Mohammad Fardin Gholami, Nikolai Severin, Jürgen P. Rabe

Folding of Graphene and Other Two-dimensional Materials

1. Introduction

1.1 Folding

The concept of the fold, from a physical standpoint, has been a subject of investigation, spanning from folding of proteins[1] and synthetic polymers[2] to packaging engineering[3]. Folding of fabrics and thin sheets of material has played an important part in advances made in tool production (folding of solar panels, for example, is crucial for efficiency in space utilization aboard satellites).

Folding allows for the transformation of a two-dimensional (2D) material into a three-dimensional (3D) material that exhibits a more complex geometry. The importance of folding can be observed in nature from the structure of plant leaves and animal tissues to protein folding; it is the most important feature of their functionality.

Nature takes a bottom-up approach to constructing functional foldable components, such as plant leaves and animal tissues, by assembling together smaller functional units, thereby giving rise to progressively more complex systems. Against this backdrop, the use of atomically thin sheets such as *graphene*, which are able to fold themselves into various geometries, is clearly interesting.

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1   Dill/McCallum 2012.
2   Shu et al. 2001; Zhuang et al. 2008; Schmidt et al. 2011.
3   Fei/Debnath 2013.

Before proceeding to discuss folding at nanoscale levels, let us first address folding and bending of materials at macroscale levels. Folding and bending are natural processes present, for example, in plant growth. At the macroscale level, in which the thickness of a sheet of material is greater than a micrometer, high enough strain across the bulk results in bending and folding.

In nature, forces, which cause bending or folding, could result from *differential growth* imposed by various external factors, such as changes in humidity or thermal expansions.[4] Differential growth can occur when layers have different mechanical properties, leading to differential stress experienced at each layer, a differentiation that results in bending and consequently folding.

Furthermore, folding and self-folding of materials could be utilized towards nanoactuation, stimuli responsive folding, and wrapping. On the nanoscale, e.g., in graphene (fig. 1), where the thickness of a sheet of material is on the order of an atomic or molecular diameter, the folding is possible with the tip of a scanning force microscope (SFM).[5]
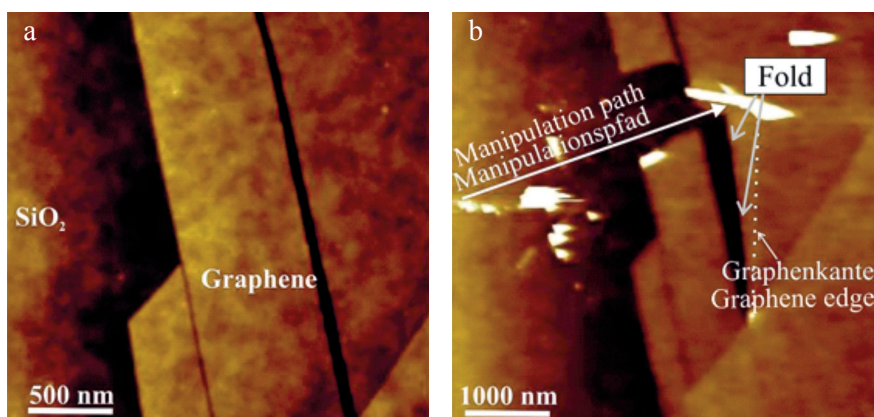

Fig. 1: Scanning Force Microscopy (SFM) height images display the topography of single graphene layers on a silicon oxide (SiO_2) surface before (a) and after (b) manipulation with the SFM. Higher regions appear brighter; a white arrow indicates the path the SFM probe was moved during manipulation; the dotted line shows the graphene edge after folding.

Also a variation of the environmental conditions and *chemical patterning*[6] may be employed. The possibility of nanoscale folding in materials promises the introduction of novel properties into matter as well as new applications for resulting products.

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4   Harrington et al. 2011.

5   Eilers/Rabe 2009.

6   By chemical patterning we mean the controlled variation of the chemistry within a single sheet of graphene or graphene oxide.

In the following, section 1.2 is devoted to describing properties of graphene and graphene oxide. Section 1.3 then continues with an overview of recent studies related to their folding. In section 2 we describe folding of 2D nanoscale sheets and the effects of defect lines on possible bending and folding. Section 3 explains the impact of folding on the electronic properties of graphene. Section 4 presents experiments and current research on folding of graphene and graphene oxides, focusing on their possible applications for nanotechnology, especially in nanopackaging.

1.2 Graphene and graphene oxide

Graphene is a single-atom thick sheet of carbon atoms arranged in a two-dimensional network of ring structures (a honeycomb lattice).[7] Andre Geim et al. were the first to isolate graphene through exfoliation of a naturally occurring graphite crystal using common adhesive tapes.[8] Subsequent studies demonstrated graphene has many promising properties such as high electrical conductivity at room temperature[9] and high thermal conductivity,[10] and on the same time high transparency[11] moreover, it exhibits a low bending stiffness,[12] and nevertheless a very high amount of force (per unit area) is required for stretching (also known as high Young's modulus).[13]

In addition, graphene has been proven to be impermeable to small molecules.[14] This impermeability is attributed to its dense delocalized cloud of electrons, effectively blocking the ring structure with a repelling field.[15] However, as with any other crystalline structure, defects and incomplete segments may exist in random locations throughout the graphene sheet.

Simulation studies and microscopic methods have already demonstrated that graphene, as a 2D sheet of atomic carbon cores, can undergo 3D deformations to minimize its energy.[16] This was attributed to structural defects.[17] Structural defects thus become a crucial element for 3D deformations on the nanoscale.

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7   Novoselov et al. 2004; Geim/Novoselov 2007; Meyer et al. 2007.
8   Novoselov et al. 2004; Wissler 2006.
9   Le/Woods 2012.
10   Calizo et al. 2008.
11   Nair et al. 2008; Cai et al. 2009.
12   See footnote 8.
13   Lee et al. 2008; Castro Neto et al. 2009; Le/Woods 2012.
14   Bunch et al. 2008; Lange et al. 2011; Li et al. 2013.
15   Sreeprasad/Berry 2013.
16   Roy et al. 1998; Zhang et al. 2010; Wang et al. 2013; Zhang/Li/Gao 2014.
17   Zhang et al. 2010.

