheet (Braga and Baughman, 2004).

Folded graphene nanoribbons have a number of potential applications. Braga, et. al. have used molecular dynamics so how that charge injection causes unrolling of nanoscrolls. (Braga and Baughman, 2004) Further possibilities could be unleashed by functionalizing the nanoribbon edges: possibly allowing the ribbons to fold or unfold upon detecting a specific molecule. If the band also structure changes with folding, this could be used at a way of detecting certain molecules. One of the most exciting possibilities is the use of nanoribbons as nanowires in microprocessors. The excellent electronic properties of graphene nanoribbons lead some to believe they are capable of sustaining processor frequencies in the range of terahertz.

Nanoribbons can be described in terms of a number of characteristics. Perhaps the most obvious is length, however density functional theory requires periodic boundary conditions, so we will consider the nanoribbons to be of infinite length. Next is width, which is on the order of Angstroms; a more appropriate unit comes in the form of the number of carbon atoms. This measure reflects an actual property of the lattice, does not vary with contraction or expansion of the bonds, and remains easy to determine when the ribbons are folded. A third and rather important property is chirality, which describes the geometric orientation of the lattice with respect to the boundaries of the ribbon. As shown in Fig. 1, the chirality is specified by a pair of lattice coordinates. There are, of course, a myriad of other properties that were not considered in this study such as band gap, elastic properties, et cetera.
II. COMPUTATIONAL METHODS

One of the principal endeavors of quantum chemistry is to determine the structure of molecules based on their chemical composition. The equilibrium structure can be found by solving the time independent Schrödinger equation for the wavefunction that minimizes the total energy of the system. Unfortunately, each particle has its own complex wavefunction, making this a problem of $3N$ dimensions (where $N$ is the number of particles).

$$\hat{H} \Psi(r_1, r_2, ..., r_N) = E \Psi(r_1, r_2, ..., r_N)$$  \hspace{1cm} (1)

Solving for the ground state energy this way tends to scale like $N^6$, and is often prohibitively expensive, as even relatively small systems could have at least tens of atoms (thus, hundreds of particles). Fortunately, in 1964, Hohenburg and Kohn proved that the ground state (time independent) energy is uniquely determined by a functional the electron density.\cite{Harrison2003} Now, in order to solve for the ground state energy we only need solve for the charge density that minimizes:

$$E_0 = E[\rho(x, y, z)]$$  \hspace{1cm} (2)

Unfortunately, their theory provided no guidance on the form of this functional. Some elements, such as the external potential (imposed by the nuclei of the atoms) are essentially trivial. The exchange correlation functionals (a result of electron-electron interactions) are still unknown. However, a variety of approximations have been developed, allowing density functional theory to become an essential part of modern computational materials science.

One such approximation is the Local Density Approximation (LDA) which assumes this functional is dependent only on the value of the electron density at that point. This approximation is simple, efficient and well understood. No DFT can account for Van der Waals interactions (without an empirical correction), however cancellation of errors LDA provides for an order-of-magnitude approximation of Van der Waals forces, usually an overestimate. This proves essential in this study, as Van der Waals forces serve to stabilize the ribbons in the folded state.

Simulations were performed using the Vienna Ab-initio Simulation Package implementation of density functional theory. The included ultrasoft potentials were used. Initial ion positions were determined using Nanotube modeller, gOpenMol, and a program written by Lee.

III. ENERGY OF FOLDS

The most intuitive quantity to study would be the energy as a function of the number of folds. This energy arises from competition between the energy associated with the Van der Waals interactions between the flat portions of the fold and the energy necessary to bend the graphene. We will refer to this quantity as the $n, m$ order fold energy (where $n$ represent the number of folds):

$$E_{n,m} = E_{m\text{-fold}} - E_{n\text{-fold}}.$$  \hspace{1cm} (3)

Unfortunately, this quantity will be negative if the $n$-folded ribbon is at a lower energy (more stable) state than the $m$-folded ribbon. Finding systems with a negative fold energy would be very interesting as this would indicate that the folded state is more stable than the unfolded state; such a structure may fold
FIG. 3 Zero-one fold energy per atom as a function of width. This data show a negative correlation between the width and per-atom fold energy. From this limited and preliminary data, it is difficult to be certain what sort of trend this is. [Preliminary Data, not fully converged, and some superlattice periodicity mismatches.]

spontaneously.
We began by investigating whether a single fold of a 28-AGNR was stable and moved onto two, three, four, five and six fold structures (for all a 28-AGNR was used). In Fig. 2 the energies of the 0, 1, 2, and 3 fold structures are stable when converged to at least $\Delta E \leq 0.001 \text{eV}$ and $F_{\text{mpatom}} \leq 0.05 \text{ eV/Å}$. The 4-folded structure has not yet converged; we are currently unsure if it is fully stable. The 5 and 6 folded ribbons were unstable and began to unfold. Figure 2 also revealed that the $n, (n+1)$ fold energy, $E_{n, n+1} = 3.99 \text{eV}$, was relatively constant for stable folds.

IV. LENGTH DEPENDENCE OF ENERGY
We were also interested in how the first order fold energy varies with the length of the ribbons. From this, we can infer the energy associated with the Van der Waals interactions between the parallel elements of the nanoribbons and the energy associated with the bending of the graphene. Fig. 3 shows some variety of nonlinear relationship between the per-atom zero-one fold energy. Although the exact nature is unclear, the best fit is a power law. As of the time of this writing, this data is incomplete. Simulations were conducted using difference periodicities (distances between neighboring nanoribbons) and none are fully converged.

V. CONCLUSIONS & FUTURE WORK
We can conclude that the fold energy, $E_{n, n+1} \approx 3.99 \text{eV}$, can be considered a constant for stable folds for any $n$. The primary constituent of the fold energy arises from the stress associated with bending the graphene; the contribution from the Van der Waals forces is small (on the order of 0.025 $\text{eV/Å}$) and it is currently unclear what its overall contribution is. The most immediate future work will be completing the relaxation of these folded structures.

Once the structures have been fully relaxed, it will be possible to move a detailed characterization of the electronic structure of these systems. We are intrigued to determine how the band structure changes when the ribbon is folded. Significant changes would allow the construction of a number of novel nanodevices that vary the current when the structures are unfolded.

Another step is to determine if these structures have any noteworthy elastic or oscillatory properties. Other graphitic structures have been shown to be gigahertz-range oscillators [citehertz]. A feature such as this would be especially interesting in the context of oscillating electronic properties, which would allow for the construction new electronic devices.

We also plan to repeat this study using the Generalized Gradient Approximation (GGA), another functional that accounts for the gradient of the electron density (rather than just the value, as in LDA). This approximation is known to be more accurate, but does not feature the same error cancellation as LDA, and may not predict bonding between the flat portions of the folded nanoribbons.

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