Consequently the discovery of folds and wrinkles in graphene (2D to 3D transformation) has attracted much interest for their possible use in various applications, involving either graphene itself or one of its most important chemical precursors for its chemical synthesis, *graphene oxide* (GO).

Graphene oxide is a highly oxidized version of graphene.[18] It was initially produced by Benjamin Brodie in 1859, while trying to measure the atomic weight of graphite.[19] The two substances differ in that graphene is an electron conductor, while graphene oxide is an insulator. This is attributed to defects and structural disruptions caused by the presence of oxygen containing groups within GO.[20]

Researchers favor it for its potential for chemical modification; moreover, GO is easily processed in large quantities, because it can be synthesized by oxidization of graphite crystals.[21] Graphene oxide is highly dispersible. It forms a suspended mixture – *colloidal suspension* – in polar solvents such as water, due to the presence of oxygen containing groups. A colloidal suspension of graphene oxide was shown to be a key requirement in the transformation of the GO sheets from 2D to 3D structures. In addition, colloidal suspension of GO is an efficient and up-scalable (large scale production) way for the chemical reduction of GO.[22]

The self-assembly of graphene oxide sheets around nanomaterials has recently been investigated; it was found to be governed for the most part by electrostatic interactions.[23] Graphene oxide has its own spectrum of applications as in super capacitors,[24] membrane technology,[25] batteries,[26] and sensors[27] or as a part of composite materials.[28]

1.3 Folded graphene

Folded graphene exhibits further interesting properties, such as alteration of electron mobility (conductivity) at folded regions.[29] The folding of graphene sheets has been observed to result in the formation of graphene rolls or *nanotubes*. Moreover, graphene and graphene

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18 Hofmann/Holst 1939.
19 Brodie 1859.
20 Dikin et al. 2007; Dreyer et al. 2010.
21 Hummers/Offeman 1958; Chen et al. 2013.
22 Lee et al. 2010; Zhou 2011.
23 Cassagneau/Fendler 1999; Yang et al. 2010; Zhu/Chen/Liu 2011.
24 Stoller et al. 2008; Chen et al. 2010.
25 Dreyer et al. 2010; Li et al. 2013; Joshi et al. 2014.
26 Tao et al. 2011; Wang et al. 2012.
27 Cheng-Long et al. 2011; Borini et al. 2013.
28 Wu et al. 2015.
29 Prada/San-Jose/Brey 2010.

oxide have each been the subject of many studies regarding their self-transformation from 2D to 3D. Examples of such studies can be found in Nano-origami,[30] Kirigami,[31] biological applications[32] and even wrapping of bacteria.[33] As a form of folded graphene, carbon nanotubes have been demonstrated useful in fast water transport at nanoscale levels.[34]

In order to transform graphene into desired geometries relevant to new applications, many methods have been introduced for shaping or patterning.[35] However, some exciting new applications, such as nanocages devised for storage purposes, have only been realized in theoretical simulations.[36] The main limitation in experimentally realizing them appears to be a lack of control at the nanoscale, while full control over the different forces operating at the nanoscale is required in order to achieve ease of transformation from 2D into a stable 3D configuration.[37]

2. Mechanics of folding in graphene

In section 2.1 we describe the folding mechanism of atomically thin graphene sheets in comparison with thick multilayered materials. In section 2.2 we follow with a discussion of the influence of structural defects on folding and present related studies.

2.1 Folding in 2D nanoscale sheets

One may consider folding as an ultimate form of bending where a sheet of material overlaps but does not intersect itself while it remains in a stable state. To understand folding at the nanoscale, bending must first be defined and understood. Recent research has shown that the process of bending in single-atom thick or multilayered graphene sheets can be modeled using finite *deformation beam theory*.[38] This suggests bending of a multilayered thick sheet of graphene is not considerably different from that of a sheet of paper.

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30 Patra/Wang/Král 2009.

31 Blees et al. 2015.

32 Chung et al. 2013; Kostarelos/Novoselov 2014.

33 Liu et al. 2011; Akhavan/Ghaderi/Esfandiar 2011; Mohanty et al. 2011.

34 Ma et al. 2015.

35 Feng et al. 2012; Wang et al. 2013; Chen et al. 2014.

36 Leenaerts/Partoens/Peeters 2008; Zhang/Zeng/Wang 2013.

37 Patra/Wang/Král 2009; Talapin et al. 2007.

38 Tarsicio/Cristian/Augusto 2002; Xianhong et al. 2013.

As a simple example, cylindrical bending along a given longitudinal direction in a sheet of graphene is conceptually the main process responsible for the formation of single wall carbon nanotubes. It is similar to the rolling of a sheet of paper. Therefore, the resistance of a material to bend – that is, its *bending modulus* – for graphene would be crucial for understanding and utilizing bending mechanics.[1]

Empirical potentials[2] and *ab initio* calculations[3] have been previously used to predict the bending modulus of graphene. Calculations of the bending stiffness of graphene are not simple, since the thickness of a single-layer graphene, which is determined by quantum mechanical methods, cannot be defined in the same as on the macroscopic scale. Introducing bending stiffness narrows further the analogy with a sheet of paper.

A bending modulus can be introduced, assuming graphene to be a homogeneous sheet with a certain thickness. Yet introducing a bending modulus is rather a mathematical trick and does not imply graphene to be a thin elastic plate, since the bending modulus for an elastic thin plate depends on cube of thickness (that is to the third power).[4]

According to Kirchhoff-Love theory of plates, the strain and stress along the bulk of a thin homogeneous elastic plate varies linearly with thickness. Lu Qiang et al.[5] used a first-generation *Brenner potential*[6] to derive a simple analytical form for the bending modulus of single-atom thick graphene. The value of the bending stiffness was found to be 0.133 nN nm, while *ab initio* calculations have shown it to be 0.238 nN nm.[7]

It is clear then that values obtained through *ab initio* methods predict a stiffer graphene. Furthermore, this suggests that the empirical model does not explain the bending stiffness of the single-atom thick graphene sheet. Qiang et al. derived a formula for the bending stiffness of single-atom thick graphene based on an empirical potential for solid-state carbon atoms. It considers the bending stiffness of graphene not only being dependent on bond angle effects but also on the out-of-plane twisting angle between carbon-carbon bonds, known as torsion angles or *dihedral angles* (see fig. 2).[8] They calculated a bending stiffness of 0.225 nN nm, very close to the *ab initio* calculations. The dihedral angle effect

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1   Qiang/Marino/Rui 2009.

2   Tersoff 1988; Tu/Ou-Yang 2002; Marino/Belytschko 2004; Huang/Wu/Hwang 2006.

3   Sánchez-Portal et al. 1999; Kudin/Scuseria/Yakobson 2001.

4   Timoshenko/Woinowsky 1987.

5   Qiang/Marino/Rui 2009.

6   This model is a function for calculating the potential energy of covalent bonds and the interatomic force. The total potential energy of a system is the sum of nearest-neighbor pair interactions which depend not only on the distance between atoms but also on their local atomic environment.

7   Kudin/Scuseria/Yakobson 2001.

8   Qiang/Marino/Rui 2009.

calls for further studies involving bending energies of graphene, as its contribution to bending stiffness of single-atom thick graphene is significant.
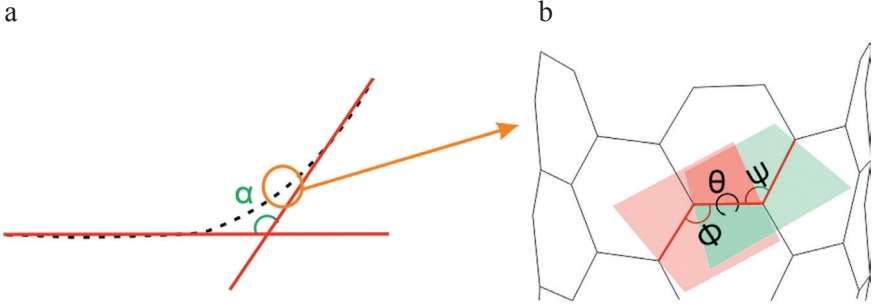

Fig. 2: (a) Graphene sheet bent to an angle α. Orange circle denotes area with bent segment, as detailed in (b). (b) Bent graphene honeycomb structure displaying the carbon-carbon bonds. Each dihedral angle θ (out of plane twisting of C-C bonds) is defined by three bonds (4 carbon atoms) connecting atoms (red lines). The dihedral angle determines the bending. Two neighboring carbon-carbon bond angles are denoted by Φ and Ψ, given by 3 carbon atoms, which define each plane (purple and green, respectively).

In the case of single-atom thick 2D sheets, such as graphene and to a good approximation also single layer graphene oxide, an external force can facilitate the bending process.[9] Researchers have shown that the self-folding of a single-layer graphene sheet can be modeled using similar considerations for calculating load-carrying and deflection characteristics of beams (deformation beam theory).[10]

Using beam theory, it was possible to predict the shape and the critical length of self-folding in graphene. Moreover, *molecular dynamics* (MD) confirmed this theoretical model.[11] A critical length is required for the process of folding in graphene to be autonomous. To visualize such a critical length, let us first define what we mean by a fold in a single-atom thick sheet of graphene.

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9   Chen et al. 2014; Guo et al. 2011.

10   Tarsicio/Cristian/Augusto 2002; Xianhong et al. 2013.

11   Molecular dynamics is a simulation method usually carried out to simulate physical movements of atoms and molecules governed by various forces such as Van der Waals forces or Coulombs forces.

At its simplest, a graphene fold is defined to be two overlapping sheets of graphene with an arc bending out-of-plane between them (fig. 3a).
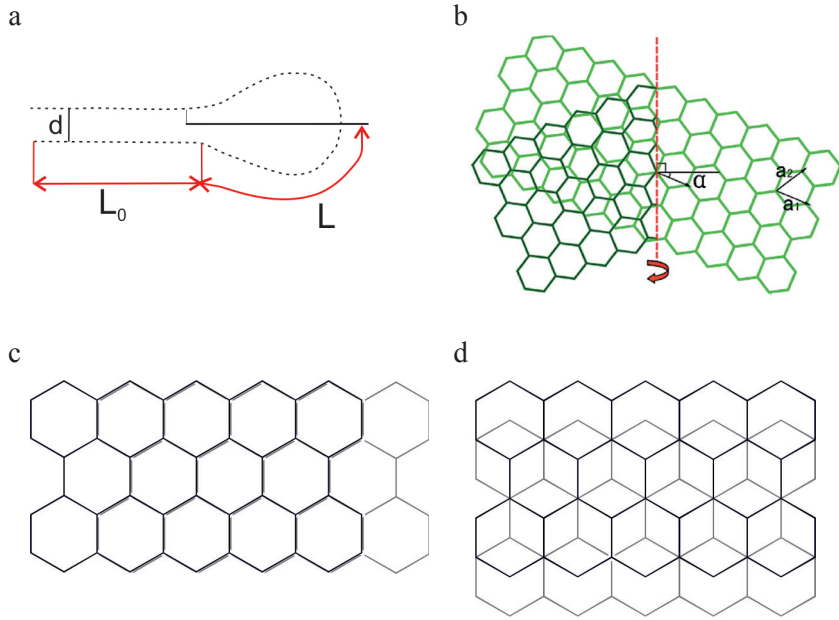

Fig. 3: Conceptual visualizations of (a) profile of a hairpin folded graphene sheet with its denoted regions, where d is the bilayer distance, L_0 and L are the lengths of the flat and half arc (hairpin) regions, respectively. (b) Schematics of a folding graphene sheet with a specific folding angle α. (c) AA stacking of the graphene sheets. (d) AB stacking of the graphene sheets.

The graphene fold involves two flat regions with an arched region in between. Flat regions can adhere to each other due to *van der Waals interactions* forces within an interlayer distance of *d*. These forces are weak attractive forces between two polarizable entities that do not stem from chemical bonding. The arched region is due to the graphene carbon-carbon bonding flexural hindrance.

Consequently, the formation of arched regions requires a certain amount of energy. For a self-folding process to take place, it is important that the adhesion energy between the flat overlapping regions – $E_{adhesion}$ – is greater than the bending energy – $E_{bending}$. Therefore, the length of the overlapping graphene sheet (fig. 3a) directly influences $E_{adhesion}$.

There exists a minimum length of the overlapping graphene segment below which $E_{adhesion} < E_{bending}$, consequently favoring unfolding.

To further quantify the total energy required for self-folding the entire length of the fold is needed. The entire length of the fold is:

$$L_{fold} = 2\,(L_0 + L)$$

where L_0 and L stand for the length of the flat region and the length of the half arc region, respectively (see fig. 3a). Meng Xianhong et al. calculate the total energy for folded graphene as follows:

$$E_{fold} = E_{bending} + E_{adhesion}$$

where $E_{adhesion} = -\gamma L_0$, with γ and L_0 standing for the binding energy per unit area of graphene and the length of the flat region, respectively. For self-folding to be possible E_{fold} must be negative. This can only happen when the overlapping length, L_0, is large enough and consequently $E_{adhesion}$ is higher in absolute value.[12] For any interlayer distance, d, between overlapping flat regions, E_{fold} can be calculated with respect to L, the half-length of the arched region. Therefore, the self-folding energy can be evaluated for different sheet geometries by:

$$(1) \qquad E_{fold} = E_{bending} - \frac{\gamma}{2}\,(L_{fold} - 2L)$$

Utilizing Eqn. (1), Xianhong et al. carried out MD simulations to investigate self-folding of graphene. MD simulations were carried out assuming a constant temperature of 0 Kelvin (K) to prevent atomic vibrations in agreement with theoretical models. To initiate the self-folding process an external force was applied in order to bring the graphene sheet ends closer together. Then energy minimization of the system was initiated. This process was repeated for graphene sheets of different lengths so as to identify metastable and stable self-folding. Using this methodology, Xianhong et al. found a critical length of graphene sheets for stable self-folding of $L_{fold} = 11$ nm. They classified the critical length of graphene required for self-folding into three regimes.

1. For graphene lengths L_{fold} below 6.5 nm, self-folding was not possible, and only a 2D configuration was stable.
2. For L_{fold} between 6.5 nm and 10.5 nm, self-folding was metastable, where both 2D and 3D configurations were stable.
3. For L_{fold} longer than 10.5 nm, self-folding or 3D configuration of the graphene sheet was stable.

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12   Tarsicio/Cristian/Augusto 2002.

Jiong Zhang et al. demonstrated that ultrasonication of graphene sheets in solution at 200 W for ten minutes, leads to the formation of folds in the 2D structure.[13] This implies suspended graphene sheets can fold under mechanical stimuli. They demonstrated that using Transmission Electron Microscopy (TEM) and computer based simulations it is possible to determine the length of the overlapping region and the shape of the curved edge. Based on simulations, the minimum length of the overlapping region should be at least 1.68 nm to form a stable fold. TEM studies of 100 graphene folds revealed that a given fold had either a 0 degree (armchair) or a 30 degree (zigzag) edge (fig. 4).
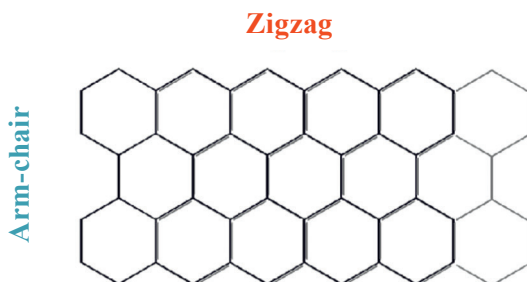

Fig. 4: 0 degree (armchair) or 30 degree (zigzag) fold edges.

To understand their results better, Zhang et al. used further simulations to minimize the energy of graphene folding at different fold edge angles. These simulations showed two prominent fold edge energy minima at 0 and 30 degrees, implying the energy of the folded graphene could be explained through lattice registry effects. Moreover, overlapping regions of graphene folds with AA and AB stacking (fig. 3c and 3d) require the highest and lowest energy states respectively. They suggested their results could be used for the design of graphene-based nanodevices.

These results agree with previous MD simulations by Niladri Patra et al., in which they demonstrated guided folding of graphene sheets.[14] Patra et al. further studied the transformation of 2D graphene sheets into 3D structures at locations where a water droplet was deposited. They observed that, irrespective of the shape of the graphene sheet, graphene could enwrap the water nanodroplets at T = 300 K (room temperature). Such enveloping causes the sheets to bend from their natural 2D configuration into a configuration maintained for a long period of time, even though it is not a minimum energy (metastable) 3D structure.

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13 Wang et al. 2013.

14 Patra / Wang / Král 2009.

They demonstrated further that, by increasing the temperature of the system from 300 K to 400 K, the shape fluctuations of water nanodroplets increases. Eventually van der Waals attraction between the graphene sheets causes the water droplets to get ejected. Patra et al. calculated the flexural rigidity of the graphene sheets and compared it to theoretically derived values. Their figure was 0.194 nN nm, which is very close to previously calculated values of 0.238 nN nm, 0.11 nN nm, and 0.225 nN nm from other studies.[15]

They therefore considered their simulations to be reasonably close to the possible experimental values. Consequently, the results of MD simulations carried out by Patra et al. imply that nanodroplets activate and guide folding of graphene sheets of complex shapes, similar to chaperones fold proteins.[16] These studies not only demonstrate the possibility of controlling the folding process using water nanodroplets and temperature changes. The latter implies possible applications of water nanodroplets packaging with graphene sheets.

Luca Ortolani et al. investigated the structure of graphene grown by *chemical vapor deposition* (CVD) on copper substrates by transferring graphene onto a TEM grid.[17] They used *high-resolution transmission electron microscopy* (HRTEM) to study graphene sheets at folded regions. In order to map out the curvature at the folds, compressions, observed in TEM images of the graphene lattice, were subject to *geometric phase analysis* (GPA).[18] Data obtained from GPA analysis then helped them to reconstruct variations in height and local curvature of edges of graphene folds within a spatial resolution of 0.5 nm. Ortolani et al. propose the analysis of apparent strains in HRTEM images of general 2D sheets as a way to achieve sub-nanometer topographic information experimentally.

2.2 Defect guided wrinkling or folding in graphene

In the structure of an atomically thin sheet of graphene, there may be regions in which structural homogeneity is disrupted. Structural defects are found where the honeycomb structure is altered by randomly occurring pentagonal or heptagonal rings (fig. 5b and 5c).[19] It has been shown that structural defects affect the mechanical properties of the graphene.[20] Both the density of defects and their regional arrangements have been shown

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15 Qiang/Marino/Rui 2009; Marino/Belytschko 2004; Kudin/Scuseria/Yakobson 2001.

16 Ellis/Van der Vies 1991.

17 Ortolani et al. 2012.

18 GPA analysis is a well-established experimental technique aimed at studying strained segments of nanomaterials.

19 Zhang et al. 2010.

20 Lusk/Carr 2008; Grantab/Shenoy/Ruoff 2010; Liu/Yakobson 2010; Rasool et al. 2013.

critical to mechanical properties.[21] For graphene grown on different substrates, such as mica or copper, individually grown crystals meet at a *grain boundary* (GB).

It is known that, in addition to the probable existence of structural defects at any location on grown crystals, the GB region always contains many structural defects. Haider Rasool et al. studied grain boundaries in graphene sheets using HRTEM and found that heptagonal and pentagonal defects are present at the GBs.[22] Rasool et al. observed a variation in carbon bond lengths at the center of the GB regions, where they were either much smaller or much larger compared with the normal length.

A bond length increase or decrease within the GB of the graphene sheet results in a tensile or compressive strain within that region. These strained regions affect the configuration of graphene by creating corrugations or bending in or out of plane of the sheet.
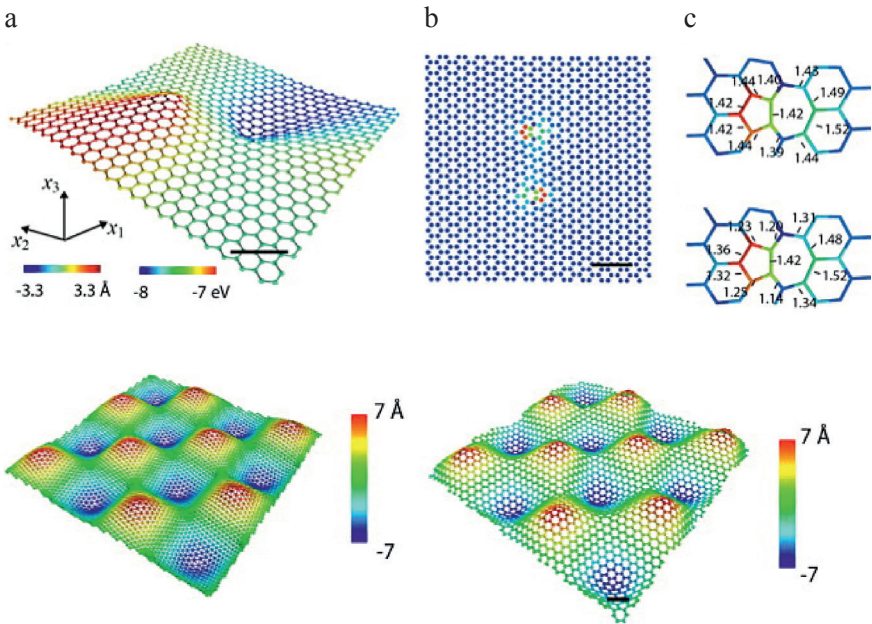

Fig. 5: Configurations of a simulated graphene sheet with dislocation dipole. (a) Perspective view of a region affected by dislocation. (b) Top view of the dislocation affected region. (c) Bond structure around the dislocation core.

21   Wei et al. 2012.
22   Rasool et al. 2013.

In a recent study, Teng Zhang et al. 2014 explored wrinkling and bending in graphene due to *line defects-disclinations* (observed where two or more planes of atoms in a crystal meet).[23] They demonstrated that a significant amount of wrinkling in 2D graphene sheets is likely the result of topological defects caused by disclinations or dislocation of atoms in the graphene lattice, which could be found at the grain boundaries. Furthermore, they examined whether inserting such defects intentionally could help control the wrinkling of graphene sheets to a desired folding or wrinkling configuration.

To answer this question they presented two examples of curved graphene sheets that can be produced and topographically tuned through the variation of topological defects. One of these examples was taken from Alexander Hexemer et al. study.[24] The latter carried out *Monte Carlo* simulations to predict the emergence of disclinations in a lattice of charged particles on a high aspect ratio sinusoidal surface.[25] Hexemer et al. predicted a periodical array of distributed disclination quadruples in a square unit cell creates a wavy graphene (fig. 5d and 5e).

This has been referred to as a *graphene ruga*.[26] Teng Zhang et al.[27] reproduced the graphene ruga through other models and its potential energies were minimized using computer molecular dynamics under periodical boundary conditions. A simple visual comparison between the graphene ruga structure produced by molecular dynamics simulations and the one produced through continuum mechanics calculations demonstrates that purely mechanics-based models (that is continuum models) are able to capture large scale wrinkling induced by structural defects in graphene.

Overall, studies by Zhang et al. have demonstrated that it is feasible to control the structural transition of graphene sheets to 3D structures by manipulation of the position of structural defects. Control over the structural defects introduces new possibilities for the design of application-specific products based on graphene. Changes in configuration introduced through topological defects have been shown to play a critical role in altering the mechanical, thermal and electric properties of graphene sheets.[28]

Apart from the alteration of graphene properties through the introduction of structural defects, Guo Wang et al. have demonstrated that the intentional creation of a line defect in

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23 Zhang et al. 2010.

24 Hexemer et al. 2007.

25 In physics, Monte Carlo methods are usually used for systems with many coupled (interacting) degrees of freedom, such as disordered materials or fluids. Monte Carlo simulations are based on a wide range of different algorithms, which rely on random resampling to obtain numerical results.

26 Zhang/Li/Gao 2014.

27 Zhang et al. 2010

28 Huang et al. 2011.

graphene offers a way to engineer further wrinkling.[29] Wang et al. carried out molecular simulations of graphene sheets containing one-dimensional periodic defects known as *Stone-Wales defects*.

Anthony Stone and David Wales, studied the icosahedral C_{60} (fullerene) and related structures with a theoretical perspective in 1986.[30] At the time, Stone et al. proposed that C_{60} has many other isomeric structures almost as stable as the icosahedral. The isomers proposed by Stone et al. required certain rearrangements in carbon-carbon bonding, which became known as *Stone-Wales rearrangements*.

A Stone-Wales rearrangement involves a change in π-bonding of two carbon atoms, allowing for a 90 degree rotation with respect to the midpoint of their bond (fig. 6). Inherently, Stone-Wales defects form an out-of-plane bending angle with respect to the longitudinal axis of the sheet, which is known as the defect angle. Wang et al. demonstrated that tuning the defect angle of Stone-Wale defects results in tuning the direction of the graphene wrinkling.
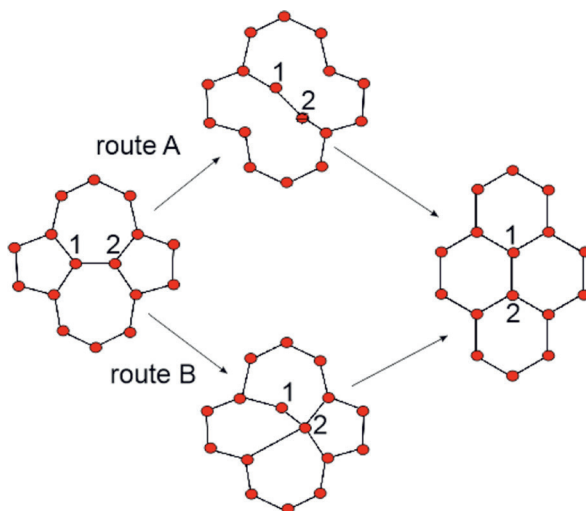

Fig. 6: Stone-Wales rearrangement routes: route A is a concerted mechanism and route B is a stepwise process. According to Stone-Wales rearrangement, two pi-bonded carbon atoms (marked '1' and '2') rotate 90 degree with respect to the midpoint of their bond. The end product of the rearrangement is an energetically more stable structure.

29   Wang et al. 2013.
30   Stone / Wales 1986.

It is known since the early 1990s that the formation of *fullerene*, as a 3D structure,[31] is due to a bottom-up mechanism involving small clusters of carbon atoms.[32] However, it was only in 2010 that Andrey Chuvilin et al. reported the formation of fullerenes *in-situ*.[33] This involved folding of a graphene nanoribbon into a fullerene after exposure to TEM. To understand this process it is important to note that TEM uses an electron beam (e-beam) to produce an image of an ultra-thin sample.

As the electron beam passes through the ultra-thin sample, it interacts with it. When graphene sheets are imaged using TEM, the graphene edges appear to be continuously changing their shapes. Chuvilin et al. observed that the high energy TEM beam of electrons causes fragmentation of larger graphene sheets into smaller ones. As TEM imaging carried on, small graphene flakes tended to transform to fullerene molecules in which the structure remained stable. The authors explained that, for the purpose of transformation of small sheets into fullerene, the creation of defects at the edges of these sheets was important. Defects induced by the electron beam at the edges of the graphene sheets underwent continuous reconstruction, leading to the most stable configuration. Note that the size of the initial 2D sheets is very important for 2D to 3D transformation: for sheets smaller than 60 carbon atoms the strain caused by defects does not suffice to bend the sheet enough to produce a fullerene.

3. Impact of folding on graphene's electronic properties

In this section we review studies concerning the effect of folding on the electronic properties of graphene sheets, especially as it is related to its geometry.

A folded region in a graphene sheet can resemble a fractional nanotube structure, in other words, a hairpin.[34] This implies the electronic properties of a folded graphene sheet are expected to differ from those of a cylindrical carbon nanotube, due to lack of symmetry in the structure of the hairpin-folded graphene.

Ji Feng et al. investigated the effect of a zigzag or armchair structural configuration of carbon bonds on the electronic properties of the folded graphene sheets.[35] The *density functional theory* (DFT) as such does not explain the long range electron correlations responsible for

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31 Icosahedral structure based on carbon rings.

32 Yannoni et al. 1991; Hawkins et al. 1991; Ebbesen/Tabuchi/Tanigaki 1992.

33 Chuvilin et al. 2010.

34 Huang et al. 2009.

35 Feng et al. 2009.

van der Waals adhesion between bilayers.[36] *Local density approximation* (LDA), on the other hand, employs a high enough level of accuracy to explain the equilibrium interaction potential between graphene layers.[37]

Following DFT-LDA optimizations, Feng et al. demonstrated that the folded graphene sheets with zigzag carbon-carbon bonds at the edge of the fold exhibit a top-bottom separation of 0.52 nm and 0.36 nm at the flat region bilayer separation. In the case of armchair carbon-carbon bonds at the fold edge, the fold top-bottom separation and the flat region bilayer were 0.72 nm and 0.37 nm, respectively. A top-bottom distance variation due to the zigzag and armchair fold edge configurations causes a variation in the scattering of the electrons in the folded region. The zigzag configuration at the fold edge results in a tighter hairpin, which causes more electron scattering and therefore lower conductance (electron mobility) at those folds.

Jhon González et al. investigated the electronic transport properties of folded nanoribbons of graphene sheets by theoretical means.[38] They considered two possibilities for folding: (1) a hairpin-shaped graphene nanoribbon folded on itself with the overlapping flat regions having a 0 degree contact direction (matching lattice), (2) a similarly folded graphene sheet only with overlapping flat regions (top layer) having 60 degree misorientation with the longitudinal axis of the bottom layer.[39]

González et al. demonstrated that, for the hairpin folded graphene nanoribbons having overlapping regions with 0 degree contact direction, conductance is similar to that of a stack of two graphene sheets with matching lattices, as a result of the fact that conductance is affected by the size of the scattering region (within the overlap and arched regions).[40] In the case of a 60 degree contact direction between overlapping regions, a slight mismatch of the sub-lattices disturbed the conductance symmetry within the hairpin-folded graphene nanoribbon. Scattering in the folded regions for both 0 degree and 60 degree caused an overall reduction in conductance of the folded graphene sheets, compared with that of flat single layer sheets. As a consequence, 60 degree folded nanoribbons of graphene have smaller sized scattering regions, giving rise to a conductance value closer to that of unfolded nanoribbons.

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36   In its simplest definition, density functional theory is a computational quantum-mechanical modeling method used to investigate the electronic structure of atoms and molecules.
37   Girifalco / Hodak 2002.
38   González et al. 2012.
39   Misorientation is the difference in crystallographic orientation between two crystallites.
40   González et al. 2010.

4. Graphene and graphene oxide folding and application-based studies

In this section we describe recent studies on the folding of graphene and graphene oxides with an emphasis on their applications to storage systems. We further present studies on their specific patterning for encoding the folds.

Toby Hallam et al. presented a method termed *Grafold* for printing folded graphene films.[41] Their method is based on using stamps with periodically varying adhesion to produce periodic waves within graphene sheets. Graphene is first transferred onto a patterned elastomeric stamp and then mechanically folded by placing the stamp over the desired substrate and slowly peeling it away. It is important to mention that folds produced in this way in the graphene sheets are more similar to wrinkles.[42] Hallam et al. found that graphene exhibited little strain at these folds (wrinkles) with a charge transport anisotropy within them. They suggested that Grafold could be utilized to produce wrinkles and folds in other 2D sheets such as MoS_2.[43]

Concerning graphene oxide folding, Fei Guo et al. observed that dried folded graphene oxide aggregates undergo a large anisotropic swelling upon rehydration to regain their hydrated unfolded forms.[44] This folding and unfolding was found to be unique to the hydration process, while drying causes a buckling in the structure that stores elastic energy.[45] The authors suggested graphene oxide could constitute a new class of stimuli-responsive materials in nanoelectronic devices or even in controlled drug-release systems.

Chen et al. studied GO-based nanosacks.[46] They demonstrated that, when graphene oxide and a secondary solute are dispersed in water microdroplets within a spray system, a spontaneous segregation into nanosack-cargo nanostructures takes place upon drying. They carried out MD simulations to understand the mechanisms behind this process. They found graphene oxide sheets tend to accumulate at the water/air interface; as drying takes place, the secondary solute is trapped within the graphene oxide sheets in the form of cargo-filled graphene nanosacks. They proposed this process to be scalable – promising for applications where nanomaterials need to be isolated from a specific environment (fig. 7).

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41 Hallam et al. 2015.

42 See ibid, fig. 2c.

43 Molybdenum disulfide is the inorganic compound with the formula MoS_2.

44 Guo et al. 2011.

45 Elastic energy is the potential mechanical energy stored in the configuration of a material or physical system as work is performed to distort its volume or shape.

46 Chen et al. 2012.

Binary suspension   **Filled graphene**

diffuse / adsorptive   water removal,
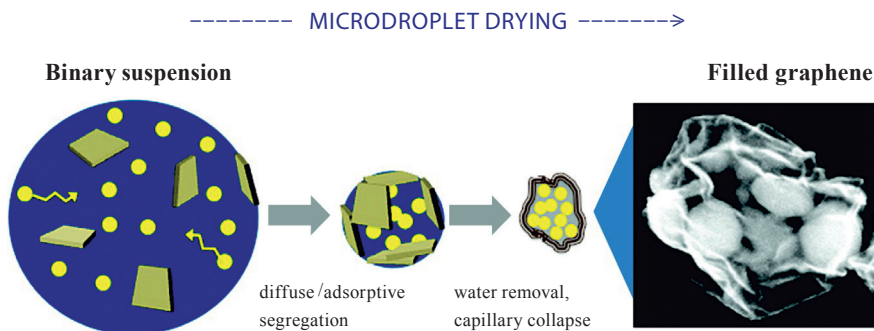segregation   capillary collapse

Fig. 7: Colloidal self-assembly of graphene oxide sheets into nanosacks containing the secondary solute. Black and white image shows a scanning electron microscope image of the nanosack filled with nanoparticles.

Soodabeh Movahedi et al. carried out edge modifications of graphene sheets.[47] They proposed a procedure for functionalizing the graphene edge using hyper-branched poly-glycerols.[48] It is important to mention the original graphene oxide sheets in their study were synthesized and later reduced to produce reduced graphene oxide sheets. Since hyper-branched polyglycerols are hydrophilic and graphene is hydrophobic, the authors argued that dispersing such a combination in water results in the bending of the hydrophobic graphene portion from a flat surface into a capsule-shaped geometry. The nanocapsules produced using such a method could encapsulate hydrophobic molecules such as doxorubicin, which is a known anti-cancer drug.

Chemical patterning of graphene has served as an important idea in the transformation of 2D flat graphene sheets into more complex 3D configurations. Elias et al. demonstrated that, albeit graphene is one of the most chemically inert materials, it could nevertheless react with atomic hydrogen, thereby transforming it from a highly conductive 2D sheet into an insulating one.[49] They found the hydrogenation process for graphene to be reversible, and conductivity could be restored through merely heating. This is an interesting fact, since it implies that the hydrogenation process affects not only the conductivity but also the 2D flat structure of graphene. This is attributed to disruptions in the honeycomb structure of graphene caused by the hydrogen atoms. Therefore, hydrogenation of graphene sheets at selected areas could be a way of encoding folding (fig. 8). The benefits of this are discussed below.

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47   Movahedi et al. 2013.

48   Hyper-branched polyglycerols are polymers with a large number of branches, very similar to a tree structure.
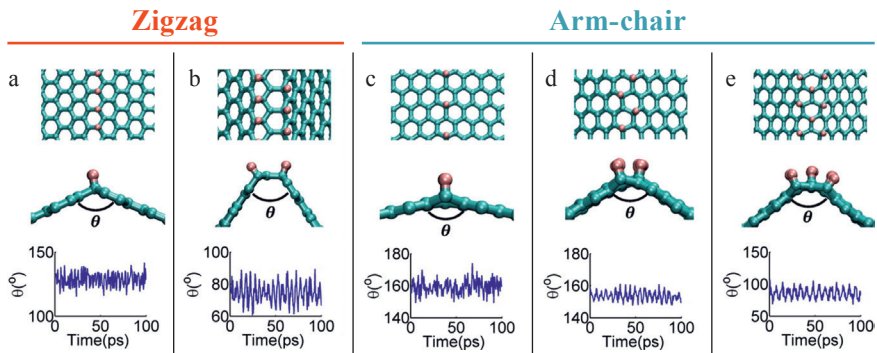
49   Elias et al. 2009.

Fig. 8: Top and side view of hydrogen-assisted graphene folding with its resulting fold angles at equilibrium. (a) One-line and (b) two-line hydrogenation are introduced along the zigzag direction of a graphene lattice. (c) One-line, (d) two-line and (e) three-line hydrogenation are introduced along the armchair direction of a graphene lattice. The bottom row plots the variation in folding angle at 300 K over time; variation in the angle of the fold throughout the simulation indicates the stability of the folded substructure.

Zhu et al. carried out systematic MD simulations to demonstrate the feasibility and robustness of *hydrogen-assisted graphene origami* (HAGO).[50] Simulations revealed that, when hydrogenation is present at both sides of a 2D graphene sheet, the structure remains planar; such a fully hydrogenated graphene structure is known as *graphane*.[51] However, when hydrogenation is introduced in a controlled manner along a line formation on any one side of graphene, a net structural distortion can indeed cause folding and bending.

Hydrogen-assisted bending occurs along the hydrogenated line in a certain angle dependent on the number of the hydrogenated rows (fig. 8). It was further demonstrated that an external electric field could further aid in controlling the folding process in HAGO. They attributed the effect of the external electric field to the polarization of carbon atoms in graphene and consequent a change in inter-graphene layer interactions. This demonstrates a decrease of the inter-wall van der Waals energy of adhesion between the graphene layers resulting from an increase in external electric field intensity.

The authors hence propose using graphene-based nanocages as a means of hydrogen storage, while controlling its release through temperature elevation and electric field variation.

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50   Zhu / Li 2014.

51   Elias et al. 2009; Sofo / Chaudhari / Barber 2007.

Another recent example in using folding for storage purposes is found in the experimental work by Hamid Reza Barzegar et al.[52] they demonstrated a facile solution-based method to insert smaller molecular structures, such as fullerene, C_{60}, into carbon nanotubes. In other words, carbon nanotubes could act as peapods by harboring fullerenes. This was previously reported as a result of simulations by Smith et al., where fullerenes were encapsulated by single-wall carbon nanotubes.[53]

The transformation of carbon nanotubes from a tube into a collapsed and flattened bilayer of graphene, tightly bound with two folded edges, can takes place only when the tube diameter is larger than a certain critical value.[54] Using high resolution TEM, Barzegar et al. observed that the fullerenes are initially packed along the hairpin tube edge and not at the center of the tube. Eventually the nanotube fills up with fullerenes.

Oliver Ochedowski et al. carried out alterations of chemical bonds of graphene sheets at specific locations using *swift heavy ion irradiation* (SHI irradiation).[55] They investigated the effect of high-energy ion beam irradiation on 2D sheets such as graphene and MoS_2. Swift heavy ion radiation specifically interacts and affects the electronic excitation and ionization of a material. Ochedowski et al. proposed two phases in graphene sheets after exposure to SHI radiation.

At the beginning, the graphene sheet bends at the regions exposed to ion radiation and forms a bilayer graphene, a process that can locally increase its mechanical strength. In the second phase, graphene forms a hairpin-folded segment, which affects its chemical reactivity and electron transports at those segments. It was found that, when exposed to the SHI radiation, graphene could transform from 2D into 3D configurations with segments including at least three folds. Such a number of folded segments were not observed, however, in the case of MoS_2 sheets. It is not yet known what is behind the number of folded segments.

Using *scanning force microscopy*, the folded regions in MoS_2 were found to be higher than their graphene counterparts. This was attributed to the inter-layer spacing in MoS_2, which is 0.75 nm and almost twice as high as that of graphene. Folding observed by Ochedowski et al. is believed to be the experimental evidence of defect formation in the exposed areas of graphene and their subsequent self-folding.

5. Summary and conclusions

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52 Barzegar et al. 2015.
53 Smith / Monthioux / Luzzi 1998.
54 Chopra et al. 1995; He et al. 2014.
55 Ochedowski et al. 2014.

Most simulations and theoretical work done so far emphasized the possibility of folding or self-folding in graphene. There have been studies regarding instances of graphene folding by externally applied forces. However, for a variety of reasons, the guided folding of graphene and graphene oxide has not been demonstrated experimentally yet. Nevertheless, simulation of chemical patterning and modification of graphene sheets was shown to be able to encode the desired folding patterns within the sheets.

Programmed self-assembly of 2D sheets into bulk material with specific properties, or the self-assembly of single sheets into 3D structures, is potentially simple and cheap, hence well suited for advanced applications such as drug delivery or nanostorage. It therefore affords promising possibilities for future industrial production of advanced materials in a way that has advantages over current production methods. Therefore, experimental methods and further investigations in controlling and defining the forces affecting folding at the nanoscale level are needed.

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Mohammad Fardin Gholami
Email: *gholami@physik.hu-berlin.de*

Image Knowledge Gestaltung. An Interdisciplinary Laboratory.
Cluster of Excellence Humboldt-Universität zu Berlin.
Sophienstrasse 22a, 10178 Berlin, Germany.

Department of Physics and IRIS Adlershof, Humboldt-Universität zu Berlin.
Newtonstr. 15, 12489 Berlin, Germany.

Nikolai Severin; Jürgen P. Rabe
Department of Physics and IRIS Adlershof, Humboldt-Universität zu Berlin.
Newtonstr. 15, 12489 Berlin, Germany